OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

This document has been produced without formal United Nations editing. The designations employed and the presentation of the material in this document do not imply the expression of any opinion whatsoever on the part of the Secretariat of the United Nations Industrial Development Organization (UNIDO) concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries, or its economic system or degree of development. Designations such as "developed", "industrialized" and "developing" are intended for statistical convenience and do not necessarily express a judgment about the stage reached by a particular country or area in the development process. Mention of firm names or commercial products does not constitute an endorsement by UNIDO.

FAIR USE POLICY

Any part of this publication may be quoted and referenced for educational and research purposes without additional permission from UNIDO. However, those who make use of quoting and referencing this publication are requested to follow the Fair Use Policy of giving due credit to UNIDO.

CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

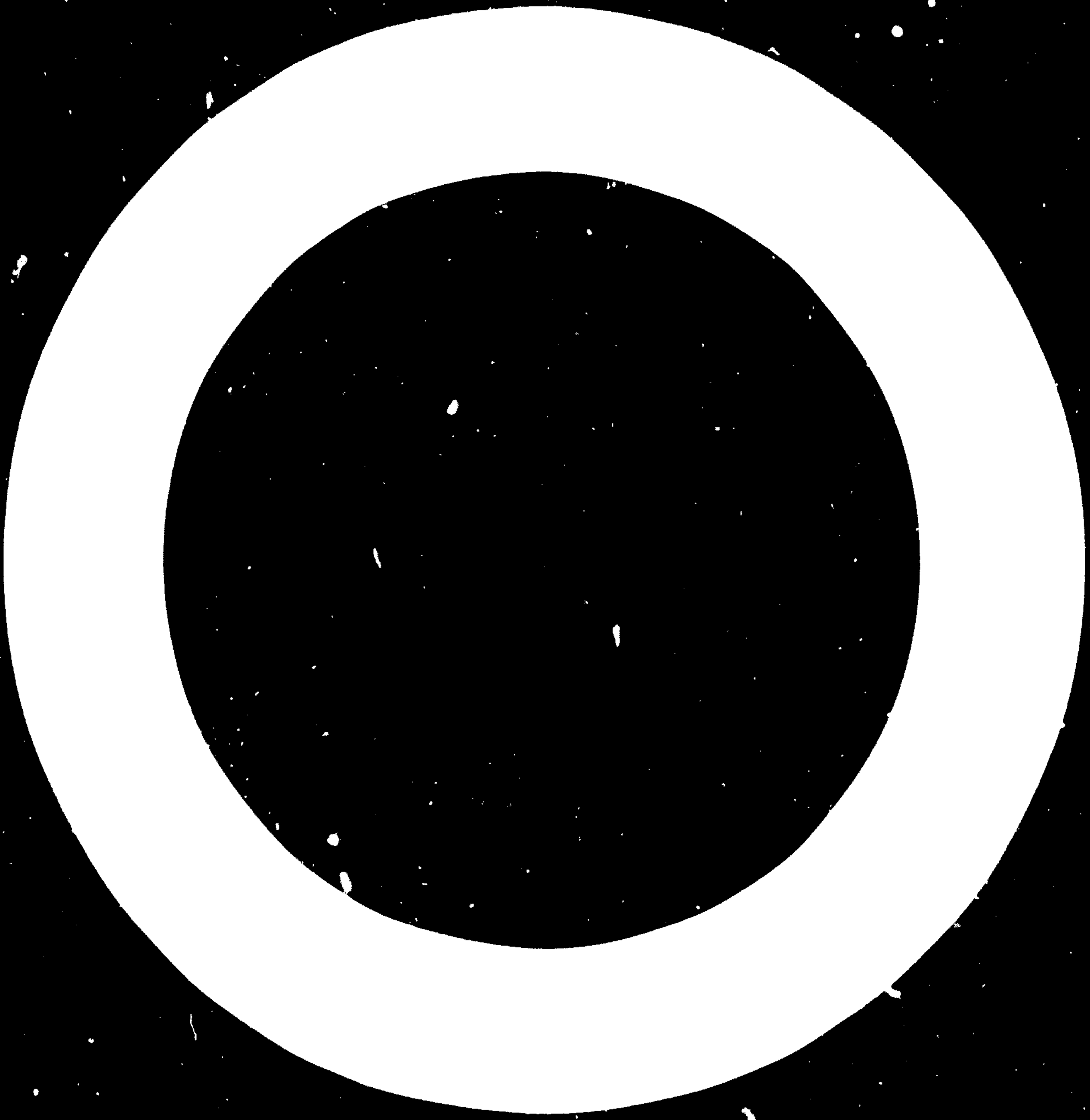
For more information about UNIDO, please visit us at www.unido.org

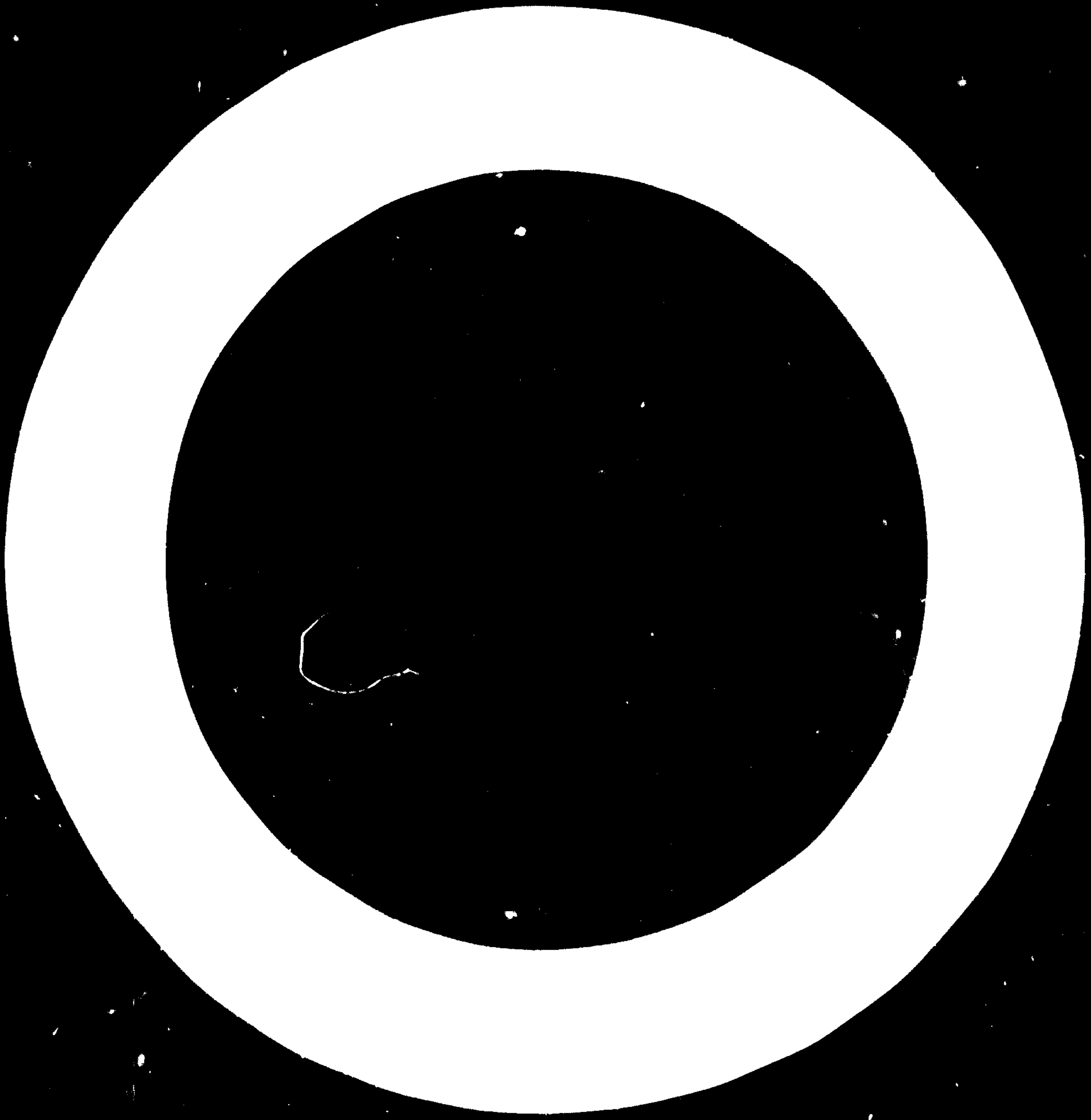
UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

06639

TRANSFER OF KNOW-HOW IN THE PRODUCTION AND USE OF CATALYSTS

report
of an expert group meeting
organized by the
JOINT UNIDO / ROMANIA CENTRE
bucharest, romania
26—30 june 1972





UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
VIENNA

TRANSFER OF KNOW-HOW IN THE PRODUCTION AND USE OF CATALYSTS

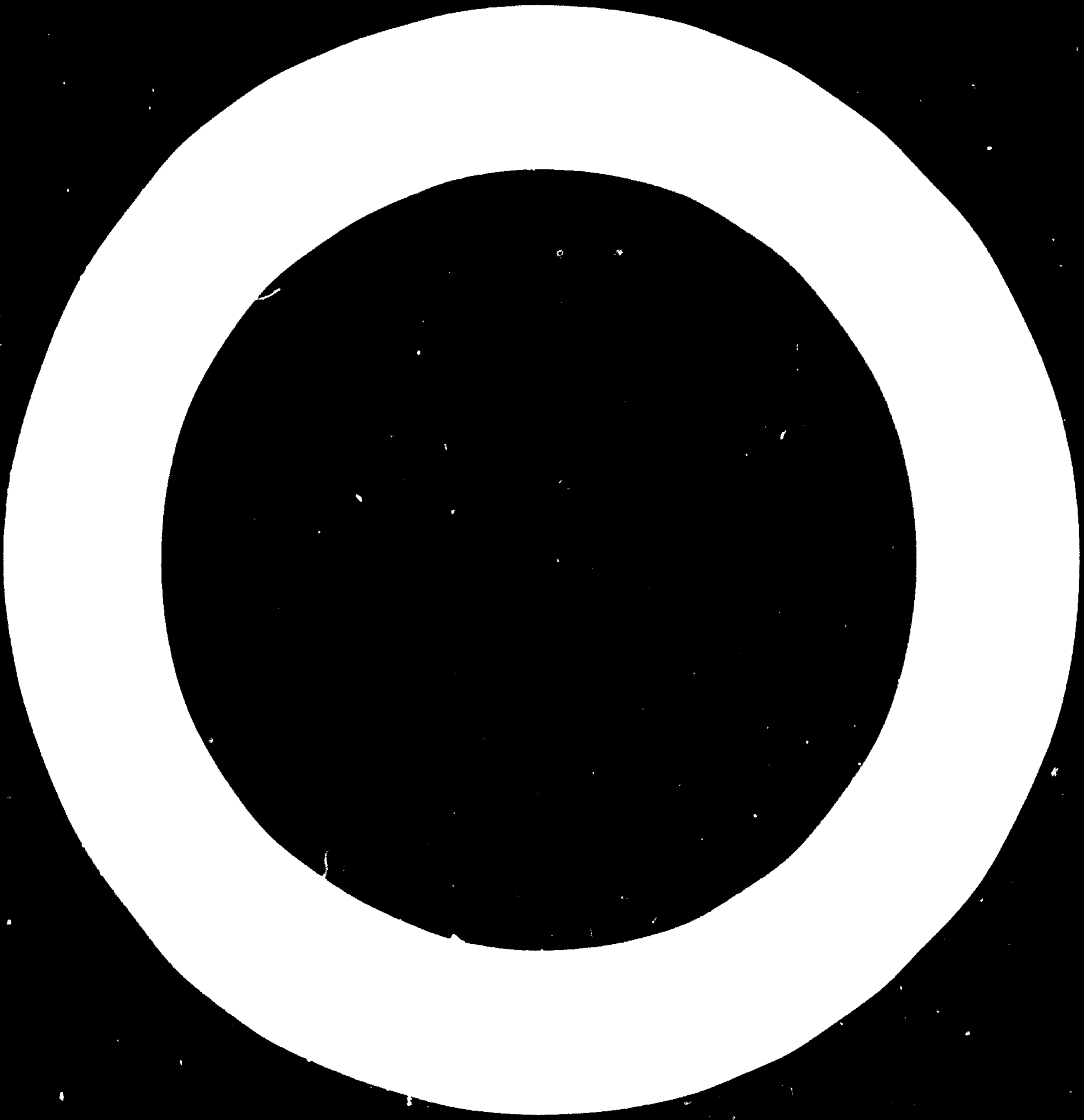
Report
of an Expert Group Meeting
organized by the
JOINT UNIDO/ROMANIA CENTRE
for International Co-operation in the Chemical
and Petrochemical Industries for the Benefit
of the Developing Countries
Bucharest, Romania
26–30 June 1972

EXPLANATORY NOTE

The term "billion" signifies a thousand million
Reference to "dollars" indicates United States dollars.
Reference to "tons" indicates metric tons.

Part one

Report of the Meeting



NOTE

The Expert Group Meeting on Transfer of Know-How in the Production and Use of Catalysts, organized by the Joint UNIDO/Romania Centre for International Co-operation in the Chemical and Petrochemical Industries for the Benefit of the Developing Countries, was held at Bucharest from 26–30 June 1972. This report of the meeting, comprising an account of the discussion and the technical papers submitted to the meeting, is issued by UNIDO as an internal document. The papers are reproduced in the form in which they were received. Only typographical errors and errors of fact or terminology have been corrected. The report was printed in Romania with the assistance of the Joint Centre. UNIDO expresses its appreciation to the Centre for its co-operation in the issue of this document.

CONTENTS

PART ONE. REPORT OF THE MEETING

PART TWO. PAPERS SUBMITTED TO THE MEETING

As part of the UNIDO programme of work for 1972 an expert group meeting on the "Transfer of know how in the production and use of catalysts" was held at Bucharest, Romania from 26–30 June 1972. This international meeting constituted the first activity of the recently established Joint UNIDO/Romania Centre for International Co-operation in the Field of Chemical and Petrochemical Industries for the Developing Countries.

The main objectives of the meeting were:

(a) To identify problems related to the production and use of catalysts for the fertilizer and petrochemical industries in developing countries;

(b) To provide guidelines for the future work programme of UNIDO in this field.

Additional objectives were:

(c) To promote investment in production facilities in developing countries;

(d) To consider ways and means of transferring catalyst technology to countries in which the chemical industry is sufficiently developed to justify domestic production;

(e) To assist these developing countries in planning the future production of catalysts;

(f) To identify future trends in the use of new types of catalysts for the fertilizer and petrochemical industries.

On behalf of UNIDO, Mr. M. C. Verghese acted as Director of the Meeting and Mr. A. Dumitrescu as Technical Secretary. On behalf of the Romanian component of the Joint Centre and the organizing committee, Mr. A. Lungu served as Co-Director and Mr. V. Ioniță was liaison officer. Mr. G. Suciu and Mr. I. V. Nicolescu of Romania were elected Chairman and Vice-Chairman respectively, and Mr. Fernando Colunga Diego, Rapporteur.

The meeting was attended by forty-seven persons from fifteen countries and one International organization: twenty experts from eleven countries (Bulgaria, the Federal Republic of Germany, India, Iran, Israel, Mexico, Romania, Turkey, the United Kingdom of Great Britain and Northern Ireland, the United States of America and Yugoslavia) and one international organization; one consultant from Romania appointed by UNIDO and twenty-six observers from eight countries (France, the Federal Republic of Germany, Iran, Italy, the Netherlands, Poland, Romania and the United States of America).

The Inaugural address was made by the Minister of the Chemical Industry of Romania, Mr. M. Florescu. Mr. Verghese read a message from the Executive Director of UNIDO, Mr. I. H. Abdel-Rahman. Mr. A. Rotival, Resident Representative of the United Nations Development Programme reviewed the projects of Romania and Mr. Dumitrescu presented the overall programme for the meeting.

Twenty-six technical and informative papers were submitted for presentation and discussion at the meeting.

The participants visited the Ploiesti Petrochemical Works and the Petrochemical and [illegible] Research Institutes. A report of this visit is given in the annex.

In spite of the complexity of the problems and difficulties involved in the transfer of know-how and in the production and use of catalysts, the participants treated the subject objectively and arrived at conclusions and recommendations related to each of the original objectives. Of particular note are the recommendations which call for:

(a) Unity of action between countries in the standardization of methods and techniques;

(b) Mutual assistance in training;

(c) Co-operative efforts in research and development;

(d) Specific tentative offers of assistance from a participant from a developed country with respect to documentation facilities, services and catalyst know-how.

The meeting closed with messages of thanks and summaries by the Deputy Minister of the Chemical Industry of Romania, Mr. V. Belizna, by Mr. Verghese and Mr. G. Suciu.

I. THE DEVELOPMENT, PRODUCTION AND USE OF CATALYSTS IN THE DEVELOPING COUNTRIES

Papers on the development, production and use of a variety of catalysts were presented to the meeting. The subjects ranged from policy questions to research, from long-term experience in catalyst development and production and local problems relating to their use to novel reactions and technologies, such as the use of phosphoric acid as a catalytic medium for organic reactions. Some of the papers dealt with the specifics of catalyst preparation for the dehydrochlorination of ethylene dichloride, the hydrodesulphurization of fuel oil using a conventional catalyst, and the preparation of aromatics by catalytic reforming of petroleum fractions; other papers were concerned with problems of education and training.

Various papers called attention to the nature of the efforts made in some developing countries to promote know-how in view of the intricacies of industrial catalysts and catalytic processes. From reports presented and discussions which took place on this subject, it was evident that many of the developing countries were already actively involved, having developed facilities for physico-chemical studies and pilot-scale evaluations of catalysts. These countries were determined to take steps which would qualify them to undertake catalyst assessment and also to produce the catalysts they needed for their industries. In fact, several of the papers concluded that in consideration of the domestic bulk consumption of catalysts, the country concerned should take such an active part in catalyst research and development that the country could eventually develop into a major catalyst manufacturer.

It was accepted as minimum requirement that users in developing countries should establish adequate facilities for catalyst assessment to allow for the examination of samples received from potential suppliers. Such facilities are needed not only because of commercial factors involved and geographical location, but also because of the unfortunate consequences that can result from total reliance on foreign catalyst manufacturers. In examples given by representatives of developing countries, some catalysts that were guaranteed for two years failed within six months, and the suppliers did not offer replacements. In spite of many obstacles to be overcome, the description of pilot units, the details given of testing procedures used and other revealing factors indicate that some developing countries were competent to proceed with the selection, development and manufacture of calatysts.

The depth of the experience achieved was clear from presentations describing reaction mechanisms, process thermodynamics, physico-chemical characteristics of catalysts and the effect of operating variables on catalyst performance. Several participants however, expressed their concern at the expenditure involved and the time required for a developing country to establish such competence, and at the uncertainty of ever gaining this objective.

Not the least of the many difficulties to be encountered was the problem of financing catalyst projects in developing countries. Local problems involved in obtaining adequate finance from industrial units applying catalytic processes were presented by one of the participants.

Difficulties in recruiting staff adequately trained in this field were also discussed. Because there were so few good technologists, there was much competition for their services. Limitations in professional scope and prospects caused professionals to change position frequently which has acted as a deterrent in developing or building up expertise.

Representatives from developing countries in which catalyst manufacture had already been initiated offered suggestions from their own experience relating to the transfer of catalyst know-how to industry. The type of tests required and the equipment and techniques needed for quality control and evaluation of catalysts were discussed. It was agreed that development batches of catalysts were best prepared in equipment that was a prototype of a full-scale commercial unit. This approach was considered essential for minimizing problems related to scale-up from the laboratory scale to operations in commercial units.

It was clear from papers presented that there was now a growing interest in the field of industrial catalysts both in universities and industrial laboratories of developing countries. However, the development of facilities for fundamental and applied research should be supplemented by courses in industrial catalysis at the university level.

Schemes for training scientists and engineers in operating catalytic units before undertaking assignments in research were considered by the participants as an important step in the generation of such expertise. One participant from a developing country believed that without such expertise the know-how of catalyst development and production alone was meaningless, because the consumer was not in a position to apply the catalysts that were manufactured. The expertise generated must include the commissioning steps in bringing a catalyst to life because without such competence even a proven catalyst may fail. The opinion was expressed that competence in catalyst technology cannot be considered established until the materials produced continue to function in commercial units for reasonable periods of time and under guarantees.

In exploring means to overcome the difficulties discussed, the Expert Group considered co-operative efforts and possible sources of assistance. It was felt necessary to examine the feasibility of establishing standards for catalyst selection. It was agreed by most of the participants that a documentation centre in catalysis would be of definite assistance. Statistics relating to the performance of catalysts supplied by different manufacturers in various units throughout the world, for example, could be of help to users in the selection of a supplier.

It was the general opinion that UNIDO could be of assistance in this regard both in supporting efforts to establish standards in catalyst characterization and by establishing a catalyst documentation centre.

II. TEST METHODS FOR CATALYSTS AND THE EVALUATION OF CATALYTIC PROCESSES

The problem of catalyst testing in developing countries was considered from two points of view (a) the general problem of establishing criteria for catalyst purchasing and use and (b) the exchange of experience and information on methods and techniques in catalyst testing.

Concerning the first aspect, representatives from developing countries stressed the importance of catalyst testing for their industries, suggesting means by which domestic competence might be realized. In order to establish a rational basis for comparison of catalysts offered by different producers, consideration should be given to the selection of properties required to characterize each particular system, the establishment of correlations between process conditions and acceptable tolerances of critical properties of catalysts and the definition of methods to be used in catalyst testing.

In regard to the standardization of methods for catalyst testing, the significance of some of the conventional criteria for the evaluation of catalysts was questioned. The basic criteria for evaluating and selecting catalysts were defined as the effectiveness of their activity and their selectivity and stability, that is their "life" under operating conditions in commercial plants. It was pointed out that the endeavours of the industry to develop reliable methods for investigating the dynamics of catalyst ageing in reactors were still active.

Representatives of several of the catalyst manufacturers expressed the opinion that catalyst users should not test catalysts themselves, but should leave testing to the catalysts suppliers. This approach, based on confidence in suppliers in lieu of effective local testing facilities, was discussed extensively and considered by most speakers as not entirely adequate. It was concluded that in spite of the numerous difficulties involved, a developing country should strive to establish competence in catalyst testing to ensure optimum performance in the operation of its chemical industry.

Consideration was given to methods applied in the investigation of the physico-chemical properties of catalysts as well as their relationship to reactor characteristics. It was noted that in this area the exchange of experience between developing countries and co-operative programmes should be encouraged.

Instrumentation and the application of numerous methods were reviewed: adsorption measurements and BET techniques, pressure porosimetry, magnetic balance, X-ray, electrical conductivity and ESR, thermogravimetry, DTA, quartz microbalance, chromatography and activity tests. With regard to the activity tests, the determination of the activity of solid catalysts, account was taken of the physical phenomena associated with catalytic reactions, and the mechanical design and functional characteristics of various types of catalytic reactors. It was pointed out that the choice of a significant test reaction for a particular catalyst involved a critical decision.

Three levels of catalyst testing were defined: (a) simple comparative testing; (b) intensive catalyst evaluation, including simulated plant operation; and (c) fundamental examination to characterize in detail the catalyst and the reactions it catalyzes. The various techniques used at each level of catalyst testing were described and their usefullness to the catalyst researcher, catalyst manufacturer and catalyst user was assessed. The testing of the several types of catalysts used in ammonia manufacture was used as an illustration, considering both those testing methods which are common to all catalysts and those which are particular to individual catalysts. The measurement of a catalyst's activity, chemical constituents, and physical properties, such as surface area, pore structure, shape and strength was discussed.

As an important step in catalyst testing, the physical and mathematical modelling of heterogeneous processes was presented. This consisted of:

Kinetic characterization of the catalyst.

Thermodynamic characterization of the reaction.

Scale-down of the commercial reactor.

Formulation of the equation for heat and mass transfer.

Subsequent adjustment of the kinetic data which characterizes the catalyst.

Highly instructive surveys of methods and procedures applied in manufacturing practice were presented by several catalyst manufacturers. These contributions conformed with the central theme of the meeting.

III. PLANTS AND EQUIPMENT FOR CATALYST MANUFACTURE AND CATALYTIC PROCESSES

The papers surveyed various aspects related to catalyst manufacture and their use in catalytic processes. The views of experts from large catalyst manufacturing companies in highly industrialized countries were confronted with the views, ideas and problems of experts from developing countries. The animated and interesting discussions of the papers presented served to underline the importance and need of examining thoroughly the various aspects of this particular field. However, time did not permit such an examination and the discussion therefore was somewhat limited.

There was a sharp divergence of ideas and opinions expressed by experts from the developing countries and experts representing large industrial catalyst manufacturers in developed countries. The latter were rather sceptical as to the possibility of manufacturing catalysts in developing countries and suggested that the production of catalysts should be limited to qualified companies in highly industrialized countries. Experts from developing countries emphasized the necessity of establishing catalyst manufacture in their countries, not only for economic reasons but also for political, social and techno-educational reasons. From the discussions, it appears that the manufacture of certain types of catalysts was possible with relatively simple production units. Such units could constitute a beginning of domestic manufacture of catalysts in developing countries. From this start manufacturing skills could be developed and experience gained in quality requirements and specifications.

The small-scale manufacture of a phthalic anhydride catalyst was presented as an example of this approach. The testing section of this kind of plant can be used for development and experimentation in this and related fields, as well as for the training of technical personnel. Several examples were given which demonstrated that the manufacture of certain types of catalysts in developing countries has been accomplished by mobilizing the intellectual potential of the country.

From the contents of the papers presented in this section and from the discussion which followed it appeared that the installation of carefully selected catalyst production units, initially limited to projects which can be realized with a relatively modest capital expenditure, was feasible in many developing countries. In certain instances these could perhaps be undertaken as joint ventures with manufacturers established in the field; this would constitute a concrete expression of the transfer of know-how to developing countries.

It was suggested that UNIDO encourage and support intentions to install such catalyst manufacturing plants and their subsequent use for technological development in developing countries by the following means:

(a) Procuring a technological small-scale model of a catalyst manufacturing plant combined with semi-technical scale demonstration units and pilot plants for the further development of catalytic processes;

(b) Organizing an information service and technological documentation centre designed to provide developing countries with information on catalyst manufacturing processes and facilities as well as on catalytic processes; this centre should contain a patent documentation section. It was suggested that UNIDO co-ordinate its own activities in this particular field with those of the newly organized International Patent Documentation Centre in Vienna, Austria. UNIDO was offered the services of data processing facilities by a participant from one of the developed countries, it was hoped that other countries would follow this initiative;

(c) Acquiring a mobile and easily transportable catalytic reaction demonstration unit which could be placed temporarily at the disposal of technical centres in different developing countries to promote development work in this field. This demonstration unit might be a corollary to the model catalyst manufacturing unit mentioned above;

(d) Appointing experts to study the feasibility of catalyst manufacture and use in developing countries requesting such services;

(e) Organizing subsequent meetings on the subject of catalysis with more detailed agenda, narrowly defined topics, and possibly with an increased number of participants. Discussions could be combined with visits to catalyst manufacturing plants and to plants using catalytic processes. Emphasis at these meetings should be placed on catalysts which appeared to be of particular interest or importance to developing countries, and which could be manufactured feasibly in these countries. It was suggested that a group of papers could be presented briefly by a rapporteur at these meetings thus leaving more time for discussion and an opportunity to exchange opinions in informal gatherings.

IV. NEW TRENDS IN CATALYSIS AND IN THE USE OF CATALYSTS

Both in papers and in discussions emphasis was placed on the increasing role of catalysis in meeting the rapidly expanding world-wide energy demand, and in providing feedstocks for an ever widening variety of products. Catalytic processes have become the most important tool in the majority of chemical conversions, irrespective of the size of the country or its economic scope. In spite of the fact that research efforts were not uniform throughout the world, and the most important achievements in catalysis were found in the developed countries, the developing countries were also becoming involved in catalytic research and development activities.

It was indicated that most of the over all research at the present time was still devoted to heterogeneous catalysis, the development of improved catalysts, and more efficient processes. An increased interest was also being shown in homogeneous catalysis, in spite of earlier reservations in this field. Research achievements in heterogeneous catalysis relate particularly to improving the economics of prevalent transformations, decreasing reaction temperature and pressure, increasing catalyst life and yields, improving product quality and other such accomplishments. The improvement of catalysts and the development of new catalytic systems would be aided considerably by advances in methods for their synthesis and characterization. The extent to which developing countries could devote efforts to research in catalysis will be dictated by domestic conditions – techno-economic, social and political. The scale of operation will greatly influence the selection of routes which might be pursued in process development. Smaller units allow for greater flexibility in considering processes which give coupled products. These units may increase the scope of the industrial development.

Some opportunities of this kind were suggested in a paper on "New trends in catalysis". Other developments were described which promised significant commercial advantages. The impact of homogeneous catalysis was emphasized in this review of the more recent processes for the manufacture of acetic acid, ammonia and methanol, nylon intermediates in ethylene epoxidation, the oxo-synthesis, the ammoxidation of propylene for acrylonitrile production, hydrogenation processes, and others.

Regarding the oxo-technology, it was suggested that in the near future, rhodium catalysts will probably replace those containing cobalt. Catalysts based on rhodium also appeared to be more efficient for the synthesis of acetic acid, showing important economic advantages over the Wacker process.

In connexion with the manufacture of ammonia and methanol, recent technological changes allowed for considerable reductions in operating pressures. It was pointed out that interest in ammonia production generally precedes that of methanol in developing countries. Because of the similarities in these technologies, consideration should be given to the design of an initial ammonia plant which at a later stage could be converted into a methanol plant when ammonia capacity is to be extended. It seemed that in such cases it would not be advisable to use the low pressure methanol technology.

In the field of hydrogenation, new and interesting catalytic systems have been announced, several of which were expected to achieve commercial implementation in the near future. New catalytic systems which combine the advantages of homogeneous and heterogeneous catalysis were described. They were indicated as being highly selective, capable of functioning under mild conditions and easily removed from the reaction product by filtration.

In the manufacture of acrylonitrile by ammoxidation, important progress has been made in the development of improved catalysts, such as uranyl antimonate and tellurium molybdate, which decreased the formation of by-product acetonitrile.

The paper entitled "Activity and life of catalysts for the production of ammonia'' stressed the importance of mutual understanding between the catalyst supplier and the customer. Because of the many factors involved, care must be taken in selecting the catalysis; quality and cost considerations must be carefully balanced, but it was indicated that even an extra cost incurred can be recovered rapidly by improved plant operation.

Trends for the improvement of contemporary catalytic processes in the oil processing industry were indicated. These processes include catalytic cracking, reforming, hydrocracking, hydrodesulphurization and others.

The paper entitled "Improved economics in catalytic reforming" concerned the advantages gained by introducing bi- or poly-metallic catalysts instead of the conventional platinum catalysts for the production of aromatics and high-octane gasoline.

The increasing importance of hydrogenation processes, which essentially cover the entire range of petroleum products, was emphasized in the paper entitled "Trends in the development of catalytic petroleum refining processes." The development of new catalytic systems for reforming and cracking has improved over-all refining efficiency and product quality, and has led to a reduction in the heavy ends of the barrel.

V. THE TRANSFER OF KNOW-HOW IN THE PRODUCTION AND USE OF CATALYSTS

The world's major basic chemical technologies, such as those used in fertilizer manufacture, petroleum refining and petrochemicals, employ processes promoted by catalysts. Success in operating such industrial installations on a viable basis depends on the judicious selection of catalysts, their proper application and their uninterrupted availability.

Reliable catalyst manufactures can provide know-how concerning the first two of these requisites, but the latter is subject to external and objective factors. Although capital costs for catalysts are high, the economic loss which may be suffered when a plant lies idle because of the lack of a catalyst may be much greater than the capital costs involved. Countries in which catalysts are not manufactured, developing countries in particular, may find themselves dependent upon manufacturers and thus in an insecure position concerning their most important chemical industries.

Relevent factors were examined to determine the extent to which pertinent know-how could be transferred to developing countries – which were particularly sensitive to the disruption of services – to guarantee continuity of supply of catalysts.

The catalysts considered were of several types classified as:
Conventional heterogeneous catalysts
Coated heterogeneous catalysts
Molecular sieves
Homogeneous catalysts
Single compound catalysts (unsupported Lewis acids, organo-metallics, peroxides etc.)

The discussions were concerned primarily with the first type, whose materials also serve as the catalyst supports for the second type. These first two types of catalysts comprise the bulk of those vital to the basic chemical industries concerned and are at the focus of the central problem discussed.

The know-how pertinent to this subject was discussed with respect to such factors as:

(a) Know-how in the selection of catalytic processes, catalysts and catalyst manufacturer.

(b) Testing and characterization know-how.

(c) Know-how in the use of catalysts.

(d) Manufacturing know-how.

(e) New processes for catalysts production.

A variety of types of materials exist even among the conventional heterogeneous catalysts, differing in complexity and volume of manufacture and uniqueness in application. Although the discussion was mostly general with respect to this point each specific situation deserves to be studied on its own merits.

KNOW-HOW IN THE SELECTION OF CATALYTIC PROCESSES, CATALYSTS AND CATALYST MANUFACTURER

Criteria for the selection of catalysts appropriate for the intended application are complex except when these are specified by the process to be applied. Reliance upon a supplier and his record of good service may be the determining factor in selection. More information with respect to both catalyst properties and manufacturers should be made available to developing countries to assist them in selection.

TESTING AND CHARACTERIZATION KNOW-HOW

The complex procedures used in the manufacture of catalysts are the propriety of relatively few producers. The nature of the materials concerned and the technologies of their manufacture has led to a situation wherein characterization and testing techniques are often empirical and vary from manufacturer to manufacturer. Catalyst performance is also often difficult to correlate with definitive material properties, which makes it difficult to specify simple evaluation procedures that would guarantee proper catalyst selection. Competent persons may also not be available in developing countries to carry out evaluation studies. Opinions expressed supported the contention that much could be done to render these techniques more uniform and to extend and intensify professional competence in developing countries. Furthermore, co-operation between research groups in developing countries could contribute to this end.

KNOW-HOW IN THE USE OF CATALYSTS

Know-how in the use of catalysts is intimately related to the process concerned and may indeed be part of the proprietary technology transmitted to the user. Such information is usually not pertinent to other catalysts, even for the same process. Operational parameters may be optimized in application, but the primary information, including training of personnel, is optimally provided by the catalyst supplier. As there is a constant danger that some trainees may not continue to work in their trained capacity, replacements should be available to meet such challenges.

MANUFACTURING KNOW-HOW

The transfer of manufacturing know-how constitutes a very sensitive and complex problem. Improvements in manufacturing have let to a situation in which smaller volumes of individual catalysts are being manufactured and an over-capacity in manufacturing facilities has developed. Manufacturers are reluctant to encourage competitors to enter this field. Members of the Expert Group appreciated the difficulties of this problem. It was agreed that there should be compensation for any such transfer of know-how. Users might expect to benefit from improvements developed by their suppliers and licensors in the field of the subject licence, without additional, burdensome royalty expenses. Such conditions should be considered for negotiation in the basic contractual agreement. In some cases, know-how could be transmitted by establishing joint companies which would employ the proprietary technology in the developing country. Means should be found for transferring the know-how in catalyst manufacture that is evolved in some developing countries and which may best benefit to other countries because of their similarity of need, economic structure, and the like.

In spite of the vital need of the basic chemical industries of many developing countries, the local domestic manufacture of catalysts in these countries may not always be desirable or even possible. Many factors must be weighed in analysing needs and the potential viability of such an industry. Many aspects of the situation including economic, technical and cultural factors such as current catalyst requirements, industrial development plans, over-all industrial structure, available markets, patent protection for processes involved, level of risks which could be supported, level of technical competence of labour force and the availability of supporting services must all be taken into consideration.

NEW PROCESSES FOR CATALYST PRODUCTION

Co-operative efforts between developing countries and manufacturers of catalysts in developed countries can be perceived in the area of joint research in new catalytic materials; these would relate to new processes for existing products or new products entirely. This effort would be mutually beneficial for the manufacturer as it would: introduce new concepts to his research and development programme, lower his research costs and make new markets available. The developing country would benefit from having access to evaluation techniques and application techniques, and from the financial aid received for research.

VI. CONCLUSIONS AND RECOMMENDATIONS

The documents prepared for the Expert Group Meeting form valuable reference material for developing countries in the field of catalyst production and use. The report and papers presented should therefore be edited and published with minimum delay and distributed. The meeting noted with satisfaction that the Joint UNIDO/Romania Centre offered to print the report and papers.

The contacts and discussions during the meeting proved to be very useful for experts from developed and developing countries; it was recommended therefore that similar meetings be organized or sponsored by UNIDO in the future. The possibility of large catalyst-producing companies or countries hosting such future meetings, and UNIDO making it possible for experts from developing countries to participate should be explored.

The test methods and procedures for analysis and use of catalysts now in use by producers, users and researchers differ considerably. Because of this a common basis for comparing physical and chemical characteristics, and tests on the efficiency and life of catalysts do not exist. The following participants were therefore invited to constitute a committee to study (by correspondence) the feasibility of setting up uniform test procedures for catalysts:

W. Bedford	(United Kingdom of Great Britain and Northern Ireland)
O. F. Joklik	(Federal Republic of Germany)
E. I. Korchak	(United States of America)
H. J. Lovink	(The Netherlands)
I. V. Nicolescu	(Romania)
Paula Putonov	(Yugoslavia)
S. P. Sen	(India)
S. W. Weller	(United States of America)

The committee is requested to report its conclusions within six months to UNIDO. If the standardization of methods is feasible, the committee should initiate action to draw up such test procedures for the catalysts used in sulphuric and nitric acids and fertilizer production, the petroleum refining industry and the petrochemical industry, starting with one sector. Mr. Weller was requested to be the convenor of this committee.

Information such as the names and addresses of catalyst manufacturers throughout the world, the types of catalysts they produce, the specifications recommended, the services they are prepared to render, test methods and precautions to be taken, is not available to many users in developing countries. UNIDO therefore should collect such information and make it available to all interested catalyst users in developing countries. Such data should be up-dated when new information becomes available. The participant from the Federal Republic of Germany tentatively offered facilities and his services in setting up a catalyst documentation centre.

It is necessary to avoid duplication of effort which might be undertaken in the field of catalysts. UNIDO therefore should establish contacts with the International Congress on Catalysis, with the relevant professional societies and with major institutes of catalyst research to minimize duplication of effort.

Some developing countries which have already built fertilizer and petrochemical industries have felt the need of training technical personnel in this field. It was recommended therefore that UNIDO should explore the possibility of establishing such training in the catalyst development centre of the Fertilizer Corporation of India, in the Joint UNIDO/Romania Centre and in other developing countries for groups of five to ten scientists, engineers or chemists, for periods of three to six months. (A request was made to the expert from India to inform UNIDO in due course about such a possibility. Other countries were also invited to offer such training facilities.)

Because difficulties exist for catalyst users in developing countries in testing the claims of various catalyst manufacturers, it is recommended that physical and chemical tests for catalyst characteristics be set up by catalyst users in developing countries. Pilot testing of catalysts in units simulating plant conditions may give adequate evaluation. UNIDO however, should consider rendering assistance in establishing such testing facilities if a country specifically makes such a request. A tentative proposal for the transfer of know-how on this subject was offered by the participant from the Federal Republic of Germany.

Difficulties are often encountered at various centres in testing catalysts using the same procedure and test methods and in interpreting the results. The Joint UNIDO/Romania Centre is therefore requested to investigate setting up such a facility to which developing countries could refer cases for testing and advice.

Visiting and studying the facilities of catalyst manufacturers in developed countries to learn testing procedures and the like presents difficulties for some people in developing countries and UNIDO is therefore requested to provide fellowships to countries which may make official requests for such training.

Some developing countries expressed the desire to go into catalyst manufacture. UNIDO therefore should assist countries which request help in performing feasibility studies for catalyst production. The participant from the Federal Republic of Germany expressed his intention to offer free assistance in this regard.

Because difficulties are encountered in the standardization of methods for catalyst testing and because it is desirable to co-ordinate the efforts made in developing countries in this direction, it is recommended that UNIDO support the realization of co-operative programmes proposed by developing countries concerning the elaboration of methods for catalyst testing.

REPORT OF THE VISIT TO THE PLOIEŞTI PETROCHEMICAL WORKS AND THE PETROCHIM AND I.C.P.T.P.T. RESEARCH INSTITUTES (25 JUNE 1972)

Mr. V. Ioniţă, Production Manager of the Petrochemical Works Ploieşti, greeted the members of the Expert Group and gave an over-all presentation of the enterprises. A film was presented on the development of this installation, followed by discussions with the participants.

The visit to the refinery included: (a) The catalytic cracking unit whose through-put is 1 million tons per year, producing C_3 and C_4 fractions for further petrochemical processing and gasoline, and (b) the catalytic reforming unit whose through-put is 1 million tons of gasoline per year, producing high octane gasoline, benzene, toluene and isomeric xylenes.

The olefins plant of the Petrochemical Works was then visited. Ethane and propane raw materials are processed to produce 35,000 tons per year of ethylene and 20,000 tons per year of propylene.

The activities of the Petrochim Research Institute were presented by Mr. G. Muscă, its Director. Mr. I. Ghejan, Scientific Director of I.C.P.T.P.T., described the work and structure of this institute. Following a period of questions and answers, the laboratories were visited.

The participants particularly enjoyed the opportunity for discussion with the personnel of the plants and laboratories.

Part two

Papers submitted to the Meeting

DEVELOPMENT, PRODUCTION AND USE OF FERTILIZER CATALYSTS IN INDIA[1]

S. P. SEN*

I. INTRODUCTION

Over the last few years there has been a spectacular world wide increase in ammonia production for intensifying agricultural productivity. Refinement in process and equipment technology has kept in step with the increasing demands for ammonia. With changing technology, catalysts have also been improved to secure better on stream efficiency. In India, the production of nitrogen has shown a steep upward trend, tending towards 3 to 4 million tons a year by 1975. This will have an obvious impact on catalyst requirements. In figure 1 the nitrogen production in India and the corresponding figure of catalysts in use have been shown.

India made its appearance in the field of fertilizer catalysts in the year 1951. Starting with nothing, the Planning and Development Division of F.C.I. is now in possession of self-generated know-how for production and utilization of nearly the entire range of fertilizer catalysts. The development, production and use of the first of our own series of catalysts was a necessary response of our R&D organization to a crisis which developed when the Sindri fertilizer factory was commissioned. Within a few weeks of the first trial runs, all 8 CO conversion units of the installation, employing 280 tons of catalyst, were de-activated and the plant had to be put out of commision because of high CO leakage. Spare charges were not readily available and at the same time it was a matter of prestige for our government to get this first state-owned chemical complex firmly established, and quickly. It was a serious crisis for a developing country as India was in 1951. The nucleus of the present day R&D division, known as the Technological Department, took up the challenge and developed a highly sophisticated technique for renovating the catalyst. The entire quantity could be regenerated and put back in line, reducing CO-leakage to less than the design limit.

This single effort resulted in a direct saving of Rs. 2.8 million in terms of foreign exchange and consequential prevention of substantial loss in production. This was the initiation of our activities in the field of catalyst development.

In the next 2 years, a break-through was achieved by developing proprietary know-how for the production of an improved CO-conversion catalyst. In 1953, large scale production of this catalyst was started in a plant based on our design, engineering and know-how. Process know-how for the production of a highly active desulphurization oxide as a substitute for imported raw materials was also generated. With the commencement

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/5.

* Fertilizer Corporation of India, New Delhi, India.

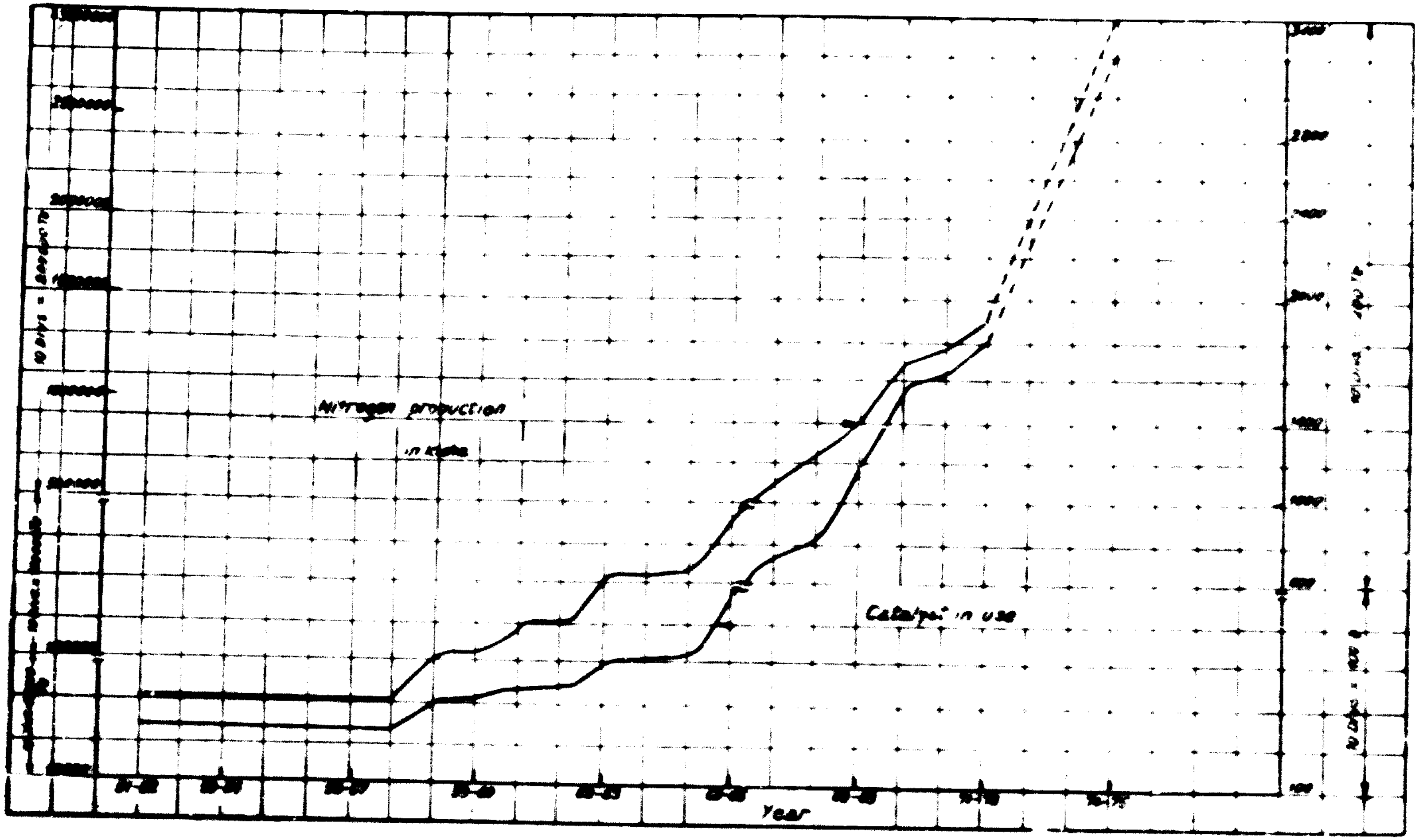


FIGURE 1

of production of the oxide mass a target of 400 tons per annum could be achieved

These developments inspired in the scientists and engineers of this organization tremendous confidence in their own abilities to improvise and to understand the nature of the role of catalysts in large chemical plants The risk involved in depending entirely on imports from abroad was realized

The invention of new and improved catalysts has greatly changed the complexion of fertilizer technology In 1951 a space velocity of only 500 was considered safe for CO conversion catalysts In 1957, the operational demand in Sindri's expansion was for a space velocity of 1,000 and in modern plants it is of the order of 4,000 Continuous improvement in the intrinsic activity of the catalyst to cope with this tremendous increase in space velocity is a real index of advancement of catalyst technology.

Even at the very early stages it was realized that unless facilities available for fundamental studies are applied judiciously, it would be difficult to cope with the growing need for improved varieties of fertilizer catalysts and keep pace with changing process demands The expertise generated and fundamental concepts developed during those early days helped us conceive these facilities and instruments which are even to-day considered modern Physical and physico-chemical instruments described below, were applied in our institution as early as 1960.

Each catalyst research institution has its own approach to investigations in catalysis and may even have its own theories. The theory and the fundamental concepts which have guided most of our activities leading to generation of know-how in this field are based on postulations by Chakravarty (1, 2)

With changes in process technology and the adoption of new processes, different catalysis subsequently made their appearance in our country. We developed the know-how for each catalyst in such a manner that our own catalyst could be put into service whenever the imported stock, supplied with the particular plant, was exhausted.

In this way, we entered the field of catalysts for pressure CO-conversion and the reforming of gaseous hydrocarbons in 1965. Within another 2 years, we were able to produce and put into commercial use our own catalyst for the primary and secondary reforming of natural gas. In 1969 there was another break-through when we put our own naphtha reforming catalyst into commercial operation.

Know-how for the manufacture of an ammonia synthesis catalyst was generated in 1965. By this time our formulations for low temperature shift and methanation catalysts were employed for regulator commercial production. By 1969 we were able to export an entire range of fertilizer catalysts excepting those for ammonia-synthesis.

The present day status can be judged from the design data of the plants given in tables I–VII, and from some typical performance data (presented in figures 2–4), for plants using our catalysts. Figures 5 and 6, showing the capacity of the various unit operations, give an idea of our catalyst manufacturing potential. In recent years the institute has applied its design and engineering know-how in two large scale plants of 600 t/day nitrogen rated capacity, based on the characteristics of our catalyst.

TABLE I

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS

Secondary desulphurization and guard catalyst

Plant	Process	Feed rate	Pressure (kg/cm²)	Inlet H_2S (ppm)	Avg-bed Temp C	Outlet H_2S (ppm)	Cat vol. (m³)	Catalyst diam. (mm)
I	Secondary desulphurization of naphtha	4,900 kg/hr	21.8	3 – 5	350 – 370	0.5 – Max	4	3 – 5 Spherical balls
II	Secondary desulphurization of naphtha	1,490 kg/hr	15.0	5 – 10	360 – 380	0.15 – 0.4	3.26	3 – 5 Spherical balls
III	Secondary desulphurization of naphtha	2,418 kg/hr	14.5	10	350 – 371	Traces	1.2	3 – 5 Spherical balls
IV	Guard for low temp. CO conversion catalyst	95,000 Nm³/hr	23.0	0.5	200 – 250	Traces		3 – 5 Spherical balls

TABLE II

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS

Primary reforming

Plant	Feedstock	Feed rate	Steam carbon ratio	Pressure (kg/cm²)	No. of tubes	Temp. C in out	Heated length (m)	Press. drop. (kg/cm²)	Cat. vol. (m³)	CH_4 exit (%)
I	Naphtha	2,418 kg/hr	6.50	14.5	176	333/800	3.0	2.7	4.0	0.7
II	Natural gas	2,400 Nm³/hr	6.50	17.0	60	400/730	10.7	1.7	4.16	7.0
III	Natural gas	6,800 Nm³/hr	3.00	25.0	132	410/800	10.2	2.0	7.0	10.0

TABLE III

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS

Secondary reforming

Plant	Feed rate (Nm³/hr)	Steam/gas ratio	Pressure (kg/cm²)	Temp. C In/out	Catalyst volume (m³)	Methane exit (%)	Catalyst size (mm)
I.	11,250	1.30	17.0	733/876	3.30	0.30	9 – 10 × 15 – 20 Extrusion
II	28,100	1.40	23.0	800/960	7.00	0.30	16 × 6 × 16
III.	43,000	0.87	28.0	670/940	14.25	0.28	16 × 6 × 16
IV	47,137	0.70	21.0	810/910	12.70	0.20	16 × 6 × 16
V.	61,494	0.75	24.0	774/960	19.40	0.40	16 × 6 × 16
VI.	55,7[illegible]3	1.26	30.5	880/976	15.52	0.25	16 × 6 × 16

TABLE IV

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS
High temperature CO-conversion

Plant	Dry gas rate (Nm³/hr)	Steam : gas ratio	Pressure (kg/cm²)	Inlet gas composition (%)				Temperature, °C: beds			Catalyst volume (m³)	CO-leakage (%): beds			Catalyst size (mm)
				CO	CO_2	H_2	Inerts (N_2, Ar + CH_4)	1st in/out	2nd in/out	3rd in/out		1st	2nd	3rd	
I.	7,309	0.80	13.0	27.0	8.6	58.0	6.40	390/480	360/385	—	9.1	5.0	3.0	—	10 × 10
II.	13,600	0.90	15.0	9.0	11.3	57.7	22.00	400/437	335/350	—	24.0	3.0	0.7		6 × 6
III.	11,000	1.50	16.5	46.0	14.0	37.0	3.00	400/530	395/410	—	18.0	7.0	2.6	—	10 × 10
IV.	16,800	1.30	28.7	45.9	2.6	50.7	0.80	372/482	404/449	380/399	22.0	14.0	10.0	5.0	10 × 10
V.	41,381	0.70	16.0	17.0	8.0	52.5	22.50	380/450	—	—	9.2	3.5	—	—	6 × 6
VI.	17,047	1.20	29.5	46.0	4.4	48.7	0.75	395/500	415/470	340/345	30.0	9.0	5.0	3.3	6 × 6
VII.	85,570	0.70	23.0	15.0	11.4	51.3	22.20	360/432	—	—	58.0	3.2	—	—	6 × 6
VIII.	64,255	0.90	21.0	15.4	10.8	51.7	21.50	400/450	400/420	—	34.4	4.0	2.0	—	6 × 6
IX.	23,466	0.90	16.0	11.7	16.2	64.5	7.50	350/420	—	—	12.2	3.0	—	—	6 × 6
X.	45,670	0.67	29.5	14.2	10.7	53.0	22.10	360/430	—	—	19.25	3.0	—	—	6 × 6
XI.	86,050	0.67	23.5	13.2	12.6	52.1	22.10	360/432	—	—	58.5	3.2	—	—	6 × 6
XII.	80,667	0.60	30.2	13.1	8.60	55.4	22.90	360/424	—	—	45.0	3.1	—	—	6 × 6
XIII.	8,780	1.40	28.0	43.3	3.6	52.6	0.50	410/520	441/463	—	11.2	3.0	—	—	10 × 10
XIV.	710	2.60	13.3	12.9	14.2	72.5	0.60	371/480	—	—	1.4	0.8	—	—	6 × 6

TABLE V

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS

Low temperature CO-conversion

Plant	Gas rate (Nm³ hr)	Steam gas ratio	Pressure (kg m²)	Inlet CO (%)	Temp. °C in/out	Catalyst volume (m³)	CO exit (%)	Catalyst size (mm)
I	52.400	0.60	18.0	3.56	220 240	16.6	0.20	6 × 6
II	95.385	0.58	21.4	3.20	200 220	53.0	0.29	6 × 6
III	94.520	0.56	21.6	3.10	200/220	53.0	0.30	6 × 6
IV	1.500	1.40	15.9	1.10	232/237	0.7	0.23	6 × 6

TABLE VI

OPERATING CONDITIONS OF PLANTS USING F.C.I. CATALYSTS

Methanation

Plant	Gas rate (Nm³ hr)	Pressure (kg/cm²)	Inlet CO_2/CO (%)	Temp. °C in/out	Catalyst volume (m³)	Outlet $CO+CO_2$ (ppm)	Catalyst size (mm)
I.	37.500	17.0	0.20/0.20	350/380	7	10	6×6
II.	75.000	22.5	0.10/0.38	367/402	16	10	6×6
III.	73.523	27.0	0.10/0.37	316/348	15	10	6×6

TABLE VII

TYPICAL OPERATING DATA OF STEAM-NAPHTHA REFORMING PILOT PLANT

1.	No. of reformer tubes	=2
2.	Diam. of the tube (o.d x i.d.) (mm)	=107.9 × 90.4
3.	Total length of the tube (mm)	=6095
4.	Heated length (mm)	=4267
5.	Volume of the catalyst (litre)	=39.33
6.	Size of the catalyst (mm)	=16 × 6 × 16 (ring)
7.	Hours of run	=500
8.	Operating pressure (kg/cm²)	=12.0

Naphtha liq. space velocity kg/lit. of cat./hour	Steam/carbon ratio	Naphtha + steam inlet temp. (°C)	Reformed gas temperature exit reformer (°C)	Flue gas temperature exit reformer furnace (°C)	Tube skin temp. (°C)		Pressure drop across the reformer tube (kg/cm²)	Methane exit (%)
					Top	Bottom		
0.60	4.20	470	810	870	870	890	0.42-0.49	1.10
0.68	3.77	475	815	875	870	890	0.42-0.49	1.40
0.72	3.60	470	810	875	865	805	0.35-0.42	1.60
0.77	3.44	470	810	875	865	890	0.35-0.42	1.80
0.80	3.31	465	800	870	870	890	0.35-0.42	2.00
0.85	3.05	450	800	870	870	885	0.35-0.42	2.10
0.85	3.03	450	795	870	875	890	0.35-0.42	2.40
0.85	3.05	450	790	870	875	885	0.35-0.42	2.70
0.90	3.00	450	790	870	875	885	0.35-0.42	2.80

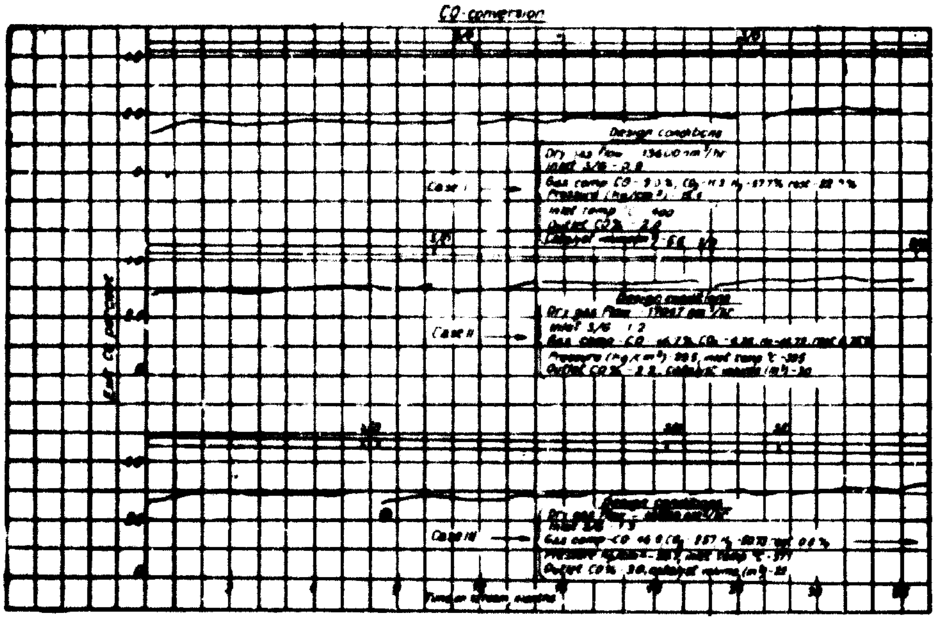


FIGURE 2 A. PLANT PERFORMANCE OF F.C.I. CATALYST

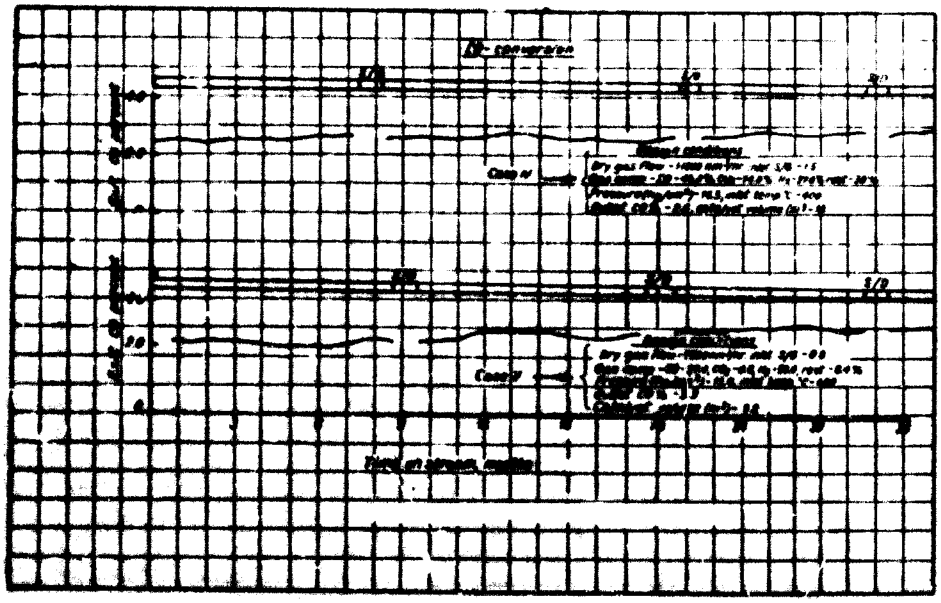


FIGURE 2 B. PLANT PERFORMANCE OF F.C.I. CATALYST

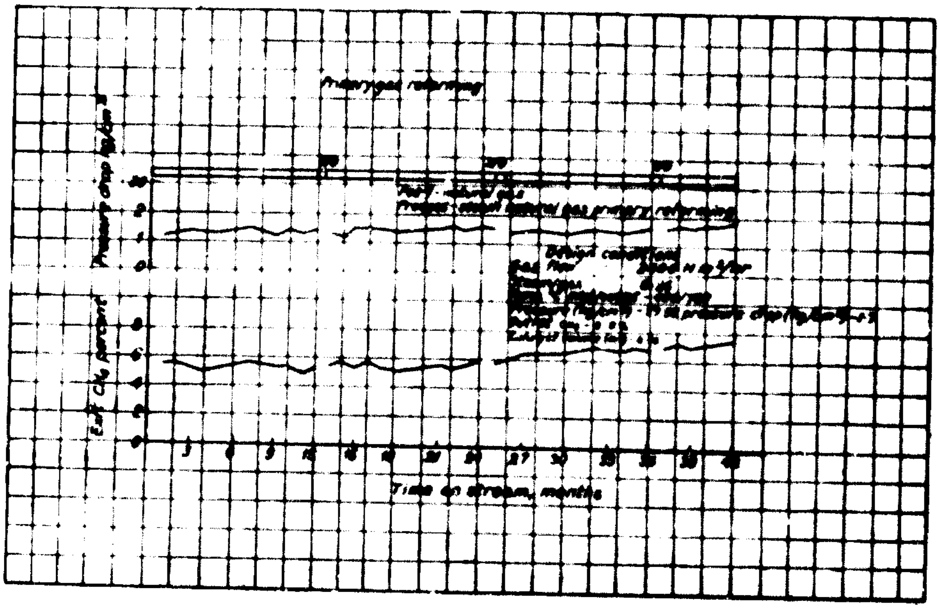


FIGURE 3. PLANT PERFORMANCE OF F.C.I. CATALYST

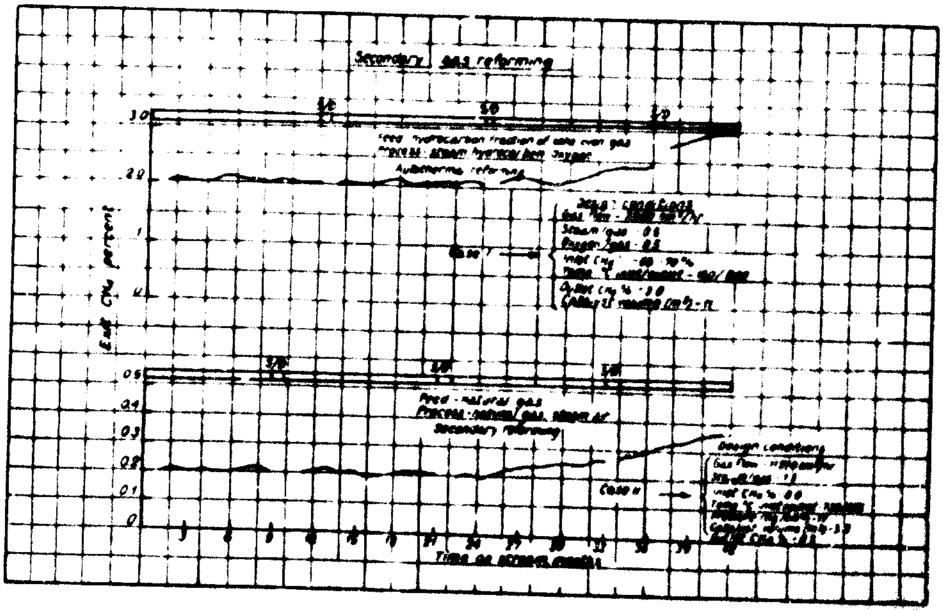


FIGURE 4. PLANT PERFORMANCE OF F.C.I. CATALYST

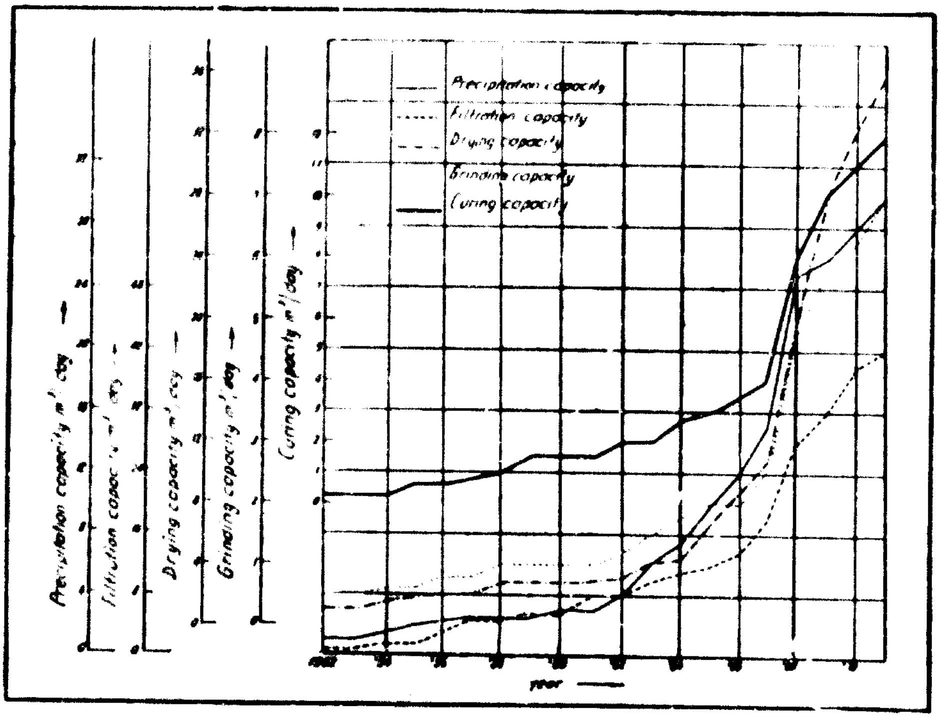


FIGURE 5

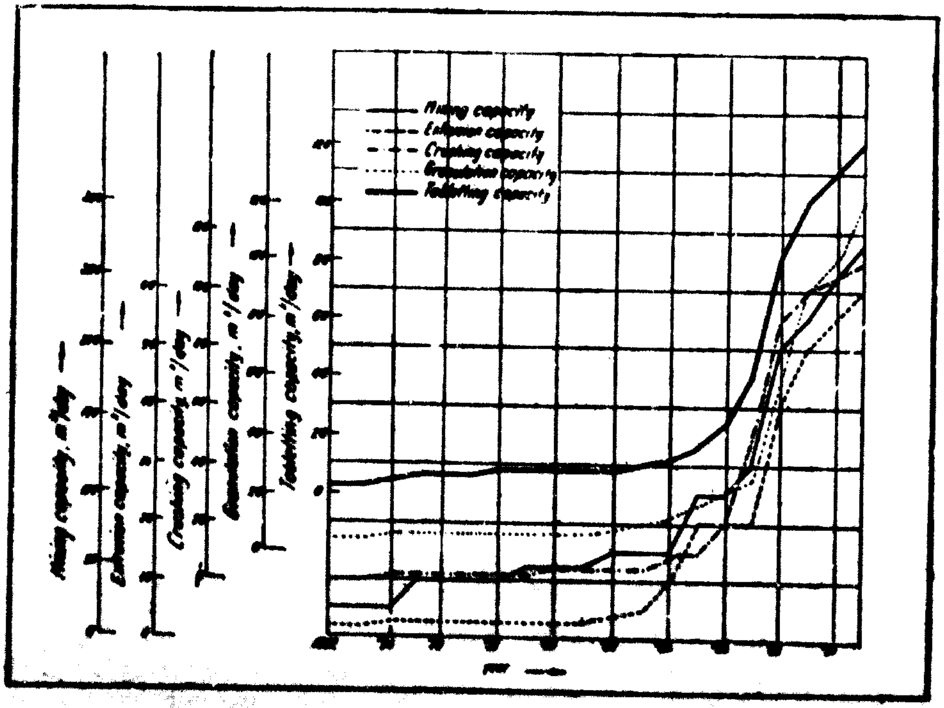


FIGURE 6

II. FORMULATION AND EVALUATION

The general characteristics of an industrial catalyst are: (a) highly developed surface, (b) appropriate pore size, (c) high mechanical strength, (d) adequate intergranular binding, (e) predictable conversion efficiency, and in some cases (f) selectivity.

All these characteristics cannot be optimally achieved in a single catalyst because of opposing factors. For example, the demand for high mechanical strength can be fulfilled (3) only by sacrificing a part of the surface area. While achieving this, there may be a growth in crystal size of the active component and elimination of favourable pores. These factors in turn will account for a fall in activity. An efficient catalyst results from a suitable compromise between these opposing factors.

While formulating a new catalyst, we have always tried to use indigenous raw materials. The objective is often to find a suitable replacement for an imported constituent. Where complete substitution is difficult, a minimum level of the imported component may be determined which would not affect activity and stability. In this way, the nickel content in our reforming catalysts was reduced to less than that in other commercial varieties. In case of low temperature shift catalysts, intensive search was made to fix the optimum copper content (4). Some of the results are given in figures 7. In our latest version, the five component catalyst system contains 23.5% CuO.

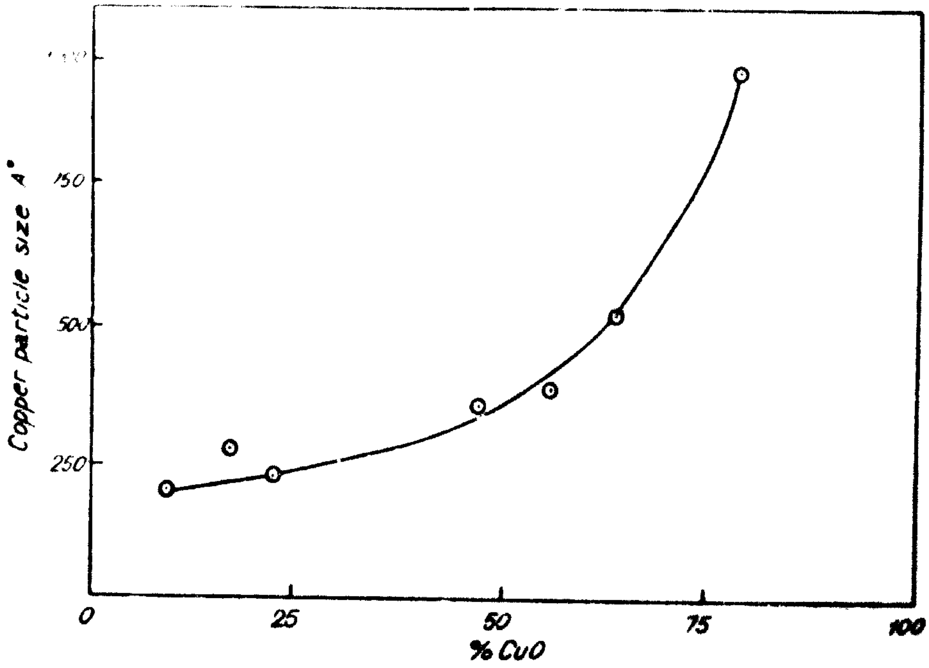


FIGURE 7. CHANGE IN THE COPPER PARTICLE SIZE WITH CuO CONCENTRATION

Some catalysts need to be highly selective. In such cases, fundamental studies are implied. In the case of a naphtha reforming catalyst for example, before attempting formulation we carried out extensive studies on the acidity of the possible carriers, the inter-action between carrier impurities and active components to form spinels, characteristics of α-and γ

-Al_2O_3 in modifying the crystal habits of the compounding medium, barriers for arresting the growth of nickel crystallites, doping of rare earths, etc. Some of the findings led us to conclude that an acceptable formulation of a naphtha reforming catalyst is possible without potash (47).

A catalyst may have all the desired physico-chemical characteristics and yet fail in a commercial reactor. Criteria for assuring the success of an industrial catalyst are as yet unknown. Only by testing the catalyst under actual running conditions, one can verify its industrial worthiness. However, it is not possible, particularly in the developing stages, to subject all the batches of the catalyst to service tests to evaluate its life. It is therefore necessary to rely on some indirect method of testing (5, 6, 15).

In our institution, the typical physical and physico-chemical methods applied are: BET technique, selective adsorption, helium and mercury density, pressure porosimetry, magnetic balance, X-ray, electron microscopy, spectroscopy, electrical conductivity, thermogravimetry, quartz microbalance, chromatography, differential thermal analysis (DTA), electron spin resonance (ESR), etc. Physico-chemical tests are extensively used at various stages of development (7, 8) in quality control of the intermediate stage and for the end product as well. These provides us with information valuable in predicting catalyst life.

The following discussion has been limited to some typical methods. These are not necessarily the best approach. Nevertheless, the approach indicated will bring into light the character of our organization as a catalyst manufacturer, and may be of help to those who intend to embark on catalyst development and manufacture.

Adsorption measurements and BET technique

Physical adsorption constitutes an important means of investigating the surface properties of heterogeneous catalysts. It can be put to good advantage in the study and assessement of the nature (9, 12) of the catalyst surface.

The estimation of surface area of solids is made by the low temperature gas adsorption using the BET equction. For reasons mentioned before, measurements are done with samples before initial activation and after, and at intervals of an actual run. Physical adsorption also forms the basis of analysis of the modification of the pore structure of carriers (10) brought about by chemical and thermal treatment.

Like physical adsorption, chemisorption is inextricably related to heterogeneous catalysis, and an understanding of the mechanism of adsorption is a prelude to the understanding of the mechanism of catalysis.

For surface area measurements and chemisorption studies, the conventional BET apparatus as well as adsorptometers and vacuum microbalance are used. The surface area values, in combination with either pore volume or pellet density, is further utilized (3, 9) in determining the average pore size and average particle diameter of a catalyst.

A new method (11) was developed for the measurement of surface areas of catalyst carriers, like silica gel.

Pressure porosimetry. Pore size distribution controls (12) the transport of reactive gases into the interior of the catalyst. If the pore diameters are very narrow, the active sites located on the finer pore walls may not be utilized at all in a flow system. From analysis of pore size distribution data of the catalyst used in commercial plants, we have seen that a fall in activity in some cases is due to the elimination of desired pores. We employ pressure porosimeters having ranges up to 15,000 lbs/sq.in. The distribution data can also be used for the evaluation of surface area (13).

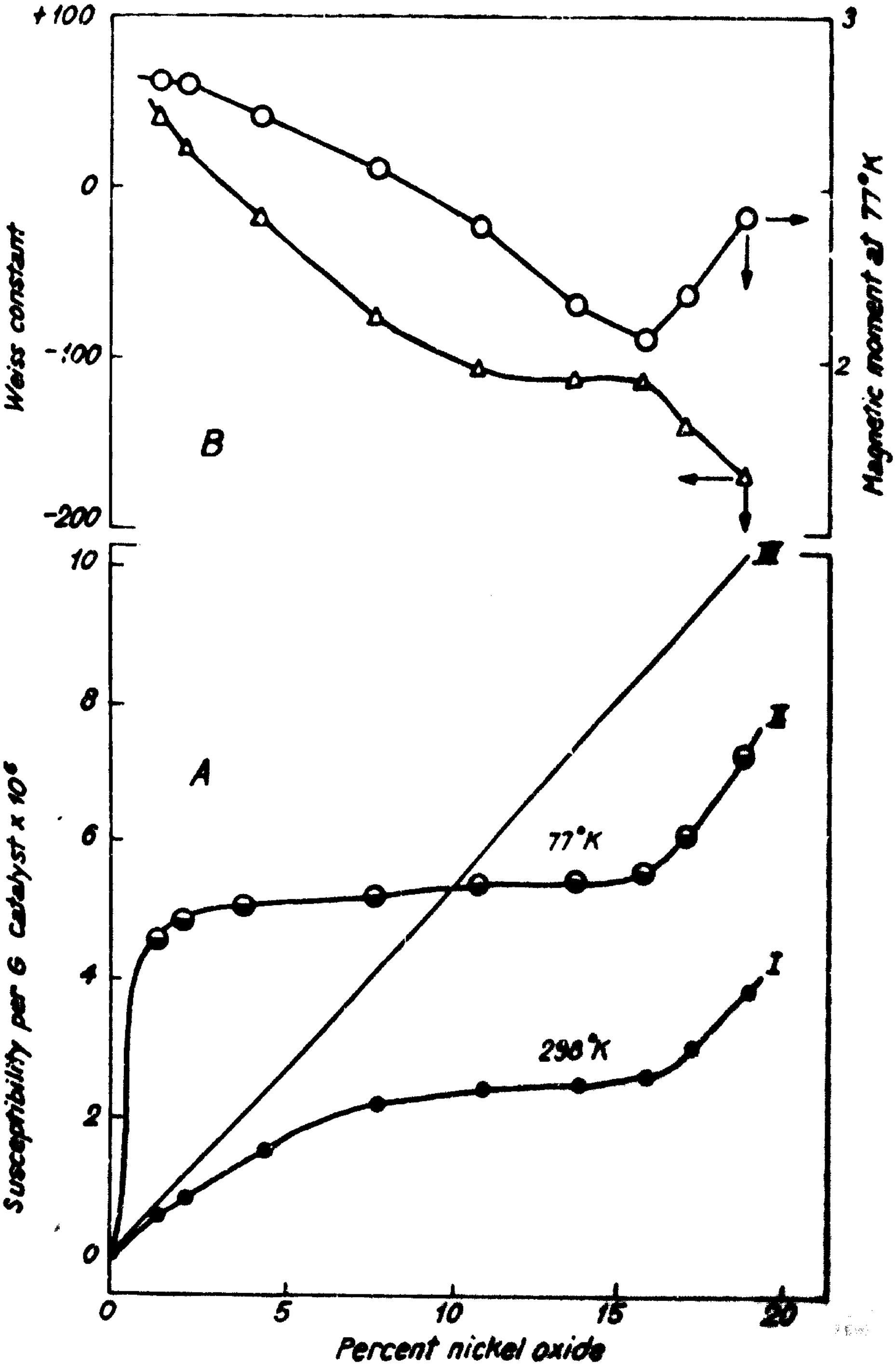

+100
0
-100
-200
Weiss constant
3
2
Magnetic moment at 77°K
B
10
8
6
4
2
0
Susceptibility per G catalyst x 10⁶
A
77°K
298°K
I
II
III
0
5
10
15
20
Percent nickel oxide

FIGURE 8

Magnetic balance. The magnetic balance is used for monitoring the dispersion of the active component of a supported catalyst during development and production, as well as for determining changes in crystal size. This technique can account for the unpaired electron in the catalyst species, the valency state, phase transformation, and the size of the crystallite. Figure 8 shows two typical applications of the magnetic technique in evaluating the dispersion and the state of oxidation of nickel as a function of Ni concentration in a nickel-alumina catalyst. Figure 8 A shows the variation in magnetic susceptibility with increasing nickel concentration.

Figure 8 B shows the changes in magnetic moment and Weiss constants as a function of nickel percentage, which is related to the nickel particle size growth.

After treating the sample under plant operating conditions for various periods of time, it is examined for growth in crystallite size of the active components as a part of the accelerated test for catalyst stability.

X-ray. X-ray analysis is one of the oldest techniques applied to the study of catalysts. In each formulation it is necessary to identify which specific phase composition contributes to the activity and which are the phases necessary for stability. Identification of these essential phases helps in the formulation of a catalyst as well as in defining the process steps for its preparation. X-ray analysis is applied by us both in development (14, 15) and in quality control work with particular reference to phase composition and crystallite size.

Electrical conductivity and ESR. The catalytic activity of a semi-conductor is determined by the position of the fermilevel at the surface of the crystal. During reaction, the concentrations of reacting and product molecules in the adsorbed phase change. This causes a change in electrical conductivity yielding valuable information on the mechanism of the surface reaction. The change in electrical conductivity of a semi-conductor is related to catalytic activity. A typical result of the work (16) done with a CuO/ZnO catalyst is represented in figure 9.

The ESR technique is applied to understand the mechanism through which heterogeneous catalytic reactions occur as well as to predict the consequence of formulation (17). While selecting the active component for a particular reaction, the state of its electron levels is examined to assess its capacity for surface interaction with reactant molecules as well as with the carrier.

Thermogravimetry. Thermograms are used for studying reduction (6), carbon deposition, gasification of deposited carbon in naphtha-steam systems, etc. The equipment in use has a working temperature up to 1,600°C, and has facilities for testing under controlled atmosphere, thereby simulating actual reaction conditions in a plant.

Thermogravimetry is also utilized for studying the decomposition of salts, such as nitrates and carbonates, and of the active catalyst components. This is of help in programming the temperature in the heat-treatment in catalyst manufacture.

DTA. A battery of such units serves to study the mechanism of release of volatiles from the surface of porous solids and the appearance of new phases in the course of catalyst preparation. Almost every batch of catalyst we produce is tested to examine the uniformity of drying, curing and grinding, in various stages of its preparation. Some typical DTA curves for a CO-conversion catalyst are presented in figure 10.

Quartz microbalance. The instrument finds application in studying the mechanism of reduction (18, 19) and for the direct measurement of carbon liberation from a hydrocarbon-steam mixture under limiting conditions, of steam to carbon ratio and temperature. This renders the instrument very useful in the development of efficient reforming catalysts. It is also used for the assessment of selectivity of a catalyst's surface by applying the process of gradual poisoning.

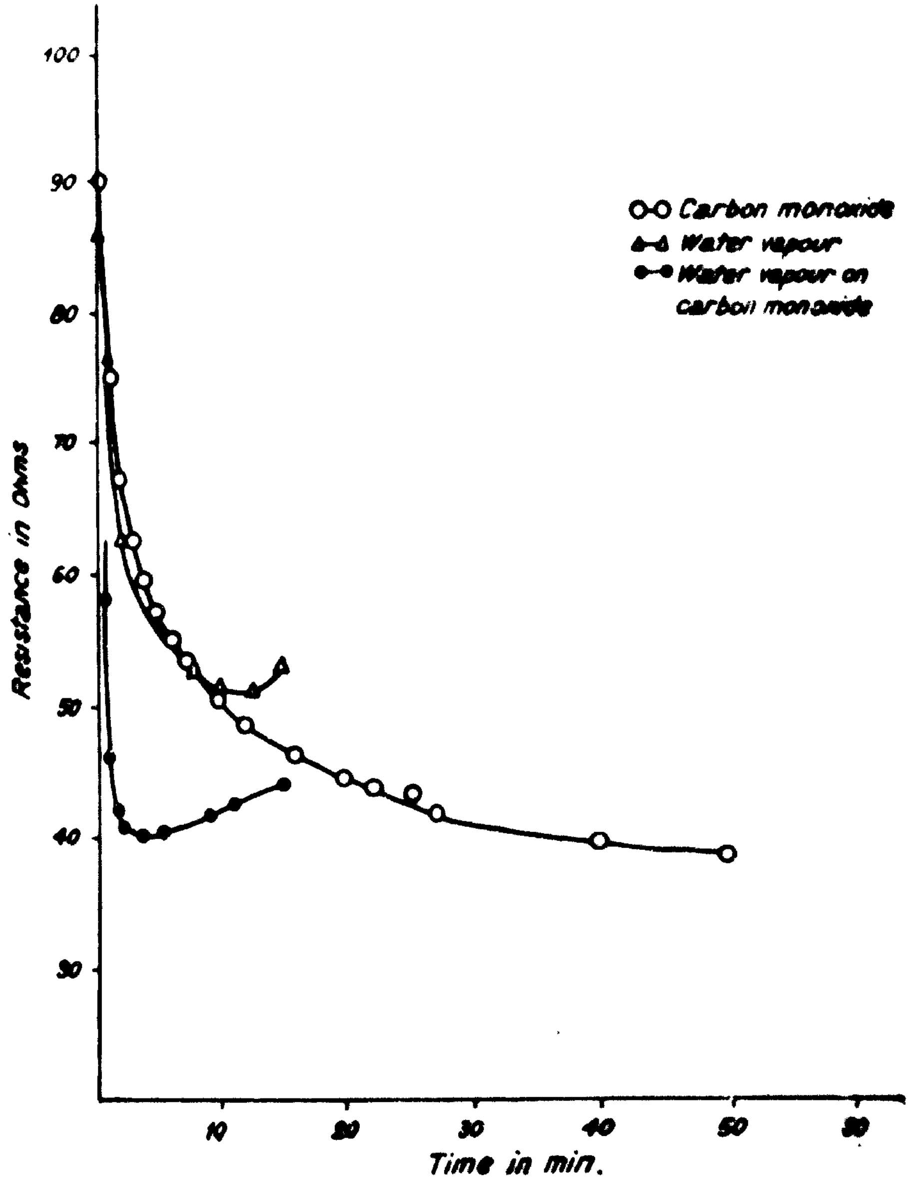


FIGURE 9

Chromatography. Gas chromatography is widely used as an analytical tool for the separation, detection and estimation of various components involved in a chemical reaction. This technique is applied in studying catalytic processes in pulse reactors for undestanding the mechanism and kinetics (20) of catalytic reactions as well as for the initial evaluation of catalyst formulations.

Activity test. All eleven varieties of catalysts manufactured by us are produced by batch processes and each batch is tested for its performance characteristics. In 1951, we had 6 units of 1,000 ml capacity employed in the measurement of activity. At present, there are 125 bench scale units, and 30 semi-pilot units. Besides these, a number of units are located in various plants. In addition, there are composite pilot plants, in which naphtha purification, primary reforming, secondary reforming, and high and low temperature CO conversion units are assembled in series.

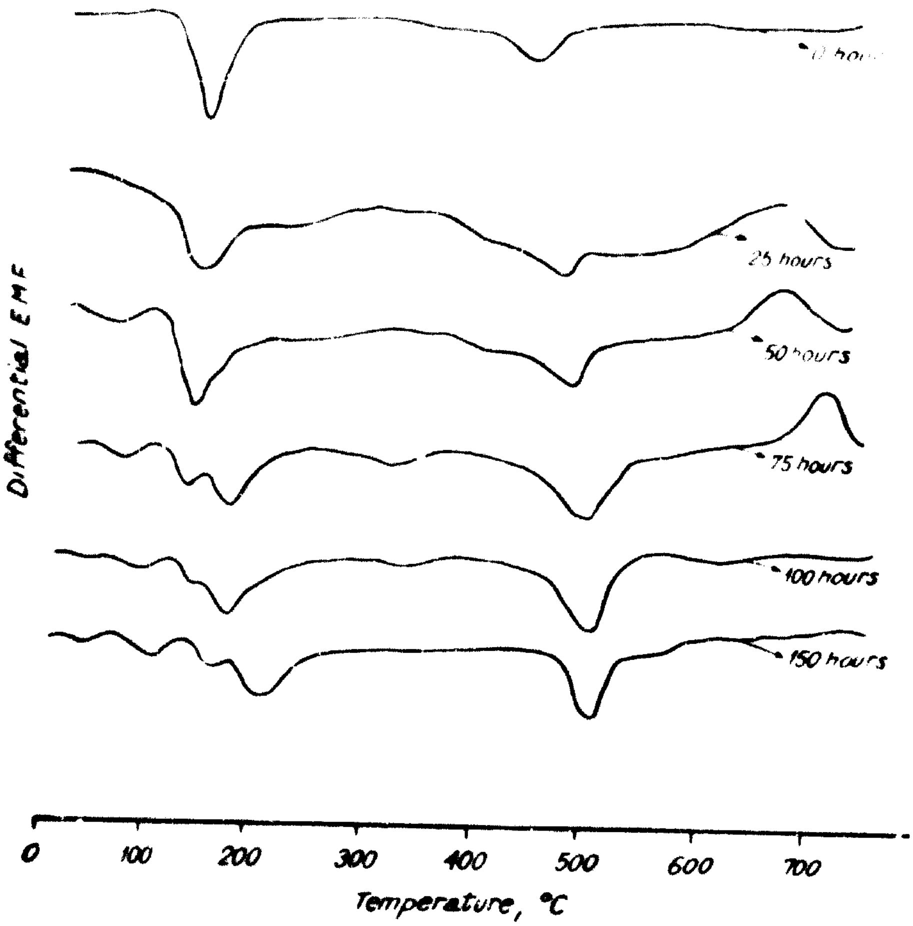


FIGURE 10. D.T.A. THERMOGRAMS OF Fe_2O_3-Cr_2O_3 SAMPLES GROUND FOR VARIOUS TIMES

III. GENERATION OF KNOW-HOW AND ITS TRANSFER TO PRODUCTION

The common unit operations involved in catalyst production are precipitation, filtration, drying, grinding, mixing, extrusion, granulation, tableting, soaking, curing etc. It is necessary to study each of these unit operations to understand to what extent it is likely to influence the quality of the product and also to assess the possible deviation of the commercial product from that of the laboratory since individually and collectively, these modify the surface and bulk properties of the solid (21).

Detailed discussions of all the variables and their effect on surface and bulk properties of finished catalyst is beyond the scope of the present paper. Some of these are discussed below in brief.

Drying. Strict control of the drying operation in the laboratory with small quantities of material can give a reproducible product but it is difficult to attain such control in large-scale operation. In commercial production, the nature of the equipment used and factors such as the thickness of the layer being dried, the ratio of the volume of the charge to the volume of the driers, rate of air recirculation, partial pressure of water vapour in the system, rate of rise of temperature etc., are much different from laboratory practice. Thus the operation of commercial units to produce a product similar to that of the laboratory can be achieved only after a number of trials.

Grinding. In the laboratory grinding is done in a mortar and pestle or pot mill. Depending on the grinding time and the reduction of size, electronic changes are induced. Grinding on a commercial scale is generally performed in a ball mill, attrition mill, colloid mill, etc. The operation in such equipment can lead to a higher degree of lattice distortion, besides changing the fermi level in the crystal of the active component (22, 23). Such changes will modify the properties of the finished product.

The energy content (22, 24) of a solid state may be expressed as Fs (δa/a, x). On grinding, the lattice distortion (δa/a) may increase from 0.05 to 0.91 per cent in the case of iron oxide, while lattice defects (x) first increase and then decrease. The nature and extent of the changes (8, 21, 25) will depend on the type of equipment and on the time of operation. A typical thermogram of a Fe_2O_3–Cr_2O_3 type shift catalyst ground for various times in a ball mill is shown in figure 10. The split which developed in the first endothermic peak probably indicates the formation of a new species, the shift of the second endothermic peak to higher temperatures represents the delayed dehydration of goethite (FeO.OH) to Fe_2O_3 and the appearance of a new exothermic peak is a phase transformation.

Tableting. In the laboratory, this operation is carried out in a hand operated hydraulic press, whereas in production plants automatic machines

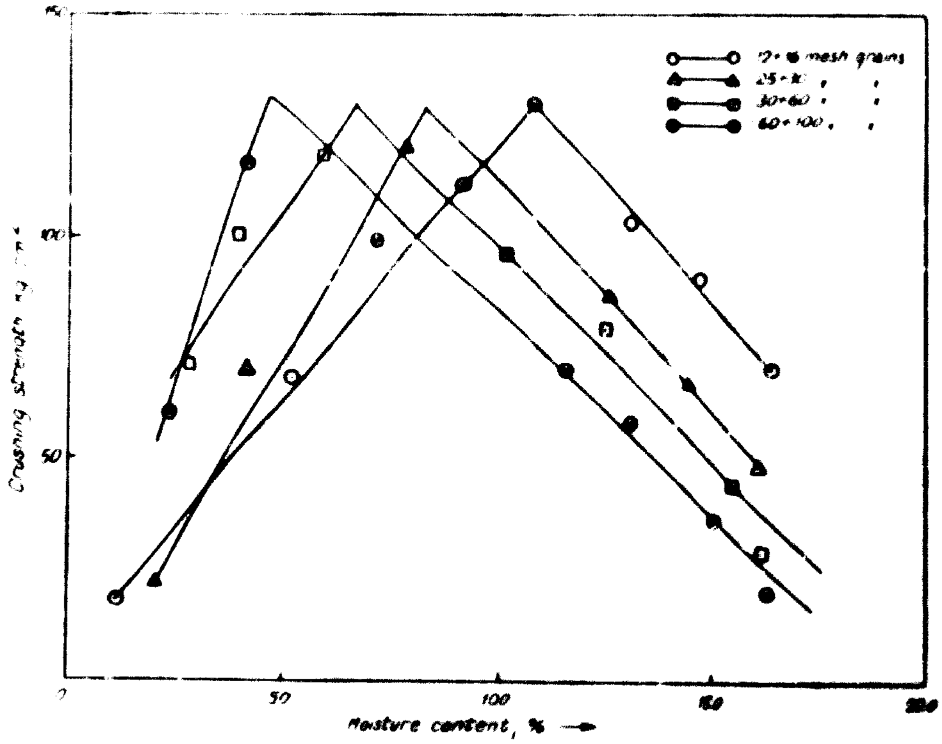


FIGURE 11 EFFECT OF MOISTURE AND GRAIN SIZE ON TABLET STRENGTH

which produce tablets of uniform size, shape and mechanical strength are used. Apart from the properties imparted by the machine, uniformity of strength of the tablets depends on particle size distribution, nature of lubricant and its mixing with the granules, moisture content, grain strength, compression etc. In figure 11, the effect of moisture and grain size on the strength of the tablet is shown. The conditions adopted in the laboratory are of little use in selecting optimum conditions in the plant. These can only be set after a series of trial runs on a large scale.

Soaking. A soaking operation is frequently adopted for incorporating promoters and active ingredients into the semifinished catalyst. The efficiency of the soaking operation depends on the concentration, impurity level (26) of the solution, temperature, the ratio of the solution to the solid and the time of soaking.

Curing. Controlled thermal treatment is necessary at various stages of production to decompose the salt of the active component or promoter, to impart adequate mechanical strength and to effect the necessary phase changes (15, 21, 27–30). Heating in any of the stages has a great influence on the activity, selectivity and stability of the catalyst. It is not possible to duplicate the laboratory conditions in an industrial furnace handling 1,000 to 2,000 kg per charge. As a result of recirculating gas in the commercial furnace, which is generally done to obtain uniformity in temperature, the curing atmosphere is laden with gases and vapours formed by the decomposition of the salt present in the catalyst. We have observed that in the case of a reforming catalyst, if oxides of nitrogen are present in the recirculation atmosphere and the curing operation is long, the material under process is non-uniform in colour, strength and activity. In the final curing, which imparts mechanical strength, a compromise between time of curing + the allowable upper limit of the temperature is to be reached, so that the active phase is not eliminated and the loss of surface area and change in pore size distribution are minimum.

The ratio of volume of the material to be charged to that of the curing furnance will depend on the amount of the volatiles expected from the material undergoing curing. This is ascertained by experimentation.

For suitable programming of the temperature rise, particularly when nitrate or carbonate are to be

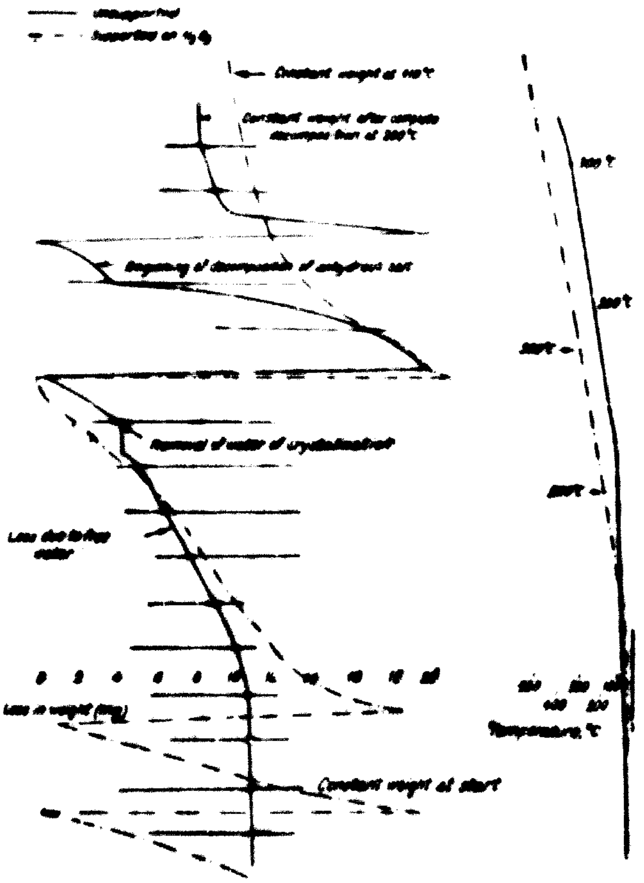


FIGURE 12. T.G.A. OF DECOMPOSITION OF [illegible]

decomposed. It is recommended that TGA investigations be carried out first. A composite DTA TGA study is useful in studying the heat treatment operation (31). Results of some typical TGA experiments are shown in figure 12.

It can be concluded that development work should be based on the preparation of samples in prototypes of the equipment employed in commercial manufacture. This will involve higher costs in the higher consumption of raw material in trial formulations of a catalyst, for example. But this will be more than compensated for by a more rapid achievement of the process know how needed for commercial production. For example, one of our reforming catalysts went into full commercial production the day our prototype studies were completed. The work started using a reaction tank of 1 m diameter and 1 m height, a steam tray dryer of 500 kg capacity, electrically heated curing furnaces 2 m deep, 1 m wide and 0.7 m high, ball mill of 0.75 m × 0.75 m size, an extrusion press and tableting machine of 100 kg/hr and 50 kg/hr capacity, respectively, etc. All the equipment used are prototypes of the commercial units. Following this route, this particular catalyst was in manufacture within 18 months of taking up the project.

IV. COMMISSIONING

The initial activation step and loading of the reactor to the designed level are ticklish operations. The catalyst may fail simply because of careless or rapid loading. Similarly, catalyst life may be in danger during periods of long shutdown if the catalyst be exposed to oxidizing conditions.

The catalyst scientists and engineers must be knowledgeable in problems of commissioning and running the commercial catalytic reactors.

A catalyst supplied to a customer must be accompanied by a commissioning schedule describing the charging, activation and loading operations, with precautions to be taken to safeguard catalyst life.

Charging. If the charging of a catalyst is not properly done there may be channelling and the catalyst may not function at its optimum. The charging procedure is comprised of cleaning the converter interior, checking the supporting grate, sieving and hand elimination of the broken tablets, careful placement to avoid tablet fall from a height which may lead to breakage leveiling the catalyst layers, and blowing air through the system to get rid of catayst dust. In case of charging reformers, certain additional steps, such, as the pressure drop measurement of each tube, are necessary. Also to assure uniform packing, a shaking device should be in operation while charging the catalyst in a primary reformer.

Activation. It is this step which imparts life to the catalyst by bringing into existence the reduced catalytic components in a fine state of division. The activation step is also responsible for bringing about changes in texture and the desired phase composition (32–35). Therefore, the reduction operation is very critical, and activity and stability both depend on the conditions under which this operation is carried out. In general, it is desirable to carry out the reduction at a very slow rate. But it is not always safe to keep the catalyst at the low temperature needed for slow reduction. It is preferable to adjust the temperature to a point where the rate of reaction is measurable and to keep the level of the reducing gas flow low.

A catalyst supplier in general stipulates an initial dose of reducing gas of 5 to 10 mole per cent. However, in most plants, the reducing gas is admitted simply by cracking the inlet valve. The gas flow is completely uncontrolled. Furthermore, insufficient inert gas or steam may be available to maintain the minimum required linear velocity through the catalyst bed. In view of these uncertainties, we have adopted the practice of sending our specialists to the plant to examine the facilities for the reduction operation before entering into a commitment to supply catalyst.

Yet another problem which catalyst manufacturers are likely to face is the attitude of the users to hasten initiating operation of the plant and start testing the functioning of the equipment. Even when there is real necessity to extend the reduction period beyond that specified, plant personnel are usually reluctant to agree to it. There are instances where such short-cut procedures have led to catalyst failure, forcing long shutdowns.

Loading. Following the reduction operation, the unit is loaded to the design level. This should be performed in steps and the system allowed to stabilize before the next increment of feed. The specialists on the job must know the temperature shock the particular catalyst can withstand without adverse effects, while recommending the incremental feed.

While commissioning, problems may arise requiring changes in accepted practice. A particular problem faced while commissioning a primary natural gas reforming catalyst in a plant is cited here. The plant employs 4 m^3 catalyst in 60 tubes of 10.5 m length each. At the site there was no provision for synthesis gas and reduction had to be carried out with natural gas. The normal reduction schedule with hydrogen did not work when natural gas was used. After reviewing the whole situation, the specialists made changes in the normal procedure. The pressure and flow of natural gas were increased and the catalyst was successfully reduced. This happened nearly four years ago and even today that batch of catalyst is at its optimum activity at 100 per cent load. Capacity to assess the problem and take appropriate and immediate decision for overcoming the problem is possible for those who have both a fundamental background and plant experience.

V. DEVELOPMENT OF EXPERTISE

The planning and development division has a catalyst commissioning group comprised of scientists and engineers well experienced in operating catalytic units and plant problems. They have also acquired thorough knowledge in the fundamentals involved in the process of commissioning. Each and every member of the specialist group performs several investigations to characterise the reduction operation with different catalysts in the central laboratory. An example of this is the reducibility of NiO dispersed on Al_2O_3 (experimental results shown in figure 13). It can be seen that the coprecipitated sample appears to be more resistant to re-

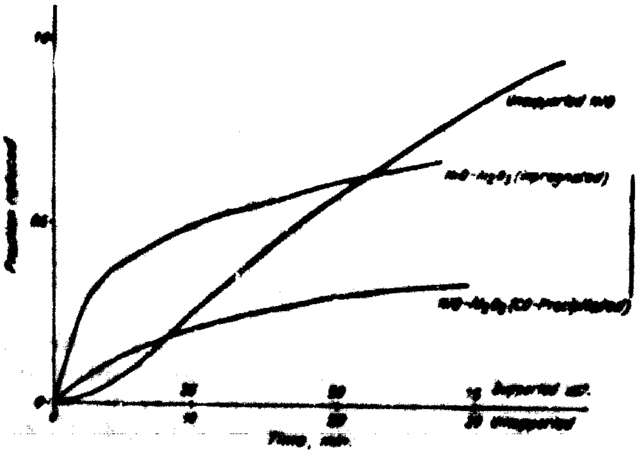
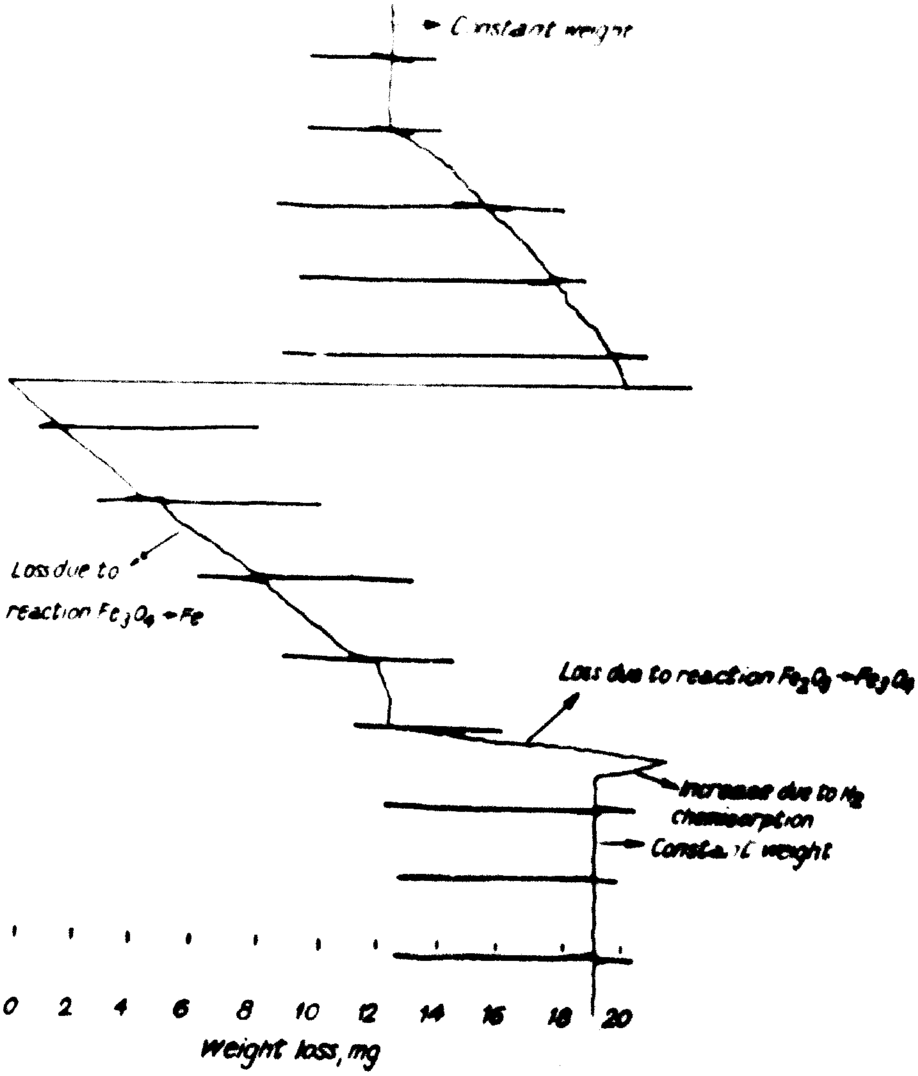


FIGURE 13. REDUCIBILITY CURVES FOR SUPPORTED AND UNSUPPORTED NiO AT [illegible] UNDER H_2 ATMOSPHERE

duction. This suggests that if necessary the reduction operation of the coprecipitated batch may be done at a higher temperature using a greater concentration of reducing gas without harmful effects on activity and life of the catalyst. Other typical reduction curves with high and low temperature shift conversion catalysts are presented in figures 14 A and 14 B.



URE 14 A. THERMOGRAM OF REDUCTION OF Fe_2O_3-Cr_2O_3 CATALYST AT 400°C IN H_2 ATMOSPHERE

The curves indicate that at the initial period, hydrogen is chemisorbed at the reduction temperature employed. Such information helps us in avoiding the danger of introducing higher concentrations of reducing gas on the basis of hydrogen consumption just at the commencement of reduction operation.

In our organization, all new hands are first sent to commercial units to understand the problems associated with the operation of converters. After completion of plant training, they are sent to various catalytic units in the country using our catalysts to collect plant data and follow the behaviour of the catalyst since the date of commissioning. They also examine the physical and physico-chemical characteristics before and after use. During this period they feed scientists engaged in fundamental work with plant data and problems. After completion of this study, which normally extends for 2 years, they are absorbed into research programmes. A similar number of research staff go out for plant studies and discussions with users. In the last two decades this procedure has yielded sufficient numbers of specialists having adequate experience in taking up the full responsibility of commissioning.

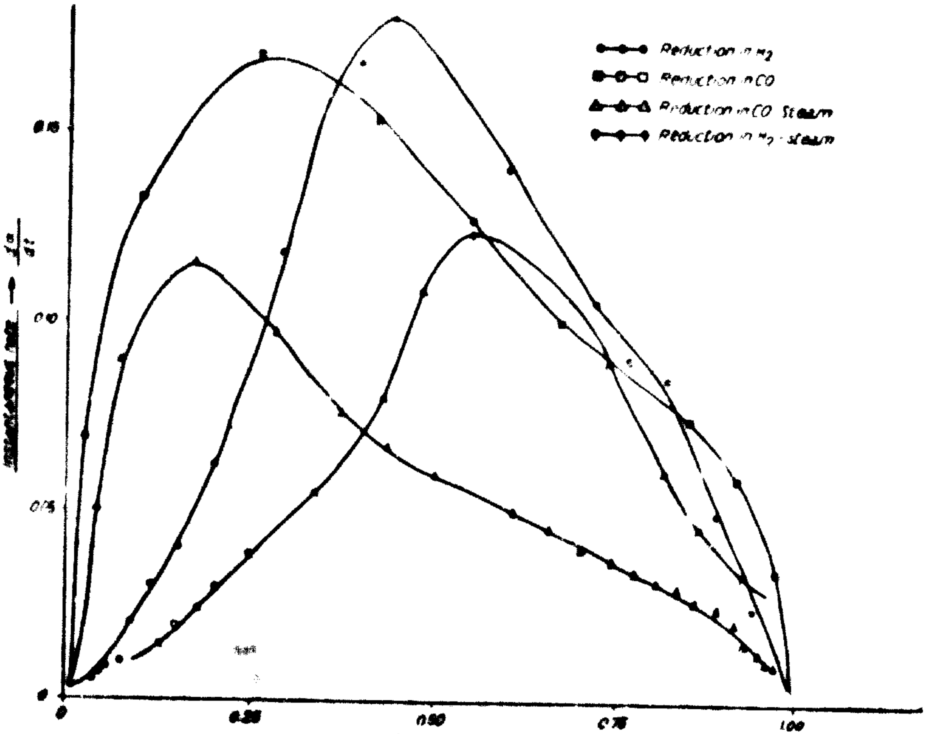


FIGURE 14 B. INSTANTANEOUS REDUCTION RATES OF CuO-ZnO CATALYST AT 200°C

VI. USE

Fertilizer catalysts in general are used in (A) desulphurization, (B) high and low temperature shift conversion, (C) primary and secondary reforming, (D) methanation, (E) synthesis, (F) ammonia oxidation, and (G) sulphuric acid. The steps leading to ammonia synthesis are considered below.

A) DESULPHURIZATION

Sulphur compounds are catalyst poisons and desulphurization of feed stock is invariably a part of the catalytic process scheme. Up to 1967, we were concerned with the purification of coke-oven and semi-water gas employing alkali scrubbing and dry box purification. Since 1953 we have been using hydrated iron oxides of our own make as a substitute for import (36–38). Our product is used both in atmospheric and pressure operated plants.

With the change in the feedstock to nuphtha, very rigorous purification steps are installed to protect the catalysts, which are highly sensitive to sulphur. The process employs a hydrodesulphurization step in the presence of either cobalt-molybdenum or nickel-molybdenum catalysts to convert organic sulphur compounds to H_2S, followed by ZnO at 350–400°C to retain the H_2S. Considering, the non availability of costly ingredients in our country, we are developing (39) an alternative to conventional hydrodesulphurization catalysts. The formulation at hand is of 80 per cent relative activity.

For retention of H_2S our product finds wide application. It retains its initial activity up to 20 per cent fouling. A second formulation is used as guard catalyst. The efficiency of ZnO depends to a great extent on the particle size and pore geometry. Our studies show that pores in the region of 300–500 Å are most effective (40).

B) WATER GAS SHIFT REACTION

(a) HIGH TEMPERATURE

Carbon monoxide reacts with steam to produce hydrogen ($CO + H_2O \rightarrow CO_2 + H_2$) in the presence of a catalyst. Since our appearance in the field in 1951, various investigations (41–43) enabled us to improve catalyst reactivity and stability to cope with the demand. of process technology for higher space velocities, lower steam to gas ratios and higher operating pressures. At present we manufacture 3 types, meeting the demand of 18 fertilizer factories in the country as well as abroad.

(b) LOW TEMPERATURE

Where as in old plants copper liquor and liquid nitrogen washes are used to remove CO from synthesis gas, in newer plants, purification is effected by methanation. Methanation could be included in the process technology because of the low temperature shift catalyst which can bring the level of CO down to 0.2 per cent. This is one of the most sophisticated and critical among catalysts. It is highly sensitive to sulphur and its fall in efficiency due to poisoning or thermal sintering leads to high purge loss.

In parallel with efficient sulphur removal to protect this catalyst, we have improved it with respect to sulphur resistivity. The improved variety has the percentage composition Cu–23, ZnO–20, Fe_2O_3–8, Al_2O_3–42 and TiO_2–5. This catalyst is characterized for its high sulphur tolerance and

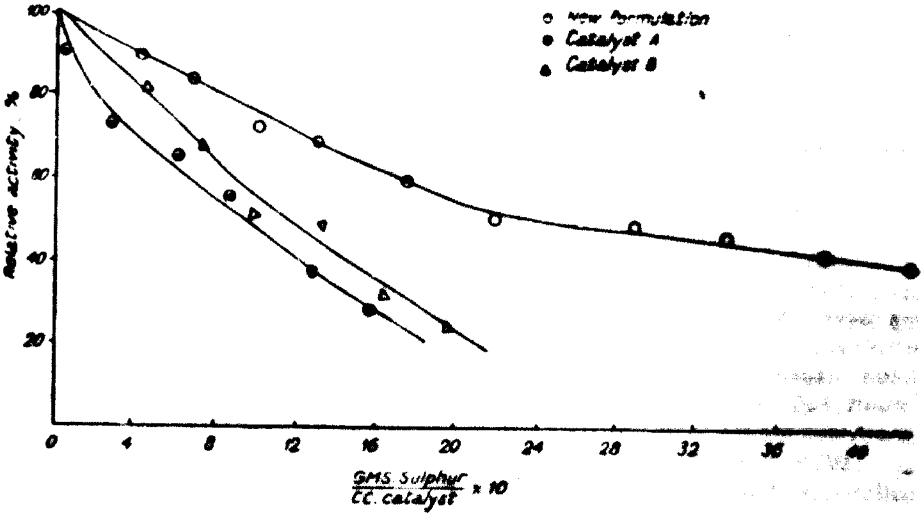


FIGURE 15. SULPHUR POISONING OF LOW TEMPERATURE CATALYST

high activity. Figure 15 shows the tolerance of the new formulation compared to that of other commercial catalysts.

C) REFORMING

Reforming is broadly classified into primary and secondary operations. The family of reforming catalysts is comprised of refractory based NiO systems (44–46).

Primary. Our first production batch of natural gas reforming catalyst employed in primary reforming has been on line at Namrup for nearly four years.

The naphtha reforming process had a very long development period prior to its industrial exploitation. Some of the elementary steps indicated below show the mechanism through which reforming takes place.

1. $C_nH_m + nH_2O \rightarrow nCO + \left(\frac{2n+m}{2}\right) H_2$
2. $CO + H_2O \rightarrow CO_2 + H_2$
3. $2CO \rightarrow CO_2 + C$
4. $C_nH_m \rightarrow nC + \frac{m}{2} H_2$
5. $C_nH_m \rightarrow$ Coke.

Carbon deposition on the catalyst under certain conditions (steps 3, 4 and 5) can lead to an increase in pressure drop, change in catalyst function and some time crumbling of the catalyst (15, 33, 46). Even today catalysts in use are still sensitive to carbon deposits. The incorporation of alkali and alkaline-earth oxides accelerates gasification of deposited carbon (47). We have developed a catalyst which possesses a high degree of selectivity and does not permit carbon formation on the catalyst surface (33). In this formulation there is no potash or other component which will volatilize and deposit on down-stream equipment. Depending on the quality of feedstock, we market two different varieties.

Secondary. Gas from the primary reformer is received by the secondary along with a calculated volume of air to give the required nitrogen content in the synthesis gas. Oxygen reacts with part of the CH_4 and H_2 as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O;\quad 2H_2 + O_2 \rightarrow 2H_2O$$

These exothermic reactions result in the development of very high temperatures, particularly at the top of the units, and the catalyst in use must have high thermal stability (29). No doubt, in the secondary reformer the conditions are predominently under thermal control (48). Nevertheless, the requirements of very close approach to chemical equilibrium, to assure a low methane content at the exit, brings in the necessity for effective catalysis as well.

Our catalyst displays high thermal resistance and low methane leakage. For reforming methane rich gas in one stage, we make autothermal reforming catalysts containing 2.5, 5.0 and 10.0 per cent Ni, to be used in series. These catalysts have been in commercial use since 1963.

D) METHANATION

Exposure of a synthesis catalyst to even traces of oxides of carbon for long periods of time causes deactivation. In new plants, liquid purification is replaced by methanation. The high throughput per volume of catalyst and the service conditions for bringing $CO + CO_2$ from a level of 0.3 per cent to a few ppm demands high intrinsic activity. At the same time, temperature shocks may occur due to surges of CO+CO_2, because of a fall in activity of the low temperature shift catalyst or trouble in CO_2 scrubbing. Therefore a commercial catalyst must have adequate thermal stability.

E) SYNTHESIS

Since the time of Haber and Bosch, the principal constituent of the catalyst used for ammonia synthesis has been Fe_3O_4 in combination with promoters. The introduction of high capacity synthesis converters and the lowering of operating pressure made it necessary to increase the activity and thermal stability of the catalyst. Keeping the primary component, Fe_3O_4, the needed improvements could be effected by altering the sequence of addition of promoters to the melt and changing the formulation of promoters. We have developed a catalyst containing four promoters which meets present day requirements.

REFERENCES

1. K. R. Chakravorty,
   – Technology, 3 (1966), 2.
2. S. P. Sen, Bhaskar Sen & D. K. Mukherjee,
   – Paper presented in the symposium on „Chemicals & Oils from Coal" held at Central Fuel Research Institute, Jealgora, Dec. 1969.
3. V. K. Puri, N. C. Ganguli & S. P. Sen,
   – Ibid.
4. N. Ray, S. K. Nath, A. Sarkar, D. P. Das & S. P. Sen,
   – Communicated to Technology.
5. B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli & S. P. Sen,
   – Technology, Vol. 8, No. 2 (1971).
6. B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli & S. P. Sen,
   – Communicated to Technology.
7. J. Mishra, D. K. Mukherjee & S. P. Sen,
   – Technology, Vol. 7, No. 4 (1970), 231.
8. B. R. Arora, N. K. Mandal, R. L. Chowdhury, N. C. Ganguli & S. P. Sen,
   – Technology, (in press).
9. S. P. Sen, B. R. Arora & N. C. Ganguli,
   – Technologie, Vol. 4, No. 3 (1967)
10. S. R. Naidu, R. N. Tewari, N. C. Ganguli & S. P. Sen,
    – Communicated to Technology.
11. R. N. Tewari, S. R. Naidu, N. C. Ganguli & S. P. Sen,
    – Technology, Vol. 7, No. 3 (1970), 134.
12. S. P. Sen & Bhaskar Sen,
    – Technology, Vol. 5, No. 1 (1968), 3.
13. S. R. Naidu, R. M. Cursetji, D. K. Gupta, N. C. Ganguli & S. P. Sen,
    – Technology, Vol. 7, No. 4 (1970), 225.
14. D. K. Mukherjee, J. Misra, S. P. Sen & K. R. Chakravorty,
    – Technology, Vol. 8, No. 3 (1971).
15. D. K. Mukherjee, S. K. Ghosh, M. Sundaram & S. P. Sen,
    – Technology, Vol. 8, No. 4 (1971).
16. G. Sengupta, S. C. Chandak, H. S. Ahluwalia & S. P. Sen,
    – Technology, (in press).
17. P. K. Ghosh, J. S. Tiwari, S. C. Sinha, N. Ray & A. Sarkar,
    – Paper presented in the symposium on „Chemicals and Oils from Coal" held at Central Fuel Research Institute, Jealgora, Dec. 1969.
18. S. R. Naidu, G. Sengupta, D. K. Gupta & S. P. Sen,
    – Technology, Vol. 7, No. 3 (1970), 191.
19. S. R. Naidu, D. K. Gupta, H. Mahapatra, N. C. Ganguli & S. P. Sen,
    – Technology, Vol. 9, No. 2 (1971).
20. S. R. Naidu, A. K. Banerjee, N. C. Ganguli & S. P. Sen,
    – Communicated to Technology.

21. S. K. Nath, B. R. Arora, S. C. Chandak, N. C. Ganguli & S. P. Sen,
   — Technology, Vol. 8, No. 1 (1971), 12.
22. R. Schrader, U. W. Stadter,
   Acta Chim. Acad. Sci. Hung. 55, 39 (1968).
23. R. Schrader,
   — Chem. Techn. 11, 159 (1959).
24. R. Schrader and W. Vogelsberger,
   — Z. Anorg. Allg. Chem. 367 (3-4), 187. (1969).
25. B. R. Arora, H. Mahapatra, T. Achari, N. C. Ganguli & S. P. Sen,
   — Technology (in press).
26. S. P. Sen & B. R. Arora,
   — Technology, Vol. 1, No. 2 (1964), 33.
27. B. R. Arora, R. K. Banerjee, N. K. Mandal, N. C. Ganguli & S. P. Sen,
   — Technology, Vol. 8, No. 3 (1971)
28. B. R. Arora, N. K. Mandal, R. K. Banerjee, N. C. Ganguli & S. P. Sen,
   — Communicated to Technology.
29. D. K. Mukherjee, H. Roy, S. K Adhya, L. Bahadur & S. P. Sen,
   — Technology, Vol. 8, No. 3 (1971).
30. M. S. Chhabra, V. K. Puri, P. K. Sengupta, N. B. Bhattacharyya & S. P. Sen,
   — Technology, Vol. 8, No. 3 (1971).
31. S. R. Naidu, B. R. Arora & S. P. Sen,
   — Technology, Vol. 6, No. 4 (1969), 190.
32. S. R. Naidu, H. Mahapatra, D. K. Gupta, N. C. Ganguli & S. P. Sen,
   — Communicated to Technology.
33. S. P. Sen, D. S. Mazumdar, P. K. Hazra, R. Prasad, S. K. Ghosh & N. Bhattacharyya,
   — Paper presented in the 24th Annual General Meeting of the Indian Institute of Chem. Engineer held at Kanpur, Feb. 1972.
34. N. B. Bhattacharyya, M. Sundaram, R. K. Sharma & S. P. Sen,
   — Ibid.
35. B. R. Arora, R. K. Banerjee, N. K. Manda, N. C. Ganguli & S. P. Sen,
   — Ibid.
36. N. Bhattacharyya and P. K. Gour,
   — Technology, Vol. 1, No. 4 (1964), 53.
37. A. R. Chatterjee, N. B. Bhattacharyya & S. P. Sen,
   — Technology, Vol. 8, No. 1 (1971), 40.
38. M. Sundaram and N. B. Bhattacharyya,
   — Technology, Vol. 1, No. 3 (1970), 130.
39. N. C. Mehta, T. S. R. Prasad Rao, S. K. Singh, N. Bhattacharyya & S. P. Sen,
   — Technology, Vol. 7, No. 4 (1970), 239.
40. P. K. Gour, A. R. Chatterjee, M. S. Chhabra & N. B. Bhattacharyya,
   — Technology, Vol. 7, No. 3 (1970), 126.
41. S. P. Sen, B. Sen & K. R. Chakravorty,
   — Indian J. Tech., Vol. 1, No. 9 (1963), 341.
42. S. P. Sen, S. K. Singh, Bhaskar Sen & K. R. Chakravorty,
   — Indian, J. Tech., Vol. 2, No. 8 (1964), 265.
43. S. P. Sen, S. C. Aggarwal & K. R. Chakravorty,
   — Indian J. Appl. Chem. Vol. 29, Nos. 5—6 (1966), 181.
44. S. P. Sen, N. B. Bhattacharyya, D. K. Mukherjee & K. R. Chakravorty,
   — Indian J. Appl. Chem. Vol. 31, Nos 1—2 (1968), 44.
45. R. L. Chowdhury, B. P. Sahay, D. K. Mukherjee, N. B. Bhattacharyya & S. P. Sen,
   — Technology, Vol. 8, No. 1 (1971), 17.
46. D. K. Mukherjee, J. Misra, S. P. Sen & K. R. Chakravorty,
   — Technology, Vol. 8, No. 3 (1971).
47. D. K. Mukherjee, J. Misra, R. L. Chowdhury & S. P. Sen,
   — Communicated to Technology.
48. S. A. Kamaev,
   — Chem. Abstr. 51 (1957), 20738.

PHOSPHORIC ACID AS A CATALYTIC MEDIUM FOR ORGANIC REACTIONS[1]

L. M. SHORR*

I. INTRODUCTION

CHEMICAL TRANSFORMATIONS IN SULPHURIC ACID. THE CO-PRODUCT AMMONIUM SULPHATE PROBLEM

Liquid concentrated sulphuric acid serves as a catalytic medium for a number of commercially important reactions. Oxime derived caprolactam and methyl methacrylate produced from acetone cyanohydrin are among the better known. At the conclusion of these transformations, the acid is commonly neutralized with ammonia to produce ammonium sulphate as co-product. In some instances, neutralization is indispensable for the liberation and recovery of the organic compound produced. In many of these processes, the acid is present in large excess. It serves both as catalyst and solvent or liquid medium for the efficient transfer of the sometimes very considerable heat generated by the reaction. Therefore, several tons of the co-product salt are often obtained for each ton of primary product.

In 1968, about 6 million tons of the sulphate were recovered from world caprolactam manufacture alone, and the figure has grown considerably since. Co-product ammonium sulphate has been the major source of this material in the United States of America in recent years. The total world consumption of the salt in 1966/67 was less than 10 million tons. The market trend is towards a reduction in consumption of this compound as a fertilizer, especially in developing countries where ammonium sulphate (20.5% N) is being replaced by urea (46% N). Not only has an over-capacity for ammonium sulphate thus developed, but a waste disposal problem may even be encountered in certain geographic areas.

EFFORTS TO LIMIT AMMONIUM SULPHATE CO-PRODUCTION

There has been a considerable development effort in recent years to find alternate routes to these organic products which avoid, or at least decrease the amounts of co-product ammonium sulphate. To accomplish this end, both new chemistries have been proposed and known routes have been modified. The photonitrozation of cyclohexane and the Union Carbide caprolactone route to caprolactam are examples of the former approach. The Stamicarbon nitrophosphate process, which halves ammonium sulphate production, is an example of the latter.

But these are at best only a partial solution to a general problem embracing many chemical reactions. Efforts to effect some of these transformations with catalytic quantities of acidic materials have so far not borne fruit. Raw material costs are generally the major cost component;

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.122/6.

* IMI (Institute for Research and Development), Haifa, Israel. The author acknowledges the co-operation of A. Baniel, R. Blumberg, M. Neuberger, J. Segall and A. Varsanyi and is grateful to IMI for permission to publish this paper.

very high if not essentially quantitative conversions are required, and these have not been achieved by conventional catalysis.

Polyphosphoric acid has been extensively studied as an acid catalyst in a wide variety of organic reactions (1). It has also been applied to the Beckmann rearrangement (2–5). Acids of concentrations equivalent to 110% H_3PO_4 or higher have been used, the impression being held that lower lactam yields were a necessary corollary to lower acid concentrations. However, the industrial application of polyphosphoric acid is seriously impeded by its high viscosity (see table I).

TABLE I

KINEMATIC VISCOSITY[a] OF PHOSPHORIC ACID SOLUTIONS

Temperature (°C)	100% H_3PO_4	110% H_3PO_4	115% H_3PO_4
25	100	2,200	
30	81	1,600	
40	53	810	
50	36	410	
60	25	270	1,500
80	14	100	600
100	9.2	50	250
120	6.2	29	120
140	4.5	18	68
160	3.5	13	41

Source: „Phosphoric Acid" by Monsanto.

[a] Viscosities expressed in centistokes.

CHEMICAL TRANSFORMATIONS IN PHOSPHORIC ACID

Studies in our laboratories have shown that contrary to the prior contention, excellent yields of caprolactum can be achieved in 100% H_3PO_4. In fact, many of the subject transformations can be efficiently catalysed by concentrated phosphoric acid. Its substitution for sulphuric acid allows for the coproduction of mineral acid derivatives, such as ammonium phosphate, of higher value than those obtained with sulphuric acid. However, it should not be assumed that this advantage can be realized by a one to one translation from sulphuric acid based processes. The chemical characteristics of the two acids are not identical, and the optimal process conditions using the one are not necessarily those when using the other.

There have been two significant deterrents to the application of phosphoric acid for such purposes in the past. Clean acid must be used lest impurities emanating from the catalytic medium contaminate the product. Pure, furnace acid is too expensive to serve in this capacity; wet process acid is too impure. Technologies developed by IMI (6) for:

(a) the production of phosphoric acid using hydrochloric acid as the primary acidulant, and

(b) the purification of wet process phosphoric acid

overcome these drawbacks and provide clean acid of the necessary characteristics at an economically viable price, being particularly attractive for developing countries.

Let us assume that an equal weight of phosphoric acid is substituted

TABLE II

PRICES OF INORGANIC CHEMICALS ($/TON)[a]

H_2SO_4	20
H_3PO_4 (100%)	70
NH_3	40
$(NH_4)_2SO_4$	15 ( )
$(NH_4)_2HPO_4$	70

INORGANIC REAGENT ECONOMICS (PER TON OF ACID)

Sulphuric acid route: $ 13.70 cost
Phosphoric acid route: $ 10.40 credit

[a] Prices for phosphoric acid and ammonium phosphate are directly related. Therefore, variations in charges for the former are balanced by credit for the latter.

for sulphuric acid in a given application, all other process parmeters being taken as equal. The cost data given in table II show the advantage of the substitution, even assuming the marketability of ammonium sulphate at $ 15 per ton. A process charge of $ 13.70 can be converted to a $ 10.40 credit per ton of acid employed.

This approach to better economics is applicable to a wide variety of chemical processes which include aromatic nitration and hydrocarbon separations. Of these, the Beckmann rearrangement for caprolactam production and the Ritter reaction used in the synthesis of N substituted amides have been selected for illustration.

II. BECKMANN REARRANGEMENT

SOURCES OF THE PROBLEM

The Beckmann rearrangement of cyclohexanone oxime to caprolactam

entails two major technological hurdles: its high exothermicity and the basic character of the product lactam.

The calculated reaction enthalpy of the transformation is −45 Kcal mol. This is one reason why it has been difficult to apply heterogeneous catalysis to this transformation. In commercial practice, a weight ratio of sulphuric acid to oxime of 4:1 is commonly used. The excess acid serves to ensure efficient heat dissipation, minimizing by-product formation. Since the lactam is a weak base, it is bound by the acidic medium and can be liberated only by neutralizing all the acid present. This leads to the coproduct problem.

BECKMANN REARRANGEMENT IN PHOSPHORIC ACID

A comparison of the viscosity data for 100% and 115% H_3PO_4 (table I) shows the marked technological advantage to be gained by the use of the more dilute reaction medium. On the other hand, hydrolysis of both the oxime and the amide is sensitive to the concentration of the acid. However, with good control of the reaction parameters, efficient, conversions are achievable. Two modes of operation on a laboratory scale were examined — batch reaction and in a continuous manner.

BATCH REACTIONS

Similar to the Beckmann rearrangement with concentrated sulphuric acid, an excess of phosphoric acid is needed to achieve high yields of caprolactam. Quantitative conversions and yields of 95% and higher can be obtained when 100% H_3PO_4 is used in a system containing weight ratios of acid to oxime between 4.5 : 1 and 8 : 1.

Reactions were performed by immersing stirred solutions of the oxime in the acid into a bath maintained at approximately 140°C for a period of 5 to 6 minutes. Even on a small laboratory scale, the high rearrangement enthalpy could not be efficiently dissipated and temperatures developed in the reaction mixture which were five to ten degrees higher than that of the bath. In view of the short reaction times required, a continuous process was indicated.

CONTINUOUS REACTIONS

The bench reactor was a stirred 35 ml jacketed chamber heated by pumping hot glycerine (140–150°C) through the jacket. The feed solutions of oxime in phosphoric acid were introduced through a 60 ml preheater maintained at 70–75°C by a hot water jacket. The residence time was regulated by the flow rate of the feed, while the reaction volume was maintained at 17 ml by regulating a reactor bleed off system.

By operating in this manner, the temperature within the reactor remained constant at 2°C above that of the bath and the residence time was only six minutes. In this apparatus quantitative yields of lactam were obtained at 97 per cent conversion using an acid to oxime ratio of 6 : 1. With half this amount of acid, 94 per cent yields were at 92 per cent conversion.

PRODUCT RECOVERY

Caprolactam can be separated from the reaction mixture by dilution with water and ammoniation of the phosphoric acid to pH 7. The behaviour of this system parallels that of solutions of caprolactam in sulphuric acid. The choice of ammoniation conditions is based on the phase diagram for the system $(NH_4)_2O-P_2O_5-H_2O$ (7), being selected to cause ammonium phosphate to precipitate directly as a solid phase. At temperatures below 40°C and pH up to 7, an upper phase of caprolactam, water and traces of phosphoric acid are obtained. The lower liquid phase is a phosphate brine saturated with respect to the solid phase. The caprolactam can be extracted from the upper phase with a solvent such as chloroform.

III. RITTER REACTION

BACKGROUND

A number of methods are known for the preparation of N-substituted amides. Thus, for example, carboxylic acids, as such or in the form of their acid halides or anhydrides, can be reacted with amines; unsubstituted amides can be alkylated on the nitrogen atom; oximes can be rearranged in the presence of acidic reagents, etc. A versatile procedure, and one which could lend itself well to industrial application because of its applicability to basic, relatively inexpensive industrial raw materials has been advanced by Ritter (8). In this method, nitriles interact with olefins or hydrated olefins (secondary or tertiary alcohols) in the presence of large quantities of concentrated sulphuric acid. The N-substituted amide is separated from the hydrolysed product after neutralization:

$$RCN + \overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}} \xrightarrow[2)\ H_2O,\ NH_3]{1)\ H_2SO_4} RCONH-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}H + (NH_4)_2SO_4$$

The [illegible] sulphate problem presents itself once again. Furthermore, the use of sulphuric acid in the application of this reaction to sensitive compounds is somewhat limited. For example benzene sulphonic acid has been preferred to sulphuric acid when aromatic compounds are employed. Easily polymerizable substrates such as acrylonitrile have also proved to be too sensitive to sulphuric acid media.

Attempts have been made to substitute the sulphuric acid use in the Ritter reaction by polyphosphoric acid. However the poor yields obtained forced the conclusion that the application of polyphosphoric acid in this transformation is impractical (16).

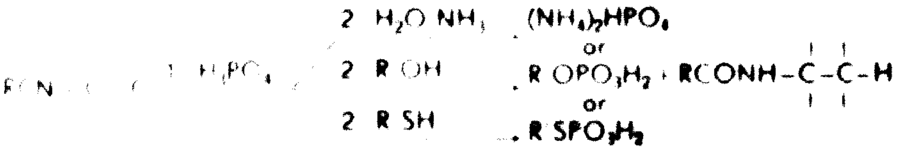
RITTER REACTION IN PHOSPHORIC ACID

Only one attempt appears to have been made previously to use phosphoric acid for this purpose (9). A yield of only 4.2 per cent of amide was obtained.

It has been found in our laboratories that essentially quantitative yields can nevertheless be obtained using 100 per cent phosphoric acid, instead of concentrated sulphuric acid, although H_3PO_4 of still lower concentration (85 per cent) can be applied with reasonably good results. Advantages are thereby provided in that (a) alkali and/or ammonium phosphates are obtained as co-product (b) aromatic and other sensitive materials present in this reaction medium are inert.

It has also been found that treatment of the olefin nitrile reaction product with compounds containing the hydroxyl or sulphhydryl group prior to the introduction of water or neutralization, produces the corresponding mono substituted phosphoric acid derivatives as by products.

The following outline represents three alternatives when using phosphoric acid.



$$RCN + C{=}C + H_3PO_4 \rightarrow \begin{cases} 2\ H_2O\ NH_3 \rightarrow (NH_4)_2HPO_4 \\ \text{or} \\ 2\ R'OH \rightarrow R'OPO_3H_2 + RCONH{-}C{-}C{-}H \\ \text{or} \\ 2\ R'SH \rightarrow R'SPO_3H_2 \end{cases}$$

The substituted phosphoric acid derivatives have found application as lubricant additives, components in corrosion resistant coatings, in leather tanning and water proofing, as insecticides and larvacides, as emulsifiers and as components in plastics to impart fire resistance and plasticity.

To effect these reactions it is only necessary to contact the olefin, nitrile, and acid in a liquid mixture at ambient temperature for approximately one hour and then add the second component, the alcohol, thiophenol, etc.

It is important to note that when using phosphoric acid, under preferred conditions for reaction, i.e. ambient temperature and absence of additional solvent or diluents, the molar ratio of acid to nitrile should be at least 2 : 1 to produce maximum yields, which in most cases are quantitative with respect to the organic reagents.

The nitrile and olefinic (or hydrated olefinic) component may be any of a wide range of aliphatic or aromatic compounds. Some of these are listed below.

RCN R =	Olefin or hydrated olefin
CH_3	i-Butene
$n-C_{17}H_{35}$	i-Butanol
C_6H_5-	i-Propanol
$C_6H_5CH_2$	Di-isobutene
$ClCH_2-$	Camphene
$CH_2=C(CH_3)$	Cyclohexanol
$p-NO_2-C_6H_4CH_2-$	Styrene
$NC(CH_2)_3$	2-Methyl-butene-2
$CH_2=CH$	

The hydroxyl or sulphhydryl component added at the termination of the primary reaction, and used to produce the substituted phosphoric acid, can be an unsubstituted or substituted primary, secondary or tertiary alcohol or thioalcohol phenol or thiophenol. The reaction is very rapid and so mild that inorganic acid esters difficult to prepare by other means (e.g. t-butoxy derivatives of phosphoric acid) can be obtained in this manner.

The product amides may find use as such, or be converted to amines by hydrogenation or hydrolysis. Thus, alkyl acrylamides, useful monomers in acrylic resins, can be synthesized by this route from organic raw materials costing less than 10 lb. In an additional example, t-butylamine can be prepared from inexpensive isobutylene and acetonitrile.

IV. SUMMARY AND RECOMMENDATION

Sulphuric acid is frequently applied in the petrochemical industry as a catalytic medium and solvent. Spent acid is subsequently transformed into a chemical fertilizer, usually ammonium sulphate. Markets for this commodity are reaching saturation, though the number of commercial processes and installations which are potential producers of the salt is on the increase. Many of the new petrochemical installations are sheduled for developing countries. These countries are also major markets for chemical fertilizers.

It is possible to replace sulphuric acid by phosphoric acid in many of these applications. New processes for phosphoric acid manufacture and purification make this substitution both technologically and economically viable.

The use of phosphoric acid in the Beckmann rearrangement for caprolactam production and in the Ritter reaction for the synthesis of N-substituted amides has been described. In addition to these, phosphoric acid can be used in aromatic nitrations, in hydrocarbon separations, etc. Spent acid can be transformed into phosphates which are more valuable and marketable co-products. This substitution should be considered for examination when concentrated mineral acid media are called for.

REFERENCES

1. a) F. Popp, et al.
   Trans. Kansas Acad. Sci. 63, No. 3, 169 (1960)
   b) C. T. [illegible]
   Ph. D. Dissertation, Univ. of Ill., June 1964
2. E. C. Horning and V.L. Stromberg
   J. Am. Chem. Soc. 74, 2680-81 (1952)
3. D. E. [illegible] and R. H. [illegible]
   Ibid. 83, 1718—17 (1961)
4. T. R. Hopkins et al.
   U. S. Pat. 3, 066, 375 (D. 1. 1962)

5 Organico
  a) French Pat 1 357 789 (2.3.1964)
  b) British Pat 1 [illegible] 197 (2 3 1966)

6. a) A Baniel et al
  Br Chem Engng 4 223 (1959)
  b) Israel Pat 21 247 (1967)
  c) Israel Pat 21 071 (1967)

7 B Wendrow and K A Kobe
  Chem Reviews 54, 890 (1954)

8. J J Ritter and P Minieri
  J Am Chem Soc 70, 4045 (1948)

9 G Glikmans et al
  Bull Soc Chim France 1376 (1966)

CURRENT PROBLEMS IN SCIENTIFIC-TECHNICAL CO-OPERATION IN CATALYSIS BETWEEN A RESEARCH INSTITUTE AND INDUSTRY IN YUGOSLAVIA[1]

PAULA PUTANOV*

I. INTRODUCTION

The chemical industry in Yugoslavia is characterized by a long tradition, but with non-uniform development, with periods of stagnation and a disproportion in development of its particular branches.

Discontinuity in the development of the chemical industry reflects itself in the development both of fundamental and applied research in the industry itself and in the collaboration with scientific institutions engaged in industrial research. The lack of a broader interest in the technological and economic aspects of catalysis in industry and the neglect of scientific research in this domain are particularly remarkable.

During the past decade this situation has changed substantially. A wide spectrum of investigations in catalysis have been studied in scientific institutes, linked closely with several large enterprises using catalytic processes. This collaboration is planned to be more intensive in the future as the role of catalysis is growing rapidly, particularly in the development of the basic organic chemical industry.

Scientific-technical collaboration in the domain of catalysis in Yugoslavia will not be restricted to internal contacts, but more and more will include the exchange of achievements at the international level. On the basis of past and future developments of the chemical industry and results already obtained in this scientific-technical collaboration, one may conclude in which direction international collaboration in catalysis is to be oriented and what are the problems to be solved by such united efforts.

II. THE DEVELOPMENT OF THE CHEMICAL INDUSTRY OF YUGOSLAVIA

The first of the basic chemical industries of Yugoslavia was installed in the second half of the nineteenth century. Among these were chemical and electrochemical plants, factories for sulphuric and hydrochloric acids, for soda etc. The period between 1908 and 1918 was characterized by the continuous development of sulphuric acid, calcium carbide, superphosphate and other chemical production. The capacities of these plants and the technologies applied were not behind production in other countries.

In the period between the two World Wars the chemical industry of Yugoslavia developed under the strong influence of foreign capital, and did not reach the expected level in spite of the previous tradition, available raw materials and energy, cheap labour and the existence of a domestic market. The growth of a great number of small scale chemical manufactures was characteristic of this period. The development of the

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG. 123/8.

* Institute for Chemistry, Technology and Metallurgy, Belgrade, Yugoslavia.

basic chemical industry was reduced. The major part of the export was based on raw materials and semi finished products: more than 85 per cent of the basic chemical industrial products were exported. Up to the Second World War, the Yugoslav chemical industry, because of a great number of circumstances, remained an undeveloped industrial branch, with a number of small economically poor firms with out of date technologies.

The development of the Yugoslav chemical industry after the Second World War can be divided into two periods: before and after the year 1956.

The main characteristic of the development in the first period, before 1956, was the favouring of the inorganic basic chemical industry, based primarily on domestic raw materials (the production of sulphuric acid, soda, chlorine, nitrogen compounds, phosphate fertilizers, calcium carbide and so on). The development of the organic chemical industry in this period was not remarkable, with the exception of polyvinyl chloride production.

In the second period, after 1956, funds were invested in the erection of larger plants for basic organic and inorganic chemicals, especially those related to petrochemistry. From 1956 to 1958 a great number of factories were put into operation as shown in table I.

TABLE I

THE MAJOR INSTALLATIONS BUILT AFTER 1956

The chemical-electro-metallurgy factory „Yugohrom“ Jegunovci	33,000 t of cyanamide 30,000 t of calcium carbide, various salts, ferroalloys etc.
The factory of sulphuric acid Bor	234,000 t of sulphuric acid
The chemical industry Kosovska Mitrovica	130,000 t of sulphuric acid 250,000 t of phosphate fertilizers
The factory of phosphate fertilizers in Prahovo	575,000 t of phosphate fertilizers
The chemical industry in Pančevo	360,000 t of calcium ammonium nitrate
Organic chemical industry „OKI“ Zagreb	20,000 t of polyethylene 10,000 t of styrene 6,500 t of polystyrene 6,200 t of phenol 4,200 t of acetone etc.
Organic chemical industry „OHIS“ Skopje	4,500 t of polyacrylic fibre 4,500 t of polyvinyl chloride 2,000 t of polyvinyl acetate 6,500 t of chlorine 7,200 t of caustic soda 6,000 t of dodecylbenzene 200 t of lindane etc.
The factory of polyamide fibres in the complex of the chemical factory of Moste	1,200 t of polyamide fibre
The factory of synthetic fibre „Progres“ Prizren	2,000 t of polyamide fibre

The capacities of some of these factories were soon increased. Thus, the production of calcium ammonium nitrate in the Chemical Industry Pančevo was increased by 480,000 t. The pharmaceutical industry was extended, too.

TABLE II

THE PRODUCTION OF THE BASIC CHEMICAL INDUSTRY

(000 t)

	1938	1964	1968	1970
Sulphuric acid	23.2	472.3	589	747
Nitric acid	—	227.8	340	579
Phosphoric acid	—	—	18	152
Ammonia	—	128.3	211	347
Chlorine	0.2	30.2	38	44
Phosphate fertilizers	27.8	985	985	1 294
Nitrate fertilizers	43.3	423	582	1 332
Viscose products	—	21	32	32
Synthetic fibres	-	47	101	110.5

In this period the development of the basic chemical industry was slow, because of insufficient investment in basic organic chemical production, especially in petrochemistry. This will be the source of many difficulties in the next period.

If we measure the development of the organic chemical industry in Yugoslavia, by the extent of production of the basic raw material components (ethylene, propylene, butadiene, benzene, toluene and xylene), we can draw the conclusion that the Yugoslav organic chemical industry is still in an early stage of development. This level is subject to the priorities established for the development of the Yugoslav economy.

As a prerequisite for future development in Yugoslavia, the organic chemical industry must be intensively expanded on the basis of raw materials for petrochemistry.

TABLE III

THE CONSUMPTION FORECAST OF SOME IMPORTANT CHEMICAL PRODUCTS

(000 t)

I. INORGANIC PRODUCTS	Consumption		
	1975	1980	1985
Sulphuric acid	1,200	1,300	1,800
Ammonia in t N	540	550	755
Chlorine	100	147	201
Caustic soda	160	205	250
Calcinated soda	253	326	437
Phosphate fertilizers in t P_2O_5	400	400	500
Nitrate fertilizers in t N	430	500	660
II. ORGANIC PRODUCTS			
Polyvinyl chloride	100—120	170—250	260—300
Polyolefin	90—130	180—260	270—400
Polystyrene	20—25	40—50	50—60
Other artificial materials	140—175	210—340	320—560
Viscose products	60	75	85
Polyamide fibres	10	15	20
Polyacrylonitrile fibres	13	20	30
Polyester fibres	13	25	30
Other fibres	2	5	8
Synthetic rubber:			
— SBR	30	35	45
— cis-polybutadiene	15	25	30
— butyl rubber	5	10	15

III. PRODUCTION, DEVELOPMENT AND PERSPECTIVES OF THE PETROLEUM INDUSTRY

There was no petroleum production in Yugoslavia until 1939. Between 1945 and 1970, 25 million tons of petroleum and about 4.8 mil. Nm³ of natural gas were produced. This increased production brought about an increase in petroleum consumption as an energy source and it supported the development of power technology and industrial petrochemical installations.

As table IV shows, the production of petroleum and natural gas during the last ten years increased constantly but not uniformly. In spite of this, domestic petroleum could not satisfy the need for consumption, so that petroleum import increased as well.

TABLE IV

PRODUCTION OF PETROLEUM AND OF NATURAL GAS BETWEEN 1960 AND 1970

Year	Production of petroleum			Production of natural gas		
	000 t	index (1)	index (2)	000 t	index (1)	index (2)
1960	944	100	—	53	100	—
1965	2.063	218	218	330	622	230
1966	2.222	235	107	402	758	121
1967	2.374	251	107	462	871	114
1968	2.494	264	105	583	1100	126
1969	2.699	285	108	730	1377	125
1970	2.854	302	106	977	1834	134

index (1) : Index relating to 1960 = 100
index (2) : Index relating to the previous year

Unless some unexpected rich source be found, we can expect a continuation of the tendency for the consumption of domestic petroleum to decrease. This tendency is shown in table V. Reserves of petroleum and natural gas amounted to about 66 million tons of crude petroleum and 40 mil. Nm³ of natural gas at the beginning of 1970. The consumption of

TABLE V

DOMESTIC VERSUS IMPORTED PETROLEUM IN YUGOSLAV MANUFACTURE

(000 t)

Year	Import	Export	Available for manufacture	Participation of domestic petroleum in the manufacture in %
1960	435	—	1,288	73.1
1965	1,107	—	2,930	71.1
1966	2,202	324	4,132	57.2
1967	2,547	322	4,495	52.6
1968	2,683	292	4,931	50.5
1969	3,300	237	5,724	47.1
1970	4,442	150	7,100	40.0

petroleum derivatives in Yugoslavia, although in remarkable growth during the last few years is still low. As can be seen from table VI the participation of the chemical industry in this consumption is continuously increasing. A marked increase in the consumption of gasoline as a fuel and for industrial purposes is expected in the future.

A constant increase is expected in the consumption of all other petroleum derivatives such as liquefied gases, special benzines, oils, lubricants, tar and petrol coke. The largest consumer of these derivatives is industry, with its participation of about 60%.

TABLE VI

PARTICIPATION OF PARTICULAR SECTORS IN TOTAL GASOLINE CONSUMPTION

(%)

Sector of consumption	1960	1965	1966	1967
Industry	14.6	24.4	23.2	23.7
Traffic	63.5	60.7	62.2	63.0
Agriculture	5.8	2.6	2.5	2.1
Personal, general and other applications	16.1	12.3	12.1	11.2

Petroleum manufacture in Yugoslavia increased particularly after 1964. Larger capacities and newer processes, led to an improvement in the quality of derivatives. They now meet world standards.

On the other hand, hasty construction of new installations has led to their incomplete use. Refineries worked at about 2/3 of nominal capacities.

We anticipate the production of about 4.5×10^6 tons of crude petroleum and about 2.5×10^9 Nm^3 of natural gas by 1975. The consumption of petroleum derivatives will also grow; in 1975 it is expected to reach the level of about 12×10^6 t with an accelerated increase, forecast. With regard to available sources of domestic raw materials, existing refinery capacities, as well as those being erected, will be sufficient if operated at full capacity up to 1975. In the next five year period, it will be necessary to build new capacities for petroleum manufacture, mainly to assure continuity in the supply of petroleum derivatives after 1975.

IV. ORGANIZATION AND SUBJECTS OF CATALYSIS RESEARCH IN YUGOSLAVIA

Although problems in catalysis have existed in the chemical industry of Yugoslavia for about a century, and although a number of catalytic plants have been constructed in Yugoslavia in the period of scientific and technical development of catalysis in the world, systematic investigation in this field in the country was organized only ten years ago. There were many causes for this situation, relating both to industrial production, and the character of our scientific effort.

In the period between the two wars, while the chemical industry of Yugoslavia was developing under the influence of foreign capital, scientific investigations were performed mainly abroad, while experts employed in Yugoslav factories applied the obtained results in production control.

In the early post war development, there was a large disproportion between the number of actual problems and the number of available experts. Later on, when the number of experts in industry increased, problems of catalysis did not receive adequate attention for many reasons. In new plants, licence conditions limited the competencies of the domestic experts and inhibited their interest in problems of this kind. In older plants the relatively small contribution of the price of the catalyst in the total cost of production did not lead to an appreciation of the real economic aspects of catalyst technology. In addition, experts employed in the chemical industry of Yugoslavia were not adequately educated toward a deeper insight into this problem.

At the University level, catalysis was treated very superficially. It was taught only as a part of other courses – general chemistry, physical chemistry, organic chemical tehnology, etc.

Catalysis, as a special subject was first taught as a one semester course at the Faculty of Technology, University of Belgrade. A year ago, catalysis including laboratory practice, was introduced as a regular subject in chemical engineering at the Faculty of Technology, University of Novi Sad. A few years ago courses in theoretical and applied catalysis were included as subjects in postgraduate lectures at the Universities of Belgrade, Sarajevo and Novi Sad.

Nevertheless, these courses are not as fully developed as other subjects and they do not include all important aspects of theoretical and applied catalysis. These deficiencies could not be compensated for adequately by training engineers on the job, because of mobility of staff.

In the postwar development of scientific research in Yugoslavia, the subject of catalysis was investigated to some extent, on an adequate level. The Institute for Technical Catalysis was founded in the chemistry department of the Faculty of Technology in Ljubljana (1946–1948). It ceased to function because of personnel changes. At the Faculty of Technology in Zagreb, in the 1950, engineering catalysis was studied, but this initiative could not serve as a basis for the systematic development of this complex speciality.

Actually the development of broader, specialized research in the field of catalysis in Yugoslavia started only 10 years ago, through the foundation of the Department for catalysis of the Institute for Chemistry, Technology and Metallurgy in Belgrade. This department is not large, but it is a well equipped specialized institution, which has initiated and coordinated all the major scientific research projects in the field of catalysis during the last 10 years.

Along with the applied research which this department performs, it is also concerned with periodic arbitration investigations for Industry.

Besides this department, other institutions are concerned with catalysis to a smaller degree. These are the Chemical Institution Boris Kidrič, Ljubljana, departments at the University of Belgrade, the University of Sarajevo, the University of Split, the University of Novi Sad and the research laboratories of some big enterprises, such as the Chemical Industry Pančevo, INA – Zagreb, etc. The major part of the investigations in industrial catalysis are performed in co-operation with the Department for Catalysis of the Institute for Chemistry, Technology and Metallurgy. This department is the subject of the following discussion.

Their more important avenues of research for industrial development are presented, excluding subjects at contract research.

One of the first problems which drew the attention of industry, was the establishment of criteria for cutalyst choice. Except for catalysts for polyvinyl chloride manufacture, there is no catalyst production in Yugoslavia. Ten years ago our firms were passive as regards selecting catalysts, trusting in the foreign producers. This attitude is changing. Another area of investigation is the influence of various process parameters on the activity and stability of catalysts. Interest in this subject varies from concern over insufficiently stabilized process conditions in the older, not automated plants, to variations in the quality of raw materials and process interruptions because of mechanical breakdown.

The subject of catalyst production has not been given too much attention until now. This seems to be unwarranted on the basis of the present capacities of catalyst in Yugoslavia. Interest has been expressed by several enterprises in making the common catalysts for selected processes. Investigations, started in order to unify process conditions and catalysts could be the first phase in preparing the domestic market for catalysts produced in the country.

There is now a growing interest in industry in the organization of a permanent co-operative effort with the institute, covering a broad research programme in the field of catalysis. The formation of a common research centre in the institute associated with industry will further this interest. Under this arrangement, a single research team can perform investigations ranging from ones in fundamental science to applied subjects.

This programme is supported by training personnel working in the industry, in the form of periodic seminars on actual problems of theoretical and applied catalysis. Such seminars were started in 1970 by the Department for Catalysis of the Institute for Chemistry, Technology and Metallurgy, Belgrade with the participation of some eminent foreign lecturers. Lecturers are invited from well known institutions.

V. SUBJECTS OF INVESTIGATION FOR INDUSTRIAL PURPOSES

Attention is being drawn particularly to the standardization of methods for the examination of catalysts, the analysis of the applicability of data given for the characterization of catalysts and the development of methods for the study of catalysts ageing in reactors.

Because of the variety of catalytic systems, the large number of factors influencing their activity and the variety of process conditions used, the problem of standardization in catalysis is particularly complex. However, practice has shown that the comparison of different samples of catalysts is necessary. In order to establish a rational basis for such a comparison, the following trend is observed:

- the selection of characteristic properties for the particular system;
- the establishment of correlations between various process conditions and variations in parameters characteristic of catalysts;
- the definition of methods for characterizing and evaluating catalysts.

Information on these subjects is not freely available.

As a result, a tendency to establish proprietory standards may be advantageous. However, this can lead to difficulties if the methods developed give different results. For example, when the term "catalytic activity" is cited, it is not usually explained whether the activity is based on a unit of area, volume or weight of the catalyst, nor by which method and under what conditions (dynamic, static) it was determined. As for data on the mechanical strength of catalysts, the terms "strength", "crush strength" or "compressing side strength" appear, but no details on the methods of determination are given.

The results are largely influenced by the method used. This situation holds for other characterization tests as well.

Some properties, given as characteristic of a catalyst, are not sufficient if complementary data are not given. For certain types of catalysts some of the data usually given are of no value. A good example is the vanadium catalyst used for the production of sulphuric acid whose activity is influenced by the thickness of the liquid layer under process conditions. Data on the magnitude of the specific surface area are of limited value if the relationship between the active mass and carrier is not known. For other catalysts, data on the percentage of active component present are insufficient if the role of other components in the mechanism of catalysis is not known and if their concentration is not cited.

The dynamics of the catalyst aging in reactors is an important subject because of the very high costs of interrupted production. Good planning is required in changing catalyst charges as well as plant discipline during shutdown periods for other reasons. The adaptation of process conditions to changing catalyst properties due to aging, would also be desirable.

These problems are very complex and their solution requires fundamental knowledge in catalytic systems, engineering experience and a familiarity with computer techniques. In the absence of all of these elements, foreign services must be and are used. However, the interest for such investigations in Yugoslavia is emphasized and collaboration in solving these problems is more than desirable.

THE PREPARATION OF AROMATICS FROM CATALYTIC REFORMING OF PETROLEUM FRACTIONS[1]

ABBAS FALLAH*, AMIR BADAKHSHAN*,
MANOOCHEHR SHAHAB*, AMIR H. AZIMIPOUR*,
FARROKH KAMALI*

INTRODUCTION

Eighty per cent of the benzene (1), 96 per cent of the toluene (2) and 98 per cent of the C_8 aromatics (3) in the world are produced from petroleum fractions. Catalytic reforming of petroleum fractions over platinum catalyst is the main source of these products in petroleum industries. Many studies have been carried out on the preparation of benzene (4, 5, 6), toluene (7, 8, 9) and C_8 aromatics (10, 11, 12) by catalytic reforming of petroleum fractions.

In this paper, data from a catalytic reforming pilot-plant are presented on two fractions at different reaction temperatures and pressure to optimize process variables. Some correlation curves on the yield of hydrogen, methane, ethane, propane and heavier than hexane (C_6+) useful for the design of commercial catalytic reforming unit are obtained.

Based on the reaction models suggested previously, in this experiment using the specific feedstock compositions, a reaction model is presented.

It has been shown that there is a lower limit of pressure for reforming below which the platinum catalyst deactivates rapidly.

Among the total conversions taking place in the experiment, dehydrocyclization of paraffins was investigated. Even under very severe catalytic reforming conditions, a small portion of naphthenic hydrocarbons remains unchanged.

EXPERIMENTAL

The two gasoline fractions containing C_6–C_7 and C_8–C_9 hydrocarbons were prepared from Aga-Jari and Ahwaz crude oil in a packed column atmospheric distillation pilot-plant having a still capacity of 350 litres.

The impurities of each fraction were removed over a cobalt-molybdenum catalyst (physical and chemical properties of the catalyst are given in table I) in a hydrotreating pilot-plant. The operating conditions of the hydrotreating unit were adjusted to remove sulphur and other impurities such as metals, nitrogen and oxigen, to the level which is harmless for

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG. 12/9.

* National Iranian Oil Company Research Centre, Tehran, Iran. The authors acknowledge the co-operation of A. Honarbakhsh, E. Barhami, N. Alizadeh, H. Hashemi and P. Sarram.

the catalytic reforming catalyst. Several test runs were carried out over a cobalt molybdenum catalyst. The optimum conditions obtained for removing impurities were as follows

TABLE I

HYDROTREATING AND REFORMING CATALYST PREPARED FROM "PROCATALYST"

	Hydrotreating catalyst HR 306	Reforming catalyst RG 701
Physical properties		
Surface area m²/gm	240	320
Bulk density gm/cm³	0.55	0.75
Pore volume cm³/gm	0.65	0.52
Crushing strength kg	8.0	—
Chemical composition,		
Wt %		
Pt	—	0.6
Cl	—	0.5
F	—	0.4
Alumina	by dif	by dif
MoO_3	19.0	—
CoO	3.5	—
Na_2O	0.09	< 300 ppm
F_2O_3	0.04	< 500 ppm
Heating loss at 550°C	1%	0.5%

Reactor temperature	325°C
Reactor pressure	30 kg/cm²
LHSV hr⁻¹	3.3
Hydrogen to hydrocarbon	70:1 1/1

The properties of the feedstock before and after hydrotreating are shown in table II.

The reforming study was carried out over a platinum catalyst with 0.6 wt. per cent platinum (physical and chemical properties of the catalyst are given in table I) in a catalytic reforming pilot-plant having a capacity of 24 litres/day. A simplified process flow diagram is given in figure 1 (15). Fresh hydrogen of 98 mole per cent purity was prepared from a hydrogen plant for start up of this unit and also for operating the hydrotreating unit. The liquid feed after hydrotreating was continuously stripped of dissolved air in a packed column. The reactor was operated to maintain isothermal conditions throughout the catalyst bed.

Gas and liquid analyses were carried out by a Varian Aerograph with EMEE (30 per cent) and glycol (30 per cent) packed columns in lengths of 16.5 ft and 5.0 ft, respectively. Helium was used as carrier gas for both analyses.

PROPERTIES OF FEEDSTOCKS BEFORE AND AFTER HYDROTREATING (H T)

	Lighter fraction		Heavier fraction	
	Before H T	After H T	Before H T	After H T
Sp Gr at 60/60° F	0.7245	0.7264	0.7422	0.7432
Sulphur content, ppm	212.0	17.0	196.0	8.0
Bromine No gm/100 gm			0.25	0.0
R V P, psig	2.5	4.5	2.0	1.5
Octane No F1 clear	53.0	56.4	47.8	50.0
ASTM distillation, °C				
IBP	93.0	94.5	106.5	107.5
5 vol % recovered	95.5	96.0	109.0	110.5
10	96.0	96.5	110.0	111.5
20	96.5	97.0	112.5	113.0
30	97.0	97.5	114.5	114.5
40	97.5	98.5	117.0	117.0
50	98.5	99.0	120.0	120.0
60	99.5	100.0	123.0	122.5
70	100.5	101.0	125.0	126.0
80	102.5	103.5	131.0	131.0
90	107.5	110.5	137.0	137.0
95	115.5	123.5	143.0	142.5
FBP	140.0	139.5	153.0	153.0
Hydrocarbon-Type Analysis, Vol %				
Naphthenes	36.5	37.0		19.0
Aromatics	7.0	7.5		13.0
Benzene	–	–		(0.2)
Toluene	–	–	–	(5.2)
C_8+	–	–		(7.6)
Paraffins	56.5	55.5		68.0
Olefins	0.0	0.0		0.0

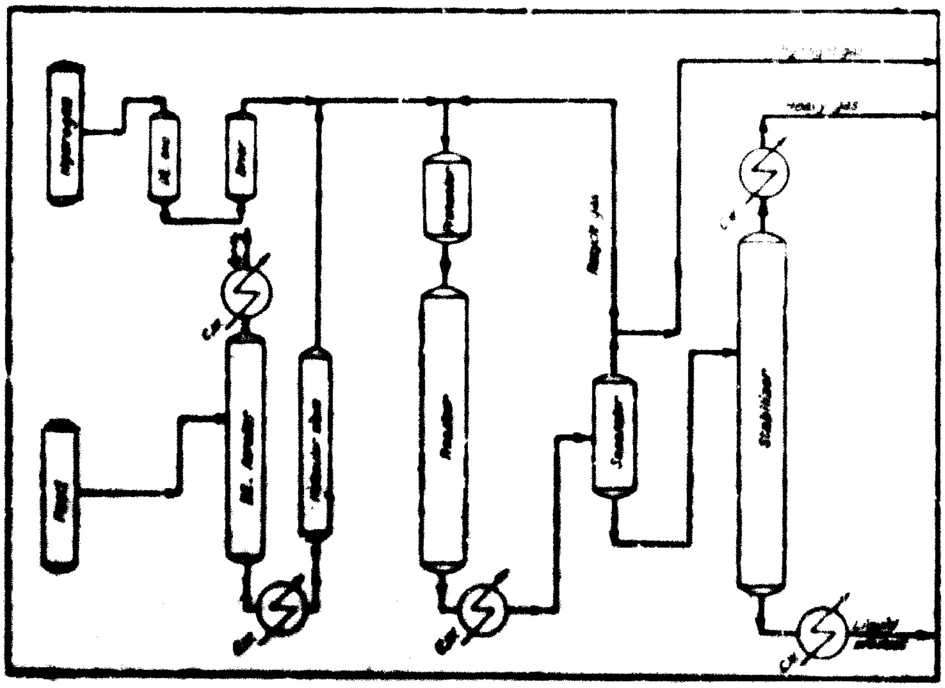


FIGURE 1. CATALYTIC REFORMING PILOT PLANT

RESULTS

Different reforming conditions were studied for the two mentioned fractions. The range of 490 to 530°C and 15 to 25 kg/cm² was examined with hydrogen to hydrocarbon mole ratios from 5.0:1.0 to 6.0:1.0 and liquid hourly space velocity around 2.0. The specifications of platformates and their aromatic compositions are given in table III for the 90-140°C fraction. The same data are given in table IV for the range of 480 to 520°C and 20 to 30 kg/cm² with hydrogen to hydrocarbon mole ratios from 7.0:1.0 to 8.0:1.0 and liquid hourly space velocity around 2.0 for the 110-190°C fraction.

Calculation of material balances on the above test runs was carried out with the aid of a digital computer. Curves on the yield of H_2, C_1, C_2, C_3, iC_4, nC_4, iC_5, nC_5 and $C_{6}+$ are shown in figures 2 and 3.

The yield of total aromatics, toluene, C_8 aromatics and the yield-octane relationship at different reforming conditions are given in figures 4, 5 and 6.

The production of hydrogen was maximum at 510°C under the pressure used for the lighter fraction and 500°C for the heavier fraction. However, the maximum yield of hydrogen in all cases was 1,350 scf/bbl of feed at 510°C and 20 kg/cm² for the lighter fraction.

Of the various reaction mechanisms suggested for the reforming of pure hydrocarbons and naphtha (13 & 14), for our feed stock composition the preferred reaction mechanism is presented in figure 7.

With the aid of the reaction model and rate equations given by Henningsen and Bundgaard Nielson (1970) and Krane et al (1959), mathematical calculations were performed on a few runs. Experimental and calculated results are in a good agreement, but the yield of aromatics obtained at any given pressure is lower than the calculated results. That was due to the rapid deactivation of our catalyst at that low pressure. Lower pressures significantly increase the amount of aromatic formed, but coking of the catalyst is increased owing to lower hydrogen partial pressure.

Production of toluene, C_8 aromatics and total aromatics increases when the process operates at higher temperature. Many naphthenes remain unconverted at low temperature. Even at very high reforming temperature (530°C) a small concentration of naphthene is found in the products.

Dehydrocyclization of paraffins to aromatics takes place under severe conditions. The results of some experiments (15) show that the production of benzene is much lower than the production of heavier aromatics in the dehydrocyclization reaction. The rate of dehydrocyclization is quite considerable because of the greater extent of reaction in the case of heavier paraffins. Aromatic hydrocarbons produced by the dehydrocyclization reaction and the conversion rate of paraffins to aromatics is shown in table V for the heavier fraction. The rate of the dehydrocyclization is actually higher than calculated because some aromatics undergo reversible reaction to non-aromatics and the conversion of naphthene to aromatics is not always 100 per cent under all conditions experienced in practice. The maximum conversion is 27.5 per cent at 520°C and 20 kg/cm².

TABLE

REFORMING CONDITIONS AND PLATFORMATE

Conditions	Case I					Case II					Case III				
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	RUN 8	RUN 9	RUN 10	RUN 11	RUN 12	RUN 13	RUN 14	RUN 15
Reactor temperature, °C	490	500	510	520	530	490	500	510	520	530	490	500	510	520	530
Reactor pressure, kg cm²	15	15	15	15	15	20	20	20	20	20	25	25	25	25	25
Liquid hourly space velocity, hr⁻¹	2.15	2.18	2.14	2.14	2.08	2.08	2.06	1.94	1.90	2.03	2.14	2.13	2.08	2.03	2.01
Hydrogen to hydrocarbon mol. ratio platforming	5.6	5.0	5.6	5.5	5.2	6.0	5.2	5.0	6.0	6.0	6.0	4.9	4.9	4.9	6.0
Sp. Gr. at 60/60°F	0.7371	0.7700	0.7410	0.7421	0.7670	0.7171	0.7675	0.7670	0.7780	0.7740	0.7346	0.7348	0.7570	0.7835	0.7543
Octane No. F₁ clear	74.3	78.0	86.0	87.7	96.9	75.0	89.7	[illegible]	94.3	98.2	75.5	79.6	87.4	90.6	93.0
ASTM distillation, °C															
IBP	41.0	50.5	42.0	38.5	39.0	38.5	41.0	40.0	44.0	[illegible]	33.4	34.5	44.0	51.6	36.0
Vol. % recovered															
5	70.5	75.0	59.0	57.0	51.5	71.5	65.0	60.0	62.0	[illegible]	76.0	69.5	69.0	79.0	49.0
10	83.0	82.5	71.0	69.0	59.5	84.0	72.0	69.0	70.0	65.0	85.0	82.0	75.5	84.0	63.0
30	95.5	96.5	93.5	92.5	88.5	96.5	95.0	94.5	94.0	91.0	94.5	94.5	94.5	97.5	89.5
50	99.0	100.5	99.5	100.5	103.5	99.5	102.5	103.5	105.0	105.5	97.0	98.5	101.5	104.5	100.5
70	104.5	105.0	107.0	107.5	113.5	104.0	109.5	111.5	113.0	114.0	101.0	103.0	107.5	111.0	108.0
90	126.0	[illegible]	139.5	143.5	152.0	115.0	130.5	133.0	135.0	140.5	115.0	121.5	122.0	119.0	[illegible]
FBP	162.5	192.0	168.5	167.0	183.0	156.6	170.0	176.0	182.5	176.5	[illegible]	151.5	169.0	179.0	[illegible]
Vol. % of charge															
Benzene	0.7	0.6	1.1	1.6	2.4	0.7	0.7	0.8	[illegible]	1.5	0.7	[illegible]	[illegible]	[illegible]	[illegible]
Toluene	18.7	18.7	20.5	21.7	21.9	22.6	23.9	[illegible]	25.8	26.8	[illegible]	20.4	[illegible]	[illegible]	[illegible]
Xylenes + ethylbenzene	2.7	3.7	3.2	3.2	3.6	0.3	4.8	[illegible]	5.4	5.0	3.0	2.9	4.0	4.6	3.6
C_9^+ aromatics	0.7	0.4	0.8	0.8	1.6	0.1	0.2	[illegible]	[illegible]	0.8	0.5	0.6	0.3	[illegible]	0.9
Total aromatics	22.8	23.4	25.6	27.3	29.5	23.7	29.6	30.6	32.9	[illegible]	[illegible]	[illegible]	28.7	28.8	[illegible]
Total naphthenes	21.0	13.0	10.7	9.8	6.6	14.3	5.1	4.1	3.3	1.9	5.1	3.5	[illegible]		1.0
Total paraffins	47.7	43.6	35.3	33.2	29.7	50.6	37.6	33.2	30.0	28.9	52.8	51.9	[illegible]		[illegible]

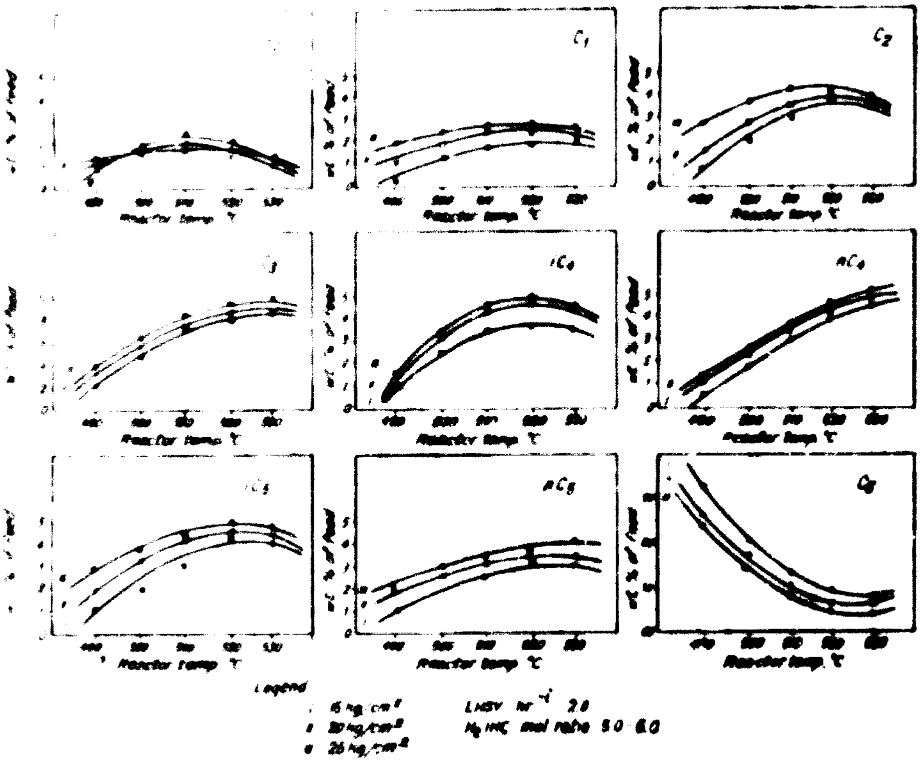


FIGURE 2. YIELDS OF H_2, C_1, C_2,... AND C_6^+ AT VARIOUS REACTOR TEMPERATURES AND PRESSURES

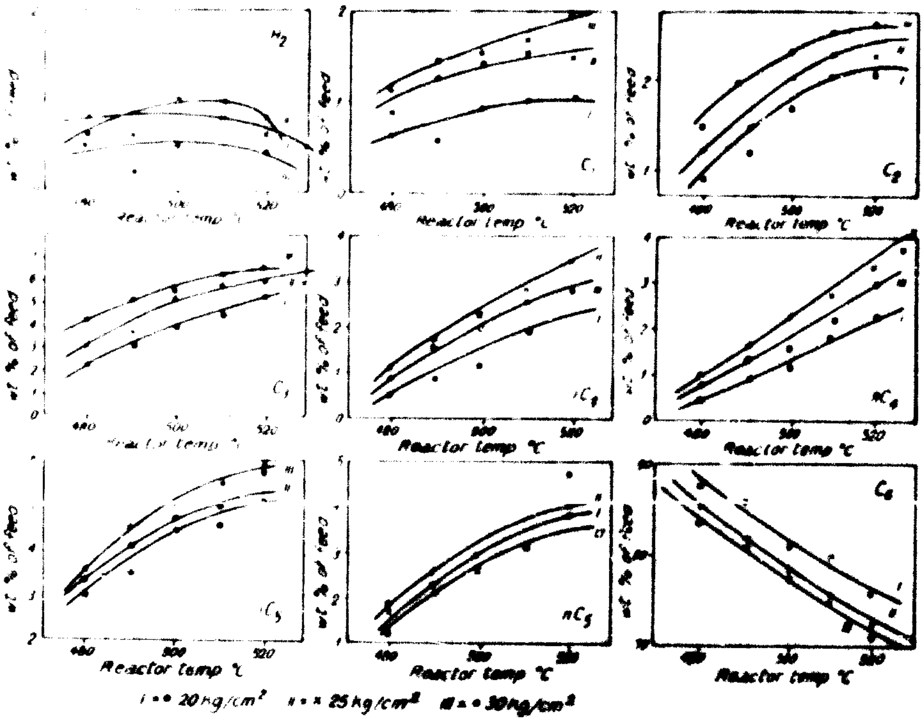


FIGURE 3. YIELDS OF H_2, C_1, C_2,... AND C_6^+ AT VARIOUS REACTOR TEMPERATURES AND PRESSURES

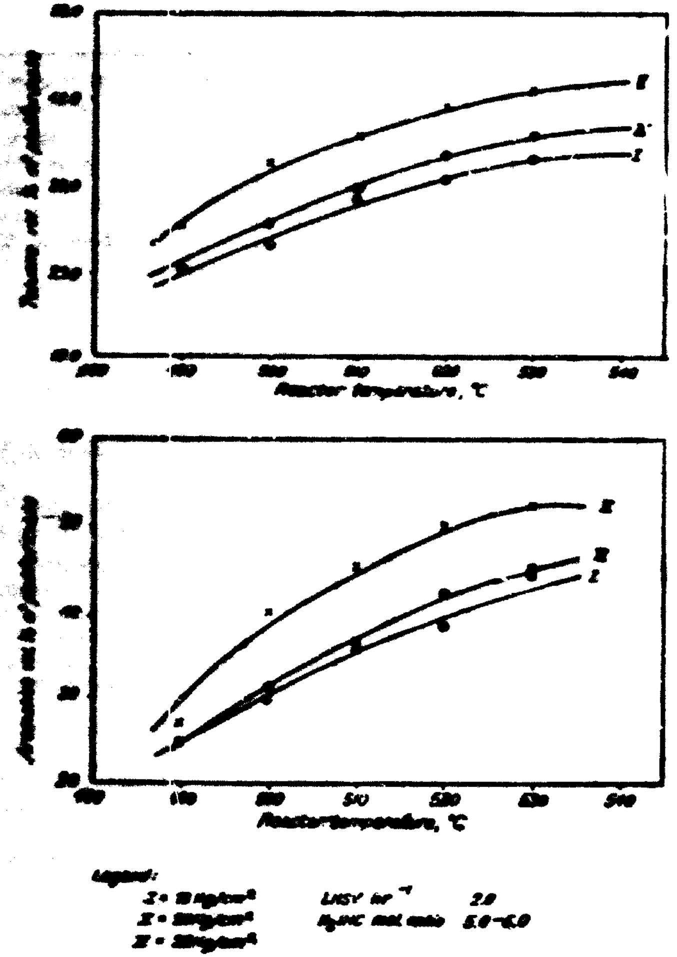


FIGURE 4. YIELDS OF TOLUENE AND TOTAL AROMATICS AT VARIOUS REACTOR TEMPERATURES AND PRESSURES

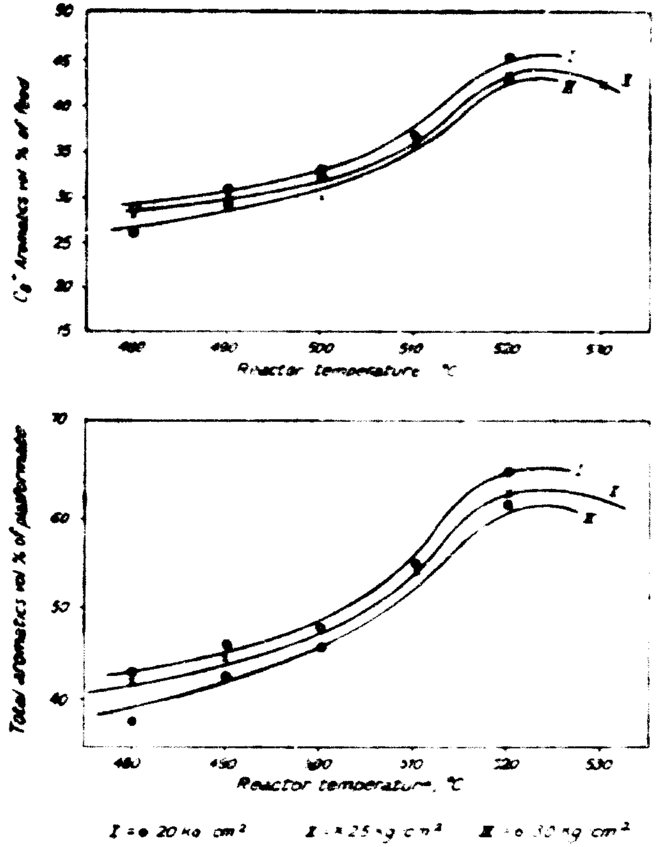


FIGURE 5. YIELDS OF C_8^+ AROMATICS AND TOTAL AROMATICS AT VARIOUS REACTOR TEMPERATURES AND PRESSURES

OPERATING CONDITIONS AND PROPERTIES OF PLATFORMATE

Conditions	Case I					Case II						Case III				
	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5	RUN 6	RUN 7	RUN 8	RUN 9	RUN 10	RUN 11	RUN 12	RUN 13	RUN 14	RUN 15	RUN 16
Reactor temperature, °C	480	490	500	510	520	480	490	500	510	520	530	480	490	500	510	520
Reactor pressure, kg/cm²	20	20	20	20	20	25	25	25	25	25	25	30	30	30	30	30
Liquid hourly space velocity, hr⁻¹	2.06	2.05	2.07	2.07	2.03	2.03	2.01	2.03	2.04	2.05	2.06	1.96	2.00	2.03	2.03	2.05
Hydrogen to hydrocarbon mole ratio platformate	7.5	7.5	7.2	8.3	6.8	6.8	7.2	6.8	7.0	8.2	8.5	8.4	8.1	8.0	7.9	7.4
Sp. Gr. at 60/60°F	0.7564	0.7544	0.7574	0.7687	0.7932	0.7624	0.7616	0.7634	0.7705	0.7815	0.7982	0.7501	0.7664	0.7704	0.7756	0.7843
Octane No. F_1 clear	83.1	85.7	90.0	93.4	99.0	84.6	90.8	94.0	97.7	98.6	99.4	82.0	87.8	92.2	96.0	98.2
ASTM distillation, °C IBP	38.0	38.0	35.0	35.0	41.0	42.0	36.0	31.5	31.0	32.5	44.0	38.0	38.0	38.0	40.0	42.0
Vol. % recovered																
5	66.5	62.0	56.0	54.0	58.0	66.0	54.0	46.0	47.0	49.0	59.0	69.0	65.0	57.0	55.0	53.5
10	83.0	76.5	71.5	66.5	70.0	80.0	67.5	59.0	59.0	60.0	71.0	87.0	79.0	69.0	65.0	64.0
30	107.5	107.5	105.5	96.0	104.5	110.0	98.0	98.0	97.5	103.5	106.0	111.0	104.5	105.0	100.0	100.5
50	115.0	120.0	119.0	118.0	122.5	120.5	116.0	118.0	120.0	123.0	124.0	118.0	118.0	119.0	120.0	122.0
70	130.0	131.0	134.0	132.0	132.0	131.5	130.0	132.0	134.0	133.0	133.0	125.0	127.0	128.0	131.0	133.0
90	151.5	158.0	161.0	156.5	147.0	159.0	156.0	155.5	158.0	149.0	146.0	140.0	143.0	143.0	145.5	146.5
FBP	174.0	174.0	185.0	183.0	175.0	167.0	176.0	175.0	178.0	166.0	173.0	161.0	164.0	166.0	168.0	171.0
Vol. % of charge																
Benzene	0.9	1.1	1.1	1.3	1.0	0.7	0.9	1.2	1.4	1.0	1.0	0.4	0.6	0.7	0.9	1.1
Toluene	12.1	12.4	12.8	14.0	14.5	11.2	11.1	11.9	12.7	14.0	13.0	9.4	10.3	11.5	13.4	14.0
Xylenes + ethylbenzene	20.1	20.5	21.1	23.0	29.6	18.7	19.0	19.7	20.1	28.2	25.5	19.3	21.0	22.9	26.6	27.8
C_9^+ aromatics	6.1	6.9	7.2	8.0	5.6	6.1	6.8	4.5	7.8	5.0	4.2	3.2	3.6	3.8	4.5	4.8
Total aromatics	39.2	41.0	42.2	46.3	50.7	36.7	37.8	37.3	42.0	48.2	43.7	32.3	35.5	38.9	45.4	47.7

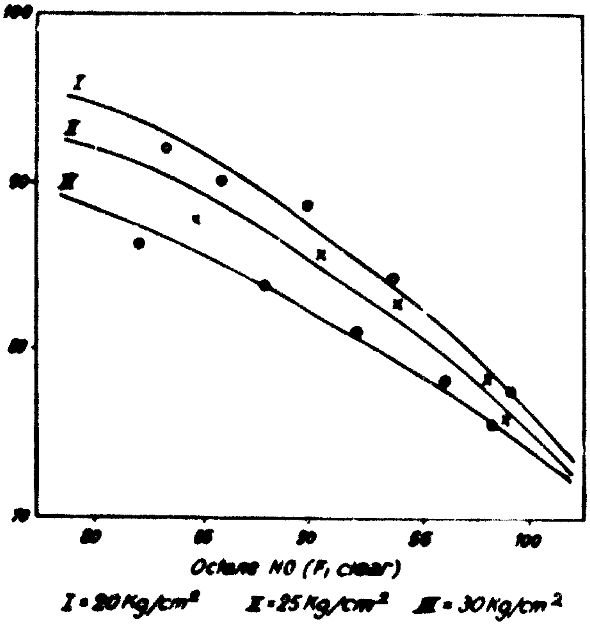


FIGURE 6 YIELD-OCTANE RELATIONSHIP UNDER EXPERIMENTAL CONDITIONS

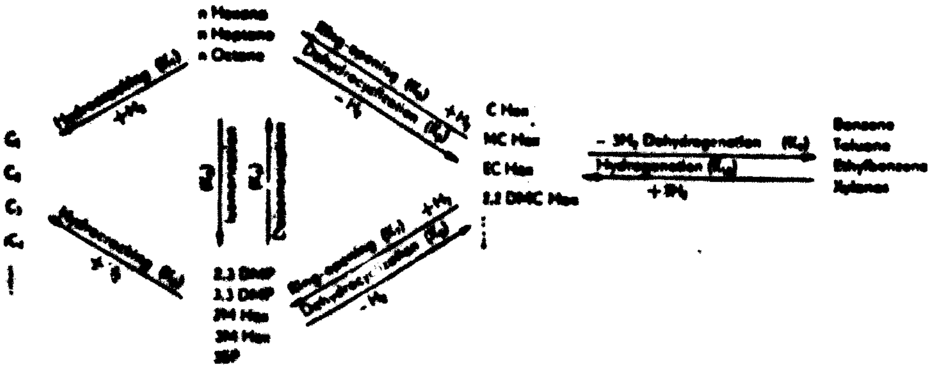


FIGURE 7

TABLE V

THE RATE OF CONVERSION IN DEHYDROCYCLIZATION UNDER VARIOUS CONDITIONS

Case I

Run no.	1	2	3	4	5
Total aromatics produced, Vol %	39.2	41.0	42.2	46.3	50.7
Aromatics by dehydrocyclization, Vol %	7.2	9.0	10.2	14.3	18.7
Conversion rate of dehydrocyclization	10.6	13.2	15.0	21.0	27.5

Case II

Run no.	6	7	8	9	10	11
Total aromatics produced, Vol %	36.7	37.8	37.3	42.0	48.2	43.7
Aromatics by dehydrocyclization, Vol %	4.7	5.8	5.3	10.0	16.2	11.7
Conversion rate of dehydrocyclization	6.9	8.5	7.8	14.7	23.8	17.2

Case III

Run no.	12	13	14	15	16
Total aromatics produced, Vol %	32.3	35.5	38.9	45.4	47.7
Aromatics by dehydrocyclization, Vol %	0.3	3.5	6.9	13.4	15.7
Conversion rate of dehydrocyclization	0.4	5.1	10.1	19.7	23.1

CONCLUSIONS

Toluene and C_8 aromatics were the major products in the reforming of both the 90–140°C fraction of Aga-Jari crude oil and the 110–150°C fraction of Ahwaz crude oil under various conditions.

A reaction mechanism for the performed experiment is presented.

The yield of hydrogen was maximum at 500–510°C for all pressures used. The maximum yield of hydrogen was 1350 scf/bbl of feed at 510°C and 20 kg cm² for the lighter fraction.

Even under very severe reforming conditions a small portion of naphthenic hydrocarbons remained unconverted.

Dehydrocyclization occurred to a maximum amount of 27.5 vol. % for the heavier fraction

REFERENCES

1. Scobaugh, R.B., Hydrocarbon Processing 44 (9) Sep. 1965.
2. Scobaugh, R.B., ibid 45 (4) April, 1966.
3. Scobaugh, R. B., ibid 45 (2) Feb. 1966.
4. Coley, J. R. Evering, B. L., McCollum J. D. (to Standard Oil Co.) U. S. Patent 2, 861944, Nov 25, 1958
5. Drehman, L. E., Hopp, Hopp, H. J. (to Phillips Petroleum Co.), U.S. Patent 3.258, 503 June 28, 1966.
6. Maslyanskii, G. N. Borkan, S. A. Int. Chem. Eng. 8 (2), 210-20, 1969
7. Kirk, M.C., Claymore, Jr. (to Sun Oil Co.) U.S. Patent 2, 4[illegible]
8. Kopf, F. W., Decker, W. H. Pfefferle, W. C., Dalson, M. H., Harlan J. A., Hydrocarbon Processing, 111-15 May, 1969.

9. Zhurba, A. S., Bryanskaya, E. K., Bondar, A. F., Smol'nik, Yu. E., Yampolski, N. G., Cherednichenko, G. I., Khim. i Tekhnol. Topliva Masel 14 (13) 1-3, 1969
10. Aliev, V. S., and Aliev, A. M., Azerb. Neft Khoz 39, 41, 1967.
11. Dnelp, L. C. Brenner, W., and Weiss, A. H., I&EC Process Design and Dev. 4 (1) 92-6, Jan. 1965.
12. Nakamura, E., Koguchi, K., Sekiyu Gakkai Sh. 12 (8) 620-26, 1969.
13. Krane, H. G., Groh, A. B., Schulman, B. L., Sinfelt, J. H., Proceding of the Eigth World Pet. Congr. Section 111 Paper 4, 1959
14. Henningsen, J., Bundgaard-Nielson, M., British Chem. Eng. 15 (11) Nov. 1970
15. Badakhshan, A., Azimipour, A. H., Kamali, F. Nersesian, A., Hashemi, M., Alizadeh, N., Sarram, P., Ind and Eng. Chem. Prod. Res. Dev. 10, 330, 1971.

HYDRODESULPHURIZATION OF FUEL OIL USING Co-Mo CATALYSTS[1]

MANOOCHEHR SHAHAB*

Rapid technological advancements have created great concern over our environment. One of the major causes of alarm is the burning of fossil fuel whose sulphur containing compound give off hazardous sulphur dioxide upon burning. SO_2, a major pollutant of today's industrial communities, is not only determintal to health but also costly to industrial installations. To remedy this problem, many institutions have set as a major goal the removal of sulphur from petroleum crudes or petroleum products.

Researchers from the young catalytic unit of the National Iranian Oil Company's Research Centre, in conjunction with scientists from other disciplines, from analytical and engineering groups, have formed a team to investigate the hydrosulphurization of an Iranian fuel oil. The challenging goals set are summarized as follows:

1. To examine sulphur removal processes with respect to a particular Iranian fuel oil containing 2.4 per cent sulphur by weight.
2. To investigate the economics of a desulphurization process in Iran where raw materials are abundant and labour is relatively cheap compared to many other countries.
3. To gain an insight into the process of desulphurization which can have valuable applications in the removal of sulphur from less problematic crude oils. This can pave the road for the competitive marketing of low sulphur crudes to world markets considering strict pollution laws and regulations.

To this end the following stages have been approved:

(a) Identification of various types of sulphur containing compounds in the fuel oil

(b) Preparation of a hydrodesulphurization catalyst

(c) Determination of physical properties of catalysts such as surface area and porosity measurements

(d) Propane deasphalting of the fuel oil for removal of asphalt and heavy metals such as vanadium

(e) Hydrodesulphurization of the propane deasphalted fuel and identification of products

(f) Determination of optimum process conditions

(g) Economic calculation of the process

(h) Implementation of the process on an industrial scale.

A commercial activated alumina having a specific surface area of 200 m^2/g was used as a support. Three catalyst samples were prepared. In all cases the alumina support was impregnated with solutions of

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/10.

* National Iranian Oil Company Research Centre, Tehran, Iran. The author acknowledges the co-operation of M. Hashemi, S. Salajedhe and F. Behbahani.

cobalt acetate and ammonium molybdate and the salt molecules adsorbed onto the support surface, were then reduced to the metals by heating in a stream of hydrogen. The techniques of impregnation varied from one case to another. An examination was made of the surface area, pore size and surface activity of the catalysts. They have been subjected to small laboratory bench experiments and pilot plant tests.

A fuel oil having a viscosity of 144.6 cs at 30°C was pretreated in a liquid-liquid extraction pilot scale. L.P.G. was used as extraction solvent to remove asphalt and heavy metals. The deasphalted fuel was pumped into the top of a reactor equipped with several thermocouples. Hydrogen was fed through a drying tube to the reactors. The reactors were operated to maintain isothermal conditions throughout the catalyst bed. The temperature distribution was kept to within ± 2°C. The pressure drop did not exceed more than 1 per cent of the operating pressure.

The reactor was warmed gradually and then the feed was introduced under steady conditions. The reactor products were cooled by a water cooler and then passed to a high pressure separator, where hydrogen rich gas was flushed from the liquid product and the products were measured and identified.

RESULTS

1. Sulphur removal increased with an increase in the reaction temperature when the liquid hourly space velocity was fixed.
2. The rate of sulphur removal increased with increasing hydrogen pressure at fixed temperatures.
3. Vanadium and other heavy metals can be effectively removed from the fuel oil to prolong the life of the hydrodesulphurization catalyst.
4. The rate of sulphur removal is decreased with the ageing of the catalyst.
5. Improved desulphurization will result with increasing total pressure or increasing hydrogen partial pressure.

The economic feasibility study is under investigation.

In conclusion, it should be mentioned that Iran with its expanding oil and petrochemical industries may be considered as one of the biggest future consumers of a variety of industrial catalysts. The country should follow an active line in catalytic research work which should, one day, lead to the establishment of the manufacture of most industrial catalysts.

PRESENT STATUS AND FUTURE POSSIBILITIES OF CATALYST PRODUCTION IN INDIA

A H LALLJEE*

I. INTRODUCTION

Soon after gaining independence in 1947, the Government of India decided to implement its plans for a chemical fertilizer factory based on coal gasification at Sindri. The plant was set up by a public company known as Sindri Chemicals & Fertilizers Limited. A small research and development cell was organized within the company to study the technologies involved in the manufacture of chemical fertilizers. During the commissioning stage of the Sindri plant, apparently due to an upset in the operations, the high temperature carbon monoxide conversion catalyst operating at near atmospheric pressures was observed to have lost some of its activity. This 270 tons of catalyst imported from the United Kingdom of Great Britain and Northern Ireland was regenerated by the efforts of the research and development cell of the Sindri Fertilizers.

The success in the regeneration of a catalyst provided the necessary impetus and confidence to undertake further developments towards the production of the catalyst itself in India. These efforts resulted in producing, before the mid 1950s, a small quantity of proprietary high temperature shift catalyst for operation at pressures close to atmospheric pressures only. Soon thereafter Sindri Fertilizers also produced some quantities of an iron oxide mass for desulphurization of raw gas obtained from coal gasification. Both these catalysts found immediate application in the Sindri ammonia plant. However the success so achieved in the production of proprietary catalysts did not result in covering much of the demands of the developing fertilizer industry.

II. TOWARDS SELF-SUFFICIENCY IN CATALYST PRODUCTION

A survey carried out as late as 1965 revealed that the requirements of every type of catalyst for all the ammonia plants then under construction, without exception, were still to be met by imports, usually through procurement by the engineering contractors concerned. Even the Sindri expansion carried out in the late 1950s had its initial and spare charges of catalysts imported, and the first Sindri plant continued to import its requirements of ammonia synthesis catalysts. This will be clear from table I, which lists the various ammonia plants in 1965 which were either using or had ordered imported catalysts for initial and spare charges.

The survey also considered the projected growth of the ammonia industry. Table II lists the various ammonia plants that had been projected

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/18.

* Catalysts and Chemicals India (West Asia) Pvt. Ltd., Bombay, India.

more or less on a firm basis for start up before 1969. It also lists the various catalyst types to be used in these plants. It was clear that establishing an additional ammonia capacity of about 2.0 million tons per annum (in terms of nitrogen) by 1969 would necessitate large scale imports of catalysts.

TABLE I

AMMONIA PLANTS IN INDIA USING ORDERED IMPORTED CATALYSTS IN 1965

	Plant	Capacity (tons/year nitrogen)	Type of catalysts	Feedstock
1	Sindri I FCI	65,000	j	Coke oven gas
2	Sindri II FCI	50,000	a, e, f, j	Coke oven gas
3	Rourkela HSL	120,000	a, f, j	By product coke oven gas
4	Nangal FCI	80,000	j, k	Electrolytic hydrogen
5	Trombay FCI	90,000	f, j	Partial oxidation naphtha
6	Gorakhpur FCI	80,000	a, f, j	— do —
7	Namrup FCI	50,000	b, e, f, j	Natural gas reforming
8	Alwaye II FACT	15,000	f, j	Partial oxidation naphtha
9	Alwaye III FACT	20,000	f, j	do
10	Neyveli NLC	70,000	a, f, j	Lignite gasification
11	Varanasi NFC	10,000	a, f, j	Coke
12	Ennore Parry	10,000	f, j	Partial oxidation naphtha
		660,000		

TABLE II

AMMONIA PLANTS IN INDIA PROJECTED IN 1965 FOR START-UP BEFORE 1969

	Ammonia plant (owner/location)	Capacity (tons/year nitrogen)	Type of catalysts	Feedstock	Start-up before
1	Visakhapatnam Coromandel	84,000	c, d, e, f, g, h, i, j	Naphtha reforming	1968
2	Baroda GSFC	96,000	— do —	Naphtha/gas reforming	1968
3	Durgapur FCI	150,000	— do —	Naphtha reforming	1969
4	Cochin FACT	140,000	— do —	— do —	1969
5	Trombay II FCI	240,000	— do —	— do —	1969
6	Alwaye IV FACT	30,000	— do —	— do —	1969
7	Baroda II GSFC	110,000	— do —	— do —	1969
8	Kanpur IEL	240,000	— do —	— do —	1969
9	Goa Zuari	150,000	— do —	— do —	1969
10	Madras MFL	190,000	— do —	— do —	1969
11	Kota Sriram	120,000	— do —	— do —	1969
12	Mangalore Mangalore Govt.	150,000	— do —	— do —	1969
13	Kothagudem Allied	60,000	a, f, j	Coal gasification	1968
14	Sindri Reformer FCI		c, d, f	Naphtha reforming	1969
15	Rourkela Reformer HSL		c, d	— do —	1969
		1,770,000			

KEY TO TABLES I AND II

a denotes	desulphurization catalysts iron oxide
b denotes	desulphurization catalysts treated carbon
c denotes	desulphurization catalysts zinc oxide type
d denotes	hydrotreating
e denotes	cracking/reforming

f denotes	high temperature CO conversion
g denotes	low temperature CO conversion
h denotes	chloride sulphur guard
i denotes	methanation
j denotes	synthesis
k denotes	de oxo
FCI denotes	Fertilizer Corporation of India Limited
HSL denotes	Hindustan Steel Limited
FACT denotes	Fertilizers & Chemicals Travancore Limited
NLC denotes	Neyveli Lignite Corporation Limited
Parry denotes	E I D Parry Limited
Coromandel denotes	Coromandel Fertilizers Limited
GSFC denotes	Gujarat State Fertilizers Company Limited
IEL denotes	Indian Explosives Limited
Zuari denotes	Zuari Agro Chemicals Limited
MFL denotes	Madras Fertilizers Limited
Sriram denotes	Sriram Fertilizers and Chemicals
Allied denotes	Allied Chemicals of the United States of America

In consultation with Catalysts & Chemicals Inc. of Louisville, Ky., United States of America a further study was carried out. The conclusions of this study were broadly that

- a minimum economic capacity for a catalyst manufacturing unit in India, such as would enable the consumer to buy proprietary catalysts at a price not exceeding the price he would pay for imported catalysts, required a market potential equivalent to catalyst requirements of
  a) operating ammonia plants of at least 1 million tons per year of nitrogen capacity and
  b) new ammonia constructions of at least 500,000 tons per year of nitrogen capacity.
- a catalyst manufacturing unit should preferably be in a position to supply the complete range of catalysts required for large ammonia plants based on modern technology.
- a catalyst manufacturing unit located in India would be advantageously placed to serve the catalyst requirements of the petroleum refineries, hydrogen and ammonia plants in the West Asian region.
- a catalyst manufacturing unit in India could also cater to the catalyst requirements of the Indian refineries and petrochemical industry.
- the successful marketing of catalysts was possible only if the catalysts being offered had proven excellence in commercial operations and the performance could be guaranteed to meet the parameters of the plant design.

On the basis of this study, collaboration was sought from Catalysts and Chemicals Inc., and an application for a licence to manufacture catalysts in India was made to the Government of India in September 1965. In June 1967, the project received preliminary approval. The collaboration agreement received preliminary approval in February 1969 and final approval in November 1970. Catalysts and Chemicals India West Asia (CCIWA)'s catalyst factory commenced commercial production by April 1971. The licensed installed capacity of CCIWA's factory in Kerala is given in table III.

Meanwhile the Fertilizer Corporation of India has also established production of a large range of catalysts (manufactured entirely on the know-how developed themselves). It is understood that at present, Fertilizer

TABLE III

CAPACITY OF CATALYSTS AND CHEMICALS IN INDIA (WEST ASIA)

	Catalysts	Tons year
1	Desulphurization catalysts	40
2	Petrochemical catalysts	50
3	Hydrotreating catalysts	200
4	Naphtha & hydrocarbon cracking & reforming catalysts	80
5	High temperature CO conversion catalysts	450
6	Low temperature CO conversion catalysts	450
7	Methanation catalysts	66
8	Ammonia synthesis catalysts	300
9	Zinc oxide type desulphurization catalysts	300
10	Petrochemicals hydrogenation catalysts	15
11	Catalytic reforming catalysts	30
		1975

Corporation of India offers to ammonia industry the following catalysts

- Naphtha and gas cracking and reforming catalysts,
- Desulphurization catalysts of iron oxide type,
- Desulphurization catalysts of zinc oxide type,
- High temperature CO conversion catalysts,
- Low temperature CO conversion catalysts,
- Zinc oxide desulphurization catalysts, and
- Methanation catalysts.

III. CATALYST REQUIREMENTS IN INDIA

The requirements of catalysts in India at present and projected up to 1974/75 are given in table IV. The requirements have been estimated

TABLE IV

CATALYST REQUIREMENTS IN THE FERTILIZER AND PETROLEUM INDUSTRY IN INDIA EXCLUDING THE REQUIREMENTS OF FCI PLANTS (FIGURES IN TONS)

	Catalysts	Average life, years	1972 – 73	1973 – 74	1974 – 75	Total
1	Desulphurization (treated carbons)	2	30	30	60	120
2	Desulphurization (zinc oxide type)	1½	130	130	200	460
3	Hydrotreating catalysts	5	250	250	350	850
4	Cracking/reforming catalysts	4	45	50	80	175
5	High temperature CO conversion	3	125	125	250	500
6	Low temperature CO conversion	1½	100	100	200	400
7	Methanation	4	20	40	80	140
8	Ammonia synthesis	7 plus	nil	100	200	300
9	Petrochemicals catalysts	various		50	90	150
10	Petrochemicals hydrogenation	various		15	15	45
11	Catalytic reforming catalysts Pt type		10	10	10	30

for only those catalysts that are presently approved for manufacture by CCIWA and excludes the requirements of catalysts for the plants operated or under construction by the Fertilizer Corporation of India

The requirements have been estimated after taking into consideration, among other factors, the following

- the total installed design volumes of operating ammonia plants as given in table V.
- the total design catalyst volumes of ammonia plants scheduled for start up before 1973/74 as given in table VI.
- average operating life of the catalysts as indicated in table IV which itself is based on the technologies involved and operating experience in the several plants as known to CCIWA's technical service division. Incidentally, tables V and VI also give the totals of the design volu

TABLE V

TOTAL INSTALLED DESIGN VOLUMES IN OPERATING AMMONIA PLANTS IN INDIA

	Catalysts	FCI plants Cu. m.	Non FCI plants Cu. m.	Total	
				Cu. m.	Tons (estimated)
1	Desulphurization (iron oxide type)	1,300	670	1,970	1,600
2	Desulphurization (treated carbons)	10	50	60	35
3	Desulphurization (zinc oxide type)	3.3	212.2	215.5	225
4	Hydrotreating	3.5	151.2	154.7	125
5	Cracking reforming	48.5	226.6	275.1	275
6	High temperature CO conversion	371.8	351.0	722.8	800
7	Low temperature CO conversion	Nil	224.2	224.2	250
8	Methanation	7.7	91.4	99.1	80
9	Ammonia synthesis	29.1	129.2	158.3	455

TABLE VI

TOTAL DESIGN CATALYST VOLUMES OF AMMONIA PLANT STARTING UP DURING 1972/73 AND 1973/74 IN INDIA

	Catalysts	FCI plants Cu. m.	Non-FCI plants Cu. m.	Total	
				Cu. m.	Tons (estimated)
1	Desulphurization (iron oxide type)	Nil	Nil	Nil	Nil
2	Desulphurization (treated carbons)	30	56.6	86.6	50
3	Desulphurization (zinc oxide type)	38.6	79.4	118.0	120
4	Hydrotreating	46.6	117.1	163.7	130
5	Cracking reforming	110.7	230.9	341.6	340
6	High temperature CO conversion	163.0	507.0	670.0	750
7	Low temperature CO conversion	156.5	268.0	424.5	475
8	Methanation	55.0	91.7	146.7	115
9	Ammonia synthesis	67.4	215.9	283.3	815

mes of plants in operation and those under construction which are scheduled for start up before 1973-74 for both FCI and non FCI ammonia plants in India,

- the requirements of the petroleum refineries and petrochemical plants as roughly estimated by CCIWA's sales division

IV. EXPORT POTENTIAL IN WEST ASIAN COUNTRIES

The principal potential for exports of catalysts manufactured by CCIWA is in countries of West Asia including Afghanistan, Iran, Iraq, Jordan, Kuwait, Saudi Arabia and the other Gulf States of Abu Dhabi, Bahrain, Dubai, Muskat, Oman etc. India's immediate neighbours Bangladesh, Sri Lanka and Pakistan are also potential markets. However their requirements have not been considered.

The total presently installed capacity of operating ammonia plants in this region is about 5,000 tons per day or about 1.38 million tons per year in terms of nitrogen, including the ammonia plants at Shahpur and Shiraz in Iran, at Dammam in Saudi Arabia, three plants in Kuwait, at Doha in Qatar, at Basrah in Iraq and one plant in Afghanistan.

Furthermore, within the next three or four years additional ammonia capacity of 1000 t/d in Iran and 800 t/d in Iraq may be expected to materialize. In addition to these ammonia plants, there are three large oil refinery hydrogen plants in this area including those at Tehran in Iran, and two in Kuwait having a total capacity of about 140 MMSCF/day of hydrogen. Additionally, three more hydrogen plants in Iran, Jordan and Saudi Arabiu may be expected to commence production within the next three or four years. Based on the operational experience in these plants related to catalyst life, the catalyst demand in these countries has been broadly estimated by CCIWA's technical service division as given in table VII.

TABLE VII

ESTIMATED CATALYST REQUIREMENTS IN WEST ASIAN COUNTRIES (IN TONS)

	Catalyst	1972 – 73	1973 – 74	1974 – 75
1	Desulphurisation (treated carbons)	30	30	60
2	Desulphurisation (zinc oxide type)	125	150	200
3	Hydrotreating	250	250	350
4	Reforming	40	50	80
5	High temperature CO conversion	125	125	250
6	Low temperature CO conversion	100	125	250
7	Methanation	20	40	80
8	Ammonia synthesis	—	100	200
9	Petrochemicals hydrogen	—	—	5
10	Petrochemicals catalysts various	—	5	10
11	Catalytic reforming Pt type	—	10	10

V. SURPLUS CATALYST PRODUCTION IN INDIA

Considering the present installed capacity at CCIWA's factory in India and Fertilizer Corporation of India's production capacity, it is estimated that about 50 per cent of CCIWA's capacity will remain surplus and available for exports after the total Indian requirements have been met for at least the next three years.

VI. INDIA AS A CATALYST SUPPLIER TO WEST ASIA

India as a supplier of proven catalysts offers many advantages to the catalyst consumers in the West Asian countries. These advantages arise primarily because of it's nearness to the region and since age old trade routes between India and these countries are well established. The consumer in West Asia can now depend on quick availability of his catalyst requirements and need not tie up his money unnecessarily in holding large inventories of spare catalysts. From India it is now possible for the catalysts to reach any of the consumers in this region within ten or fifteen days, whereas previously it required six to eight weeks or more. Further, it is now possible for them to obtain the services of a technical service engineer for any emergency situations within a few hours. Experience has shown that the importance of this prompt availability of technical service cannot be over emphasized. The scope of technical services has been elaborated elsewhere in this paper.

India as a major fertilizer importing country, offers an outlet for the surplus fertilizer production in West Asia and their purchase of the catalysts produced in India would assist, though in a small measure, towards balancing of trade between the West Asian countries and India.

VII. CATALYST PRODUCTION AS AN INDEPENDENT INDUSTRY

The function of a good catalyst is to increase the rates of chemical reaction such as to make possible the production of products under much more favourable conditions of temperature and pressure than if no catalyst or an inferior one were present. Hence, the right catalyst is often the secret to successful manufacture of a particular chemical product.

Until 1950, catalysts were developed and produced only by very large chemical companies usually for use in their own chemical plants. These chemical companies jealously guarded the know-how on catalysts both with regard to their production and use. Only when the chemical companies chose to do so, would they agree to sell the process together with the catalysts to another party on payment of huge licence fees in addition to exhorbitant prices for the catalysts, the exact formulations of which were seldom or never disclosed.

Since that time, however, a few companies have been organized specifically to manufacture and market catalysts, no longer just as adjuncts to another main chemical product. These companies began manufacturing catalysts that were either developed by others or by themselves. Catalysts for specific applications then became available outside the group of the then existing large monopolistic chemical companies. Engineering contractors were now able to offer to build economic chemical plants for new entrepreneurs without having to pay large licence fees and catalyst prices. To be sure, this also contributed, in no small measure, towards a wider ownership of larger chemical plants, particularly in the ammonia fertilizer industry, all over the world.

VIII. SUCCESSFUL MANUFACTURE OF CATALYSTS

The successful manufacture of catalysts requires, amongst other things, a clear appreciation of the fact that catalysts are not simple chemical compounds or mixtures of chemical compounds having a set or predetermined analysis. It must also be understood that the manufacture of catalysts can only be carried out batchwise or at best on a semicontinuous basis, since it is not the mere compounding of materials in set proportions that yields a good catalyst but the various techniques of controlled precipitation, treatment, compounding and forming that results in high activity catalysts. The proper selection of raw materials and the avoidance of any poisonous contaminants even in the smallest concentrations is no less important in the manufacture of a good catalyst. The mastery of these techniques, which is almost an art for producing catalysts, requires years of experience and the strictest quality control checks at various stages of manufacture. Having recognized the specialized and sensitive nature of catalyst manufacture, CCIWA opted to obtain this know-how by collaborating with Catalysts and Chemicals Inc whose skills in production had been clearly proven.

IX. TECHNICAL SERVICE

The marketing of catalysts also requires special technical competence which is not generally available. This is because the successful performance of a catalyst depends substantially on know-how regarding its use, which is provided by the catalyst supplier. Often, more than one catalyst is suitable for a particular chemical reaction and usually several will give the same result if the operating conditions be modified.

Thus a chemical design can be fitted to an available catalyst or alternatively a different catalyst may be employed to suit a more acceptable process design. A less active catalyst can also be made to perform but in doing so, the user would probably have to adopt a less economic process design involving higher capital and operating costs.

The catalyst supplier therefore has to have facilities and technical competence to provide:

- Process information to the engineering contractor or the customer during the initial stages of design and construction of the plant. Reliable information obviously can be provided only if the catalyst offered has been fully proven in commercial operation under several varying conditions of operations. Bench scale or even pilot plant data alone cannot possibly form the basis for providing such information.
- Start-up services of competent, experienced engineers, when the catalyst is first being placed on stream, are needed because overheating could sometimes totally spoil the entire charge of costly catalyst.

- Subsequent follow up service to assist the customer in maintaining optimum operating performance of the catalysts and to assist in the solution of any problems which relate to the use of the catalysts. This service has often assisted an operating company in keeping its through put at the maximum while maintaining the desired quality of the product by recommendations of changes in operating conditions to compensate for any damage to the catalyst resulting from upsets in operation or unexpected contamination of the feed material

The engineering contractors and the customers, particularly ammonia manufacturers are becoming increasingly conscious of the importance of these services and often insist that a clause providing for them is written into the contract while purchasing the catalyst At the same time, they demand suitable performace and life guarantees on the catalyst There is no doubt that the catalyst vendor recognizes the right of the purchaser to demand these services.

Among other services that a catalyst vendor provides is operator training which includes discussions of the theoretical aspects relating to the catalysts with special emphasis on the practical application of the catalysts in the customer's plant It also includes discussions on the evaluation of various factors that influence the performance of the catalysts, the physical properties of the catalysts, various precautions necessary in using the catalysts, loading and unloading procedures, start up and shut-down procedures and methods of evaluating the performance of the catalysts.

X. CONSIDERATIONS FOR SETTING UP NEW MANUFACTURING UNITS

It will be clear from the foregoing that a good catalyst per se does not ensure success in its marketing. Price also therefore, is not the only, or even major consideration when an unproven catalyst is being marketed against a proven catalyst A prerequisite for setting up a catalyst producing unit, in a developing or any country is firstly availability of acceptable know how either developed from commercial experience over several years or obtained by transfer through licensing or outright purchase.

Price assumes considerable significance when selection is to be made between two proven catalysts for the same service. There are at least three or four renowned catalyst suppliers competing severely for the limited markets presently available

The mushrooming of the ammonia industry all over the world during the early and mid 1960s resulted in large catalyst manufacturing facilities being established not only in the United States of America but also elsewhere in the world For instance, Catalysts and Chemicals Inc., in collaboration with Mechim (Société Générale) and Mitsui Toatsu, established catalyst manufacturing plants in Belgium and Japan respectively, in addition to the CCIWA plant in India At the same time catalysts are produced by other companies in the United Kingdom, other European countries and the United States. With the subsequent slackening of growth in the fertilizer industry, there now exists a large surplus catalyst production capacity resulting in severe competition and very low sales prices.

Raw material availability at competitive prices therefore has assumed greater importance. Not every country, developed or developing, is assured of low priced raw materials.

Similarly, of great importance is the cost of technical expertise. India is particularly well placed in this respect because of the high order of technical competence available in the country at rates perhaps one third or less than those in developed countries.

XI. CONCLUSIONS

Successful manufacture of highly sophisticated and sensitive catalysts requires a mastery over the production techniques. The manufacturing know-how must be available, either developed independently or obtained by transfer through licensing or outright purchase. Only a very few companies in the world possess this know-how.

A necessary factor in the successful marketing of catalysts, apart from price and product acceptability, is the capability of the catalyst vendor to provide competent technical service assistance during the design stages of a chemical plant, at the time of catalyst loading, during initial plant start-up and thereafter throughout the lifetime of the catalyst. The catalyst vendor must also provide acceptable performance and life guarantees on his catalysts. Yet another very important factor in this regard is that the catalyst vendor must be in a position to meet the emergency requirements of catalysts and technical service promptly, sometimes at very short notice.

There is surplus capacity for ammonia catalysts on a wold-wide basis resulting in severe competition between the manufacturing companies for the limited markets presently available. Long-term growth of demand, however, may be expected on the premise that ammonia production must be stepped up considerably to meet the desired levels of fertilizer use, particularly in the developing countries.

TECHNICO-ECONOMIC ASPECTS RELATED TO HEAT RECOVERY IN HETEROGENEOUS CATALYTIC PROCESSES[1]

V. CIORT*, D. CIOCÎRTOIU*, I. ZÎRNĂ*, ST. DESPA*, D. GRIGORIU*

1. INTRODUCTION

Due to the fact that the reaction products resulting from heterogenous catalytic processes are later processed at temperatures lower than those at which the reaction occurs, the reactor effluent must be cooled.

This necessity is even more evident in catalytic processes which occur under hydrogen pressure, recirculation of which requires its separation from the reaction product, in liquid phase, at the process pressure and at the lowest possible temperature. Due to this fact and considering that the effluent contains a large quantity of heat and it is at a high thermal level, partial recovery of this heat is possible.

The typical diagram of such a process (figure 1) shows that the charge stock, blended with hydrogen, is preheated by heat exchange with the reactor effluent, and brought up to the reactor operating temperature while passing through the heater. The reactor effluent, following heat transfer in the charge stock preheater, is cooled to the temperature at which the liquid-vapor blend can be separated, obtaining hydrogen rich gas which is recycled and the liquid phase, which is processed later.

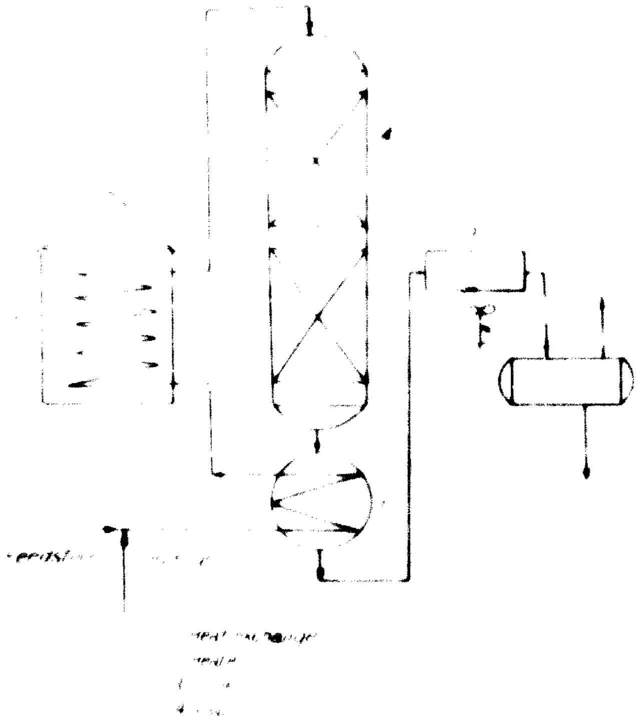


FIGURE SCHEMATIC DIAGRAM OF HYDROGEN TREATING UNIT

The heat exchange equipment may be so sized as to obtain a more or less complete recovery of the heat contained in the effluent which in turn determines the heat requirements of the heater.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/11.

* Romanian Research and Design Institute for Petroleum Refineries, Ploieşti, Romania.

The economic implications of heat recovery are discussed in this article, and the effect of effluent outlet temperature from the charge stock preheater is analysed as an independent variable, on the operating cost (cost of heat introduced in the heater, cost of effluent cooling, following heat exchange with charge stock) and investment charges (cost of effluent-charge stock heat exchanger, heater, effluent cooler).

II. THERMAL DUTY OF EQUIPMENT

A hydrogen treating process is considered, as an example, of 100,000 t/year capacity, the charge stock being a heavy oil fraction.

It is assumed that the charge stock at 40°C, blended with the hydrogen, is preheated by heat exchange with the reactor effluent, and further heated in the heater up to the reactor operating temperature.

The reactor effluent, following the transfer of a part of the charge stock heat, is air cooled to the high pressure separator temperature (60°C) where a pressure of 150 atm. was considered.

The calculations were carried out by changing as an independent variable the effluent outlet temperature from the charge stock preheater for which four values were considered.

319°C, 274°C, 218°C and 156°C.

The thermal duty variation of the preheater, heater and cooler is plotted in figure 2 as a function of the above-mentioned parameter.

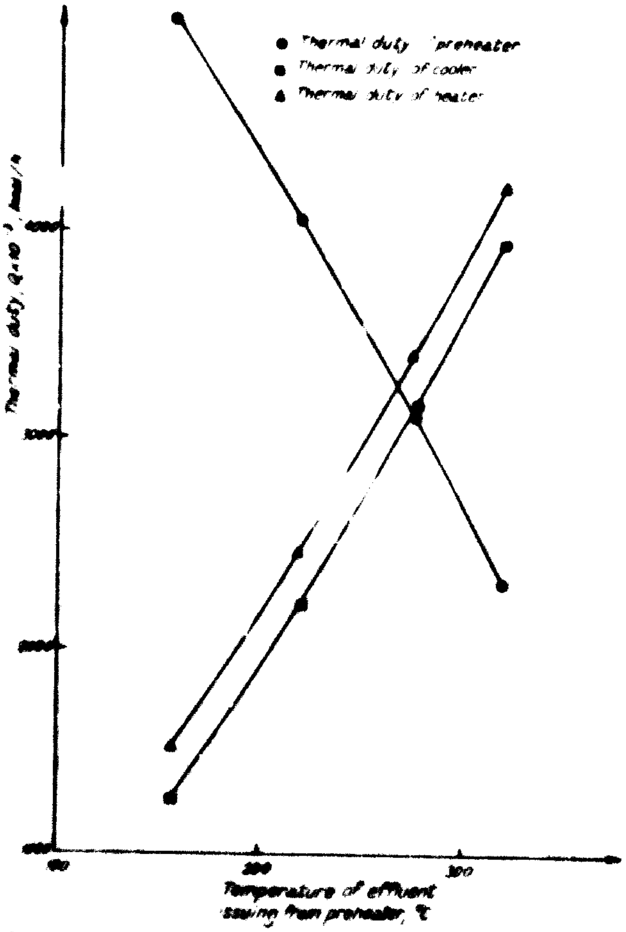


FIGURE 2. VARIATION OF EQUIPMENT THERMAL DUTY IN RELATION TO TEMPERATURE OF EFFLUENT ISSUING FROM FEEDSTOCK PREHEATER

In order to carry out the respective calculations, the charge stock and effluent TBP curve was taken into account (respectively, the distribution of reaction products) and the quantity of hydrogen recycled in the heater.

The percentage of vaporized product from the streams concerned was calculated each time first assuming and then checking the partial pressure of vapours and liquid on the basis of equilibrium vaporization curves plotted in accordance with the Edmister (1) method. The enthalpies for liquid and vapour product were taken from (3), those for gas, from (4). Heat calculations were carried out by multiplying the quantity of product by the difference of enthalpy corresponding to the two temperature levels in order to exclude the calculation basis of the enthalpies.

III. INVESTMENT CHARGES

Investment charges were estimated according to data given in literature (2) for which it was required to know the heat exchange surfaces and thermal duty of the heater.

The prices obtained from the data specified above were corrected according to the procedure as a function of the quality of materials used and the operating pressure.

In the following paragraphs only the results of these calculations are presented, with all the sizes required to determine the cost.

A 10 per cent amortization rate per year was established, considering that the unit would be paid off within 10 years.

Ultimately, the cost variation of the equipment as well as the variation in amortization rate was plotted as a function of the effluent outlet temperature from the exchanger.

In order to emphasize the effect of the material (although in the example considered, the equipment should be fabricated of alloy steel), the cost prices were calculated for cases where the exchanger and cooler would be either carbon steel or alloy steel, the heater being of alloy steel in all cases.

a. COST OF CHARGE STOCK PREHEATER

In order to establish the cost of the charge stock preheater the heat exchange surfaces were calculated considering, an overall heat transfer coefficient of K = 400 Kcal/m²h°C, according to practical operating data for similar equipment.

The costs of the heat exchanger for the four alternatives are given in table I. The variation of the cost price with the effluent outlet temperature from the preheater is plotted in figure 3.

TABLE I

COST OF CHARGE STOCK PREHEATER

Effluent, °C	Charge stock, °C	$Q \times 10^{-3}$ Kcal/h	S, m²	Cost of exchanger, $		Annual amortization, $	
				Carbon steel	Alloy steel	Carbon steel	Alloy steel
319	200	2,300	24	11,400	24,400	1.140	2.[illegible]
274	250	3,100	42	16,100	34,700	1.610	3,470
218	300	4,050	74	29,400	63,000	2.940	6,300
156	350	5,000	146	58.800	126,000	5 880	12,600

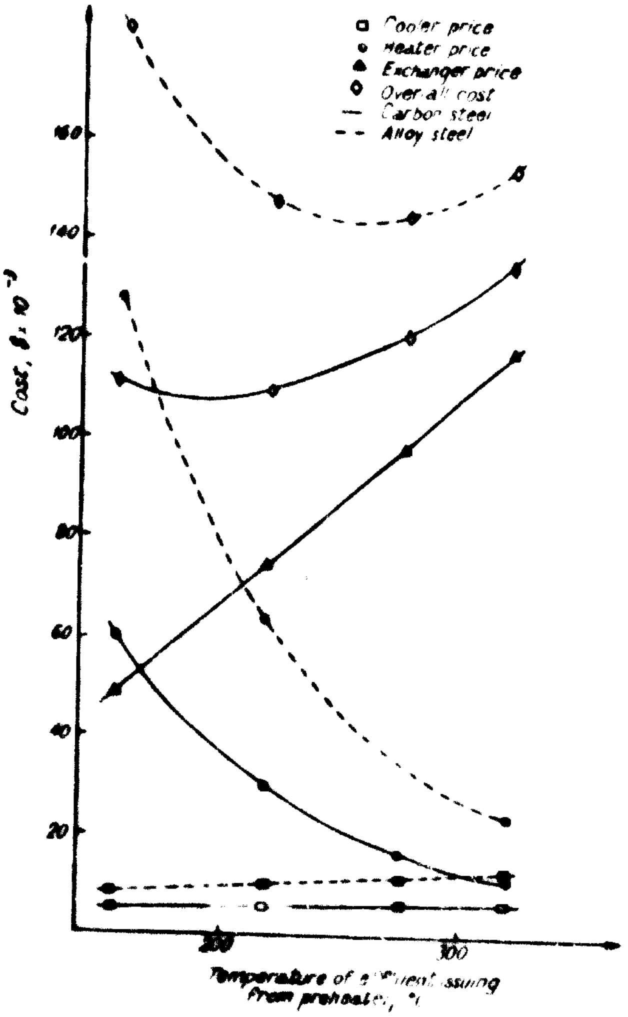


FIGURE 3. VARIATION OF EQUIPMENT COST IN RELATION TO THE TEMPERATURE OF EFFLUENT ISSUING FROM PREHEATER

b. COST OF HEATER

According to data given in literature (2), the cost of the heater was established as a function of the thermal duty of the heater. The results are given in table II. A graphical presentation of the variation of heater cost as a function of exchanger outlet temperature is given in figure 3.

TABLE II

COST OF HEATER

Effluent, °C T_0	Charge out, °C T_1	$Q \times 10^{-6}$ kcal/h	Heater cost, $	Annual amortization, 10 %
319	[illegible]	4,200	117,000	11,700
174	[illegible]	3,400	98,000	9,800
218	[illegible]	2,480	73,600	7,360
186	[illegible]	1,300	47,200	4,720

c. COST OF EFFLUENT COOLER

Air coolers were suggested to be used for effluent cooling, considering the advantages of these as compared to water coolers (deposit of scale in certain points, conservation of water, easier to maintain, etc.).

Heat exchange surfaces were calculated according to the procedure proposed by the Hudson Engineering Corporation, allowing an over-all heat transfer coefficient against a finless tube surface of 317 Kcal/m²h°C. The air used in the calculations, is dried, at 21.1°C and 760 mm Hg pressure. Results obtained are given in Table III, and a graphical presentation, in figure 3.

TABLE III

COST OF COOLER

Effluent, °C T_e	$Q \times 10^{-3}$ Kcal h T_i	S, m²	Cost of cooler, $		Annual amortization, 10%	
			Carbon steel	Alloy steel	Carbon steel	Alloy steel
319	3.950	135	6.700	12.800	670	1.280
274	3.150	122	5.800	11.200	580	1,120
218	2.200	105	5.200	10,000	520	1,000
156	1.250	77	4.100	7.800	410	780

d. TOTAL INVESTMENT CHARGES

The variation of investment charges for the 4 calculation alternatives is obtained by totallizing the cost of the 3 units (carbon steel or alloy steel fabrication).

As can be seen from figure 3, when the units are of carbon steel, investments are minimum at 180°C effluent outlet temperature from the exchanger, while for alloy steel, the investments are minimum at 280°C. The influence of operating costs on the position of this minimum will be studied further.

IV. OPERATING CHARGES

In order to establish operating charges, only the cost variation of heat transfer in the heater and the power consumed by the fan, are considered below.

The cost of power consumed by the pump and compressors was not taken into account as these are practically constant. The pressure drop variation is small as compared to reactor operating pressure, and the total surface of heat exchanger and effluent cooler, varies within small limits with respect to that of the exchanger and charge stock heater.

Operating charges were established for one year of operation, taking literature data for the cost of heat $ 0.11/1000 Kcal (5) and for power, the value of $ 0.01/kWh (6).

a. COST OF HEAT TRANSFER WITHIN THE HEATER

Knowing the absorbed heat for the four alternatives and assuming a value of 0.75 for over-all heater efficiency, the consumption of heat per year was determined. The results of the calculation are given in table IV, and the variation in cost of heat, as a function of the exchanger outlet temperature (of the effluent) is plotted in figure 4

TABLE IV

COST OF HEAT

T Effluent, °C	$Q_a \cdot 10^{-3}$ Kcal/h heater	Cost of heat, $/year
319	4,200	49,200
274	3,400	39,900
218	2,400	28,000
156	1,500	17,600

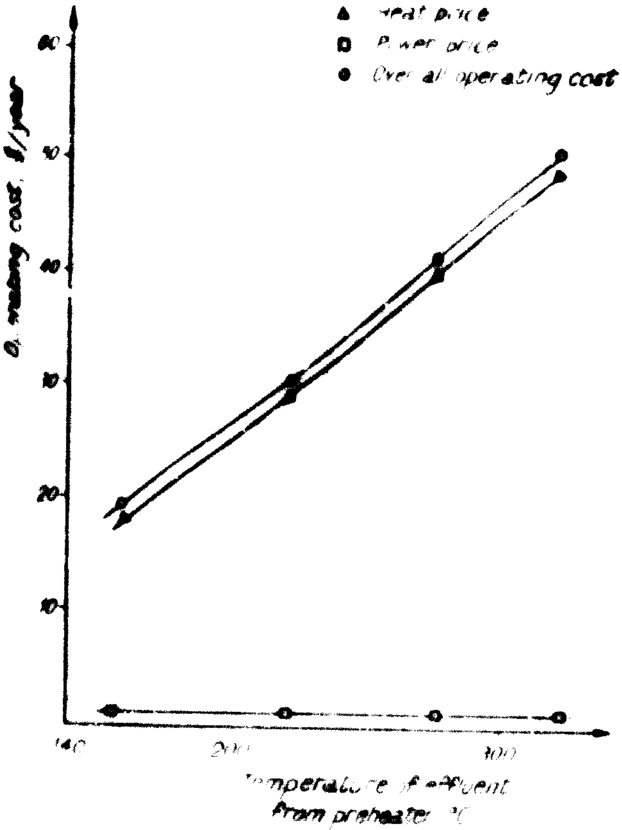


FIGURE 4 VARIATION OF POWER PRICE, HEAT PRICE AND OVER-ALL COST IN RELATION TO EFFLUENT TEMPERATURE OF PREHEATER

b. COST OF FAN POWER CONSUMPTION

According to the procedure specified for the design of coolers, the power consumption for the fan was estimated. In table V are given the

→

75. 11. 20

2 OF 4

06639

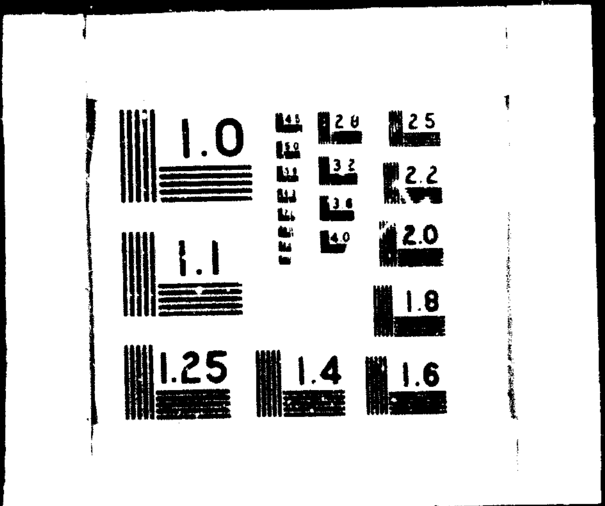


TABLE V

COST OF POWER

T Effluent, °C	S, m²	kWh year	Cost of power $/year
319	135	136,000	1,360
274	122	120,000	1,200
218	105	104,000	1,040
156	77	80,000	800

results of these calculations, and in figure 4 are plotted the cost variations of electric power for the four alternatives.

c. TOTAL OPERATING COST

The variation of the total cost with the exchanger outlet temperature was obtained by totallizing the operating costs in the four calculation alternatives.

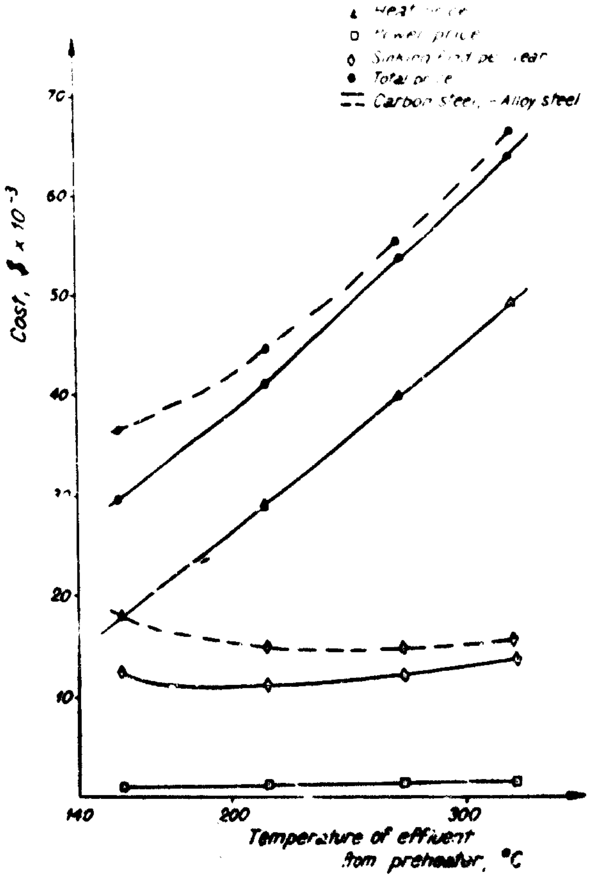


FIGURE 5. VARIATION OF OVER-ALL OPERATING COST IN RELATION TO EFFLUENT TEMPERATURE OF PREHEATER

As can be seen in figure 5, the cost of power for the fan represents only 5 per cent of the total operating costs. Operating costs increase rapidly with the increase of effluent temperature at the exchanger outlet,

V. CONCLUSIONS

In order to establish the effect of heat recovery on the total cost (annual amortization plus annual operating charges), the total cost variation, as a function of effluent temperature at the exchanger outlet was plotted (figure 5).

As may be observed, operating costs have a great influence on the position of minimum investments established earlier, giving the total cost curve an aspect of continuous increase from the high pressure separator operating temperature to a practically complete recovery of the effluent heat.

Since more complete recovery of heat leads to more expensive equipment, while the annual cost (amortization + operating costs) does not emphasize this aspect, the initial cost must be taken into account.

Only the general approach is given in this article. For each actual case, the specific conditions of the country, company, and the industrial complex within which the unit is located, must be considered. Particularly for developing countries, a careful study must be made of the economic aspects of suggested technical solutions and the choice of the optimum alternative prescribed by the operating conditions.

REFERENCES

1. W. C. Edmister, Applied hydrocarbon thermodynamics, vol. 1, Houston, Texas, 1961, ch. 12,116—132 pp.
2. K. M. Guthrie, W. R. Grace & Co., Chemical engineering vol. 76, No. 6, 1969 114—129 pp.
3. I. B. Maxwell, Data book on hydrocarbons, New York, 1967, 10—127 pp.
4. L. N. Caujar, F. S. Manning, Thermodynamic properties and reduced correlations for gases — Houston 1967.
5. Oilweek, 19, Nr. 33, 7 October 1968, 27 pp.
6. Chemical engineering progress, Nov. 1969, 62 pp.

CATALYSTS USED IN THE FERTILIZER INDUSTRY IN TURKEY[1]

REFIK S. OENUER[*]

Catalysts used in the fertilizer industry were first introduced in Turkey when the first nitrogen based fertilizer plant was completed in Kütahya at 1961. After this one phosphoric acid-triple super phosphate, and two nitric acid-calcium ammonium nitrate plants were completed and the ammonia plant in Kütahya was expanded. Some difficulties were encountered with the catalysts and catalyst beds of the ammonia plants at Kütahya. The CO conversion catalyst of the old plant was oxidized twice during the opening of the reactor for maintenance purposes. Even though both of the oxidizing processes had been carried out with extreme care it was not possible to prevent local over heating. Consequently, in both cases, considerable amounts of the catalyst had been found severely sintered. Since then, a nitrogen atmosphere has been used in the maintenance loading and unloading operations. The catalyst of the new plant however was oxidized successfully. The only difference between these two catalysts that we observed is that the new one is tableted and the old one is not.

The heater cover tube of the new ammonia converter (which was put into operation in the middle of 1968) was damaged at the end of 1968 and in May 1969 it was damaged again. In both cases catalyst was unloaded and loaded under nitrogen atmosphere. After these two operations, the converter could not reach 80 per cent of its nominal capacity. So the catalyst was changed with fresh stock.

Unfortunately in 1971 the cooling tubes of the same converter were deformed and broken. Catalyst was unloaded, tubes were repaired and then new catalyst was loaded.

Thus, during a period of three years ammonia production was stopped at three different times for repair purposes and once for changing the catalyst, for a total of eighteen weeks.

The reasons of these troubles are explained as follows:

1) Heating of catalyst to the reaction temperature at start is possible using a small amount of gas and a small heater in a reasonable time. This causes a great temperature differences between the lower and upper part of the catalyst bed and between the heater tube and the catalyst bed. These thermal stresses can damage the converter seriously. To obtain uniform temperature distribution throughout the converter at start-up, the heater capacity should be sufficiently high.

2) In developing countries like ours start-up and shut-down can occur in ammonia plants, because of electricity power interrupting. In every shut-down and start-up, thermal stresses can cause great damage. The design of such installations should take such points into consideration.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/17.

[*] Turkish Nitrogen Industries, Kütahya, Turkey.

VINYL CHLORIDE PRODUCTION BY CATALYTIC DEHYDROHALOGENATION OF 1,2-DICHLOROETHANE[1]

F. COLUNGA D.*, J. M. FERREIRA F.*

The present paper is concerned with research on the production of vinyl chloride by the dehydrochlorination of 1,2-dichloroethane. Specially treated aluminas were prepared in the Instituto Mexicano del Petróleo and were used as catalysts.

In this particular dehydrochlorination reaction the influence of temperature (300, 325, 350°C) and the influence of space-velocity (0.63, 1.86, 3.75 g/g/hr.) on conversion yield and carbon deposit on the catalyst were studied.

Experiments were run in a pilot plant with a tubular, fix bed reactor of 2.5 cm internal diameter, and charged with 20 g of catalyst. Each run took ten hours and included a gas chromatographic and volumetric analysis of the reaction products hourly

The regeneration of the catalyst was examined also, and the results showed the possibility of operating in an intermittent cycle process by using at least two reactors. The conversion obtained (which may still be improved) was from 80 to 90 per cent, per pass, with a stoichiometric yield of vinyl chloride of 40 to 57 per cent (theoretical yield is 63 per cent) and a selectivity of 95 to 99 per cent. Therefore, it appears to offer a competitive route to the classical thermal process.

I. INTRODUCTION

In Mexico the demand for vinyl chloride is about 35,000 tons per year (1). The current process is based on the use of a tubular furnace which produces vinyl chloride and hydrochloric acid from the pyrolysis of dichloroethane, with a maximum conversion of 60 per cent. Several attempts have been made to obtain a better conversion in this process. During the course of studies on the production of vinyl chloride by catalytic pyrolysis of dichloroethane, it was found possible to increase the total yield of vinyl chloride.

There are two main routes to vinyl chloride production. One is via the addition of hydrochloric acid to acetylene; the other route is via the chlorination of ethylene producing dichloroethane which can then be thermally decomposed, yielding vinyl chloride and hydrochloric acid. Both of these processes are described in the literature (2, 3, 4, 5).

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/19.

* Mexican Petroleum Institute, Mexico City, Mexico. The work described in this paper was carried out at Instituto Mexicano del Petróleo. Thanks are due to the management for making it possible to carry out this work and for granting permission to publish the results. Special thanks are due to E. Aguilar for valuable co-operation.

The pyrolysis reaction involves a free radical chain mechanism (6,7) in which a free radical of chlorine starts the chain.

$$\dot{Cl} + CH_2Cl-CH_2Cl \rightarrow HCl + CH_2Cl-\dot{C}HCl \qquad (1)$$

$$CH_2Cl-\dot{C}HCl \rightarrow CH_2{=}CHCl + \dot{Cl} \qquad (2)$$

These two steps are thought to occur primarily, if not exclusively, in the gas phase. The first step of the chain has not been established with certainty, but there is some evidence that initiation occurs at the wall of the reactor to some extent. When a catalyst is used, initiation apparently occurs at the catalyst surface. This means that characteristic properties of the catalyst (8, 9, 10, 11) such as the crystallographic morphology, the surface area, the pore volume, the acidity, etc., affect the reaction.

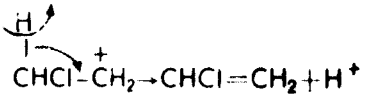
The mechanism of the catalytic reaction may also be ionic because it has been proved that the alumina surface can have an acidic character. Two possible ways for the reaction to take place are assumed:

$$CH_2Cl-CH_2Cl \rightarrow CH_2Cl-\overset{+}{C}H_2 + \overset{-}{Cl} \qquad (3)$$

a) The formation of a carbonium ion by interaction with acid centres (catalyst).

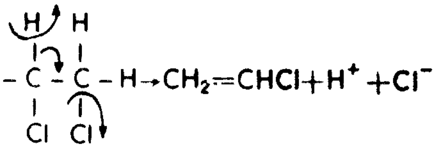
$$CH_2Cl-CH_2Cl \xrightarrow{catalyst} CH_2Cl-\overset{+}{C}H_2 + \overset{-}{Cl} \qquad (4)$$

and the rearrangement of molecule by the elimination of a hydrogen ion as the molecule is deadsorbed from the catalyst.



$$CHCl-\overset{+}{C}H_2 \rightarrow CHCl{=}CH_2 + H^+ \qquad (5)$$

b) By a concertated mechanism



$$-C-C-H \rightarrow CH_2{=}CHCl + H^+ + Cl^- \qquad (6)$$

At present the I.M.P. laboratories are investigating the influence of the acidity in the reaction by controlling it on the alumina surface or by the addition of other compounds in the production processes.

Catalytic dehydrohalogenation processes. Numerous patents are claimed in this area. Some references (12, 13, 14, 15, 16) refer to the use of the system $CuCl_2/Al_2O_3$, $CuCl_2/C$ for vinyl chloride. Others (17, 18) work with $HgCl_2/SiO_2$, $HgCl_2/C$ at low temperatures. By utilizing Al_2O_3 (14, 19, 20), good yields and selectivity are claimed.

II. EXPERIMENTAL

PRODUCTION OF CATALYSTS

The properties of aluminas used as catalysts depend on their preparation (8, 9, 21, 22, 23). In general they are obtained from aluminium, aluminium chloride, aluminium sulphate or from organometallic compounds such as alkyl aluminium. In all cases, an alkali treatment, is involved, and hydroxide is precipitated. Subsequent heating yields alumina with distinct chemical characteristics.

Some aluminas (A-4, A-5) were synthesized in the Instituto Mexicano del Petróleo and their catalytic activity was compared with that of commercial aluminas.

All the aluminas used were analysed by X-Ray micro-diffraction spectroscopy, electronic microscopy (E.M.) and surface adsorption. Also pore volume, particle size, absolute density, bulk and compact density were measured. See table I.

TABLE I

PHYSICAL PROPERTIES OF THE CATALYSTS

Physical property	A – 1	A – 2	A – 3	A – 4[a]	A – 5[a]
Surface, BET m²/gr	350	250	100	100	250
Pore volume Å	65.0	90	120	—	—
Absolute density	1.3813	—	—	2.6321	1 0228
Bulk density	0.6097	0.6097	0.6410	0.7178	0.6931
Compact density	0.5814	0 5555	0.5814	0.6931	0.7143
Size (mesh)	18 – 14	18 – 14	18 – 14	10 – 14	10 – 14
Shape	spherical	spherical	spherical	rolls	rolls

a) These were produced in the Instituto Mexicano del Petróleo.

PRODUCTION OF VINYL CHLORIDE

Pilot plant (figure 1) studies, carried out in a tubular fixed bed reactor, were used to provide a measure of the distribution of products

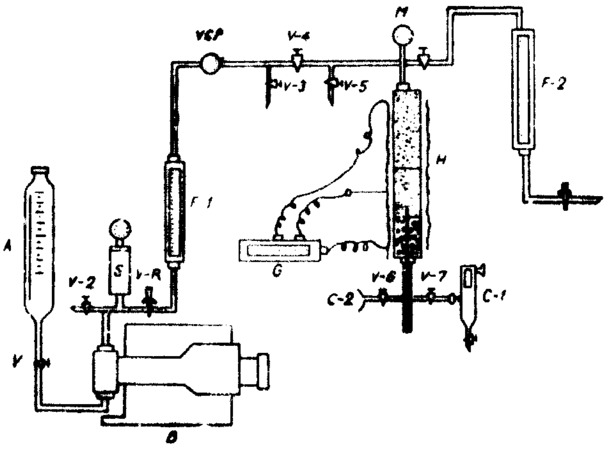


FIGURE 1. PILOT PLANT DIAGRAM

and to establish the space-velocity and the temperature. Feed container A (for technical 1,2-dichloroethane) is connected to piston pump S, which has a device for controlling the impulses of the pump and a micrometric control of piston displacement, so that liquid pumping can be changed rapidly from 0.3 ml/minute to 4.5 ml/minute. These changes were verified by turning on the valve V-3 and measuring the outlet liquid with a graduated cylinder. The installation also has a liquid flow rotameter (F-1). Reactor E (0.25 m in length and 0.025 m in internal diameter) is made of stainless steel. It was heated by a tubular and electrical furnace (H), and the temperature was regulated by a proportional control (G). The reaction temperature was measured by a thermocouple. In all the experiments, 20 gr of catalyst were used.

Each run started by heating the system with N_2 as carrier, controlled by gas flow rotameter F-2. It took one hour for the fix bed catalyst to reach 350°C. Simultaneously, the flow feed was measured and was passed into the reaction zone. The products were collected in cold trap C-1 and in special traps C-2 (figure 2). Analysis (24, 25, 26).

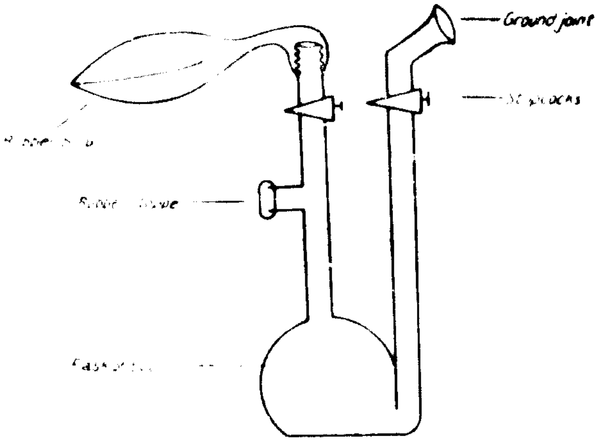


FIGURE 2. **SPECIAL TRAP C-2**

The reaction products in the vapour phase were bubbled at room temperature through N-methyl-2-pyrolidone for 60–120 seconds. The special design of the trap permitted the quantitative dissolution of reaction products without changes of pressure in the reactor.

The analysis of organic products (27) was done in a Perkin Elmer F-11 gas chromatograph, with a flame ionization detector. Two steel columns of a length of 0.45 m and 1.8 inch internal diameter were used, filled with porapak Q (80–100 mesh). The injection temperature program was from 30 to 200°C at a rate of 30°C/minute. The carrier gas was nitrogen (150 ml/minute).

Ethanol was used as an internal reference standard and the sample size was 3 microlitres.

Under these conditions the analysis time was 9 minutes, after which the N-methyl-2-pyralidone was vented into the atmosphere through the backflush system of the chromatograph. Vinyl chloride, 1,2-dichloroethane, ethanol and acetylene were identified.

Hydrocholoric acid was analysed by pouring all the reaction products and solvent of the trap except for the 3 microlitres used for organic analysis into an Erlenmeyer flask, washing with 50 ml of water and titrating with 1.0 N NaOH. The content of carbon in the catalysts was determined by burning at 450°C for 18 hours while air was passed through.

CATALYST ACTIVATION

The dehydrohalogenation reaction was carried out at relatively low temperatures (275–400°C). However, cracking reactions were detected by the gas chromatographic analysis and by the deposit of carbon on the alumina surface. This diminished the conversion with time and therefore the activation of catalysts was studied after 10 hour runs. The results for some experiments are given in table II.

TABLE I.

CATALYST REGENERATION

Exp.	Time (h) / Temp. (°C)	% Conv. 2 h.	% Conv. 4 h.	% Conv. 6 h.	% Conv. 8 h.	% Conv. 10 h.	% Conv. average
1	—	70.0	65.0	56.0	44.5	37.5	54.6
2	7/450	59.0	66.5	57.0	45.0	44.0	54.3
3	10/450	67.0	75.0	67.0	57.0	49.0	[illegible]
4	18/450	66.0	82.0	67.0	60.0	47.5	[illegible]
5	18/450	63.5	60.1	52.0	38.7	20.0	46.9
6	18/450	61.0	54.0	47.0	45.5	38.0	49.1
7	18/450	65.0	56.2	53.0	40.5	30.0	48.9

III. RESULTS

Table I to IV and figures 1 to 6 show the experimental results. All the experiments were run at atmospheric pressure (585 mm Hg) and at least 2 runs were made with the same catalyst. Ten samples were trapped and analysed in each experiment.

The calculation of yield, conversion and selectivity were obtained from the average content of traps during each run.

The carbon deposited on the catalysts was determined after each 10 hour run.

IV. CONCLUSIONS

THE EFFECT OF CATALYST

Catalyst plays an important role in this dehydrochlorination reaction. With the aid of the data of table I and table III, it was possible to deduce the effect of the catalyst. In the case of catalysts A-1, A-2, A-3, the effect of the surface area is shown in figure 3. By comparing experiments 1, 10 and 25 or 4, 13, 28 or 7, 16, 31 it is possible to infer that as the surface area of the catalyst increases, the conversion also increases.

THE EFFECT OF TEMPERATURE

Figure 4, (experiments 11, 14, 17, 19, 23 and 24) illustrates the effect of temperature on yield of vinyl chloride from 1,2-dichloroethane in a fixed catalyst bed, at space velocity of 1.87 gr/gr/hr. Thus an increase from 275°C to 400°C increases the yield from 2.0% to 38.6%. Simultaneously, the selectivity decreased from 100.0% to 80.8% and this was corroborated by the increase of carbon deposit from 4.2% to 23.0%; However, the best yield of vinyl chloride was at 375°C. Nevertheless, 350°C is recommended as the optimum operation temperature — because the yield is still high and the carbon deposit is lower than that attained at 375°C.

THE EFFECT OF SPACE VELOCITY

The effect of space velocity on results at 350°C is shown in figure 5. Experiments with the increasing space velocity (16, 17, 18, 20, 21 and 22) from 0.63 to 7.5 gr/gr/hr decreased the yield of vinyl chloride from 47.4 to 15.5 per cent.

TABLE III

EXPERIMENTAL RESULTS

Exp.	Temp. °C	Space vel.	% Conv.	% Yield	% Select.	% Carbon
CATALYST A-1						
1	300	0.63	23.5	14.2	95.0	2.6
2	300	1.87	10.3	6.2	95.6	4.3
3	300	3.75	5.7	3.6	100.0	5.0
4	325	0.63	64.2	38.6	95.1	3.8
5	325	1.87	21.0	13.3	100.0	5.3
6	325	3.75	19.0	12.2	101.7	6.6
7	350	0.63	90.1	57.0	100.0	6.6
8	350	1.87	80.6	48.5	97.3	8.1
9	350	3.75	31.5	18.4	92.6	7.0
CATALYST A-2						
10	300	0.63	18.4	11.7	100.0	3.9
11	300	1.87	14.2	9.1	100.0	4.8
12	300	3.75	7.0	4.4	100.0	4.2
13	325	0.63	55.0	33.4	96.0	4.1
14	325	1.87	39.8	23.5	93.8	6.1
15	325	3.75	25.0	15.7	100.0	6.7
16	350	0.63	80.0	47.4	94.0	6.1
17	350	1.87	67.0	41.0	97.4	7.8
18	350	3.75	33.1	21.3	101.6	12.5
19	275	1.87	3.1	2.0	100.0	4.2
20	350	1.25	80.5	41.2	81.4	6.9
21	350	5.6	27.1	15.9	92.9	8.9
22	350	7.5	33.5	15.5	73.2	12.0
23	375	1.87	80.7	45.0	88.3	16.6
24	400	1.87	75.6	38.6	80.8	23.6
CATALYST A-3						
25	300	0.63	2.3	1.4	100.0	1.2
26	300	1.87	1.9	1.2	100.0	1.6
27	300	3.75	4.5	2.8	100.0	4.9
28	325	0.63	28.0	17.6	99.0	4.3
29	325	1.87	4.0	3.0	100.0	2.7
30	325	3.75	3.8	2.4	100.0	2.9
31	350	0.63	79.0	49.0	97.0	7.3
32	350	1.87	51.3	3.16	97.7	13.2
33	350	3.75	36.9	23.7	101.5	6.2
CATALYST A-4						
34	300	0.63	19.9	12.0	95.3	1.34
35	300	1.87	2.4	1.5	100.0	1.34
36	300	3.75	12.4	7.8	100.0	4.56
37	325	0.63	69.6	36.9	84.1	1.65
38	325	1.87	43.5	30.5	113.1	4.7
39	325	3.75	58.0	34.8	95.8	4.6
40	350	0.63	81.1	44.2	86.3	3.2
41	350	1.87	52.5	31.0	95.0	6.2
42	350	3.75	64.1	39.7	98.1	9.2
CATALYST A-5						
43	325	0.63	--	—	—	—
44	325	1.87	31.6	19.3	97.0	—
45	325	3.75	18.1	11.3	99.0	—
46	350	0.63	82.0	43.0	83.0	6.9
47	350	1.87	6[illegible].5	38.0	100.0	15.0
48	350	3.75	36.0	16.5	72.9	7.3

TABLE IV

THE DEGREE OF EQUILIBRIUM DEHYDROCHLORINATION FOR THE FOLLOWING REACTIONS :

T (°K)	ΔH cal mol	ΔG cal mol	Kp
$CH_2Cl-CH_2Cl \rightarrow CH_2{\equiv}CHCl + HCl$			
300	0.173×10^5	0.712×10^4	0.650×10^{-5}
400	0.174×10^5	0.370×10^4	0.946×10^{-2}
500	0.174×10^5	0.270×10^3	0.762×10^0
600	0.174×10^5	-0.316×10^4	0.142×10^2
700	0.174×10^5	-0.659×10^4	0.115×10^3
800	0.173×10^5	-0.100×10^5	0.546×10^3
900	0.172×10^5	-0.134×10^5	0.182×10^4
1000	0.171×10^5	-0.168×10^5	0.479×10^4
$CH_2Cl-CH_2Cl \rightarrow CH{\equiv}CH + HCl$			
300	0.410×10^5	0.219×10^5	0.972×10^{-15}
400	0.415×10^5	0.155×10^5	0.323×10^{-8}
500	0.418×10^5	0.900×10^4	0.116×10^{-3}
600	0.420×10^5	0.242×10^4	0.132×10^0
700	0.420×10^5	-0.418×10^4	0.205×10^2
800	0.420×10^5	-0.108×10^5	0.893×10^3
900	0.419×10^5	-0.174×10^5	0.167×10^5
1000	0.417×10^5	-0.239×10^5	0.173×10^6

Effect of pressure: $K_p = P \frac{\alpha}{1-\alpha^2}$

for vinyl chloride:

$$\Delta H = 0.169 \times 10^5 + 0.168 \times 10 \times T - 0.152 \times 10^{-2} \times T^2$$
$$\Delta G = 0.174 \times 10^5 - 0.344 \times 10^2 \times T + 0.188 \times 10^{-2} \times T^2$$
$$\log K_p = -0.142 \times 10^2 + 0.373 \times 10^{-1} \times T - 0.197 \times 10^{-4} \times T^2$$

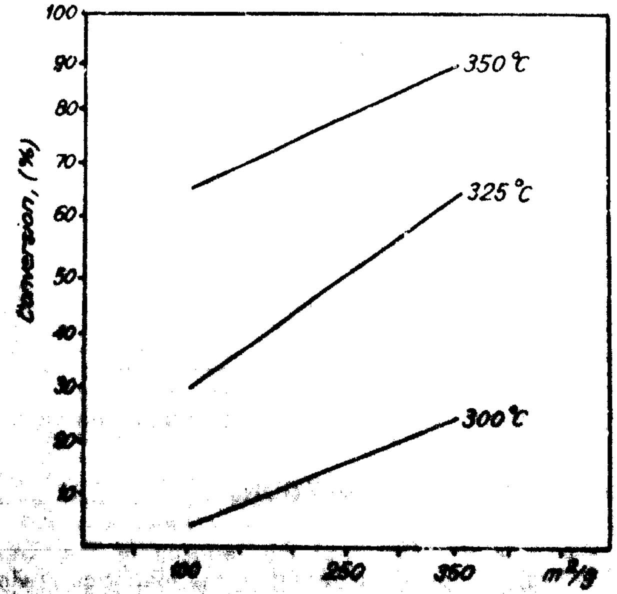


FIGURE 3. THE EFFECT OF SURFACE AREAS OF CATALYSTS ON CONVERSION

Independent of the temperature, the ratio of vinyl chloride and carbon formed remained practically constant when the space velocity was greater than 3.75

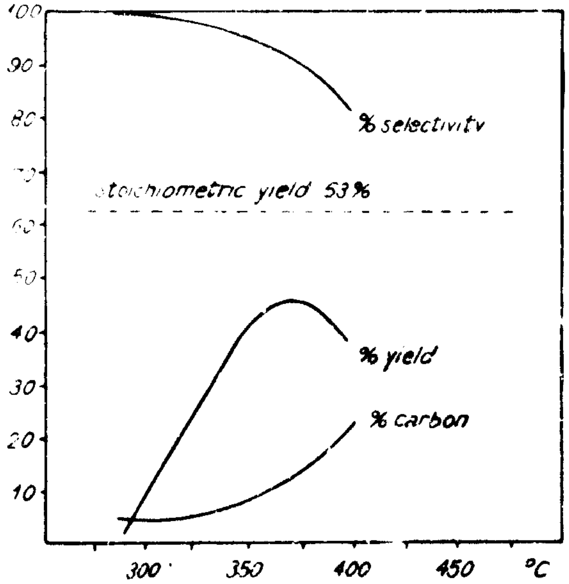


FIGURE 4. THE EFFECT OF TEMPERATURE

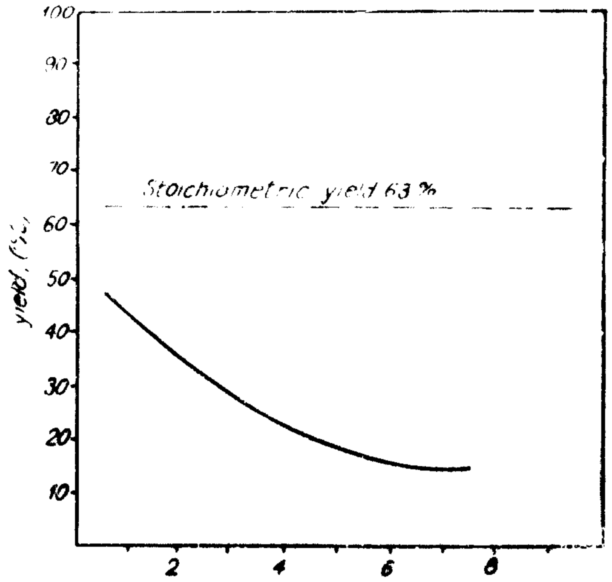


FIGURE 5. THE EFFECT OF SPACE VELOCITY (g/g/hr) ON YIELD

THERMODYNAMIC CONSIDERATIONS

It was shown earlier (28) that the reaction of the catalytic interaction of 1.2 dichloroethane which results in the formation of vinyl chloride and hydrochloric acid is peculiar not only to these simplest products, but to the other different classes of dehydrohalogenations. The results of

It will be the formation of molecules with less molecular weight by the substraction of hydrochloric acid. The thermodynamic calculations show (see table IV) (29) that the dehydrochlorination of 1,2-dichloroethane can be successfully realized with temperatures exceeding 500°K.

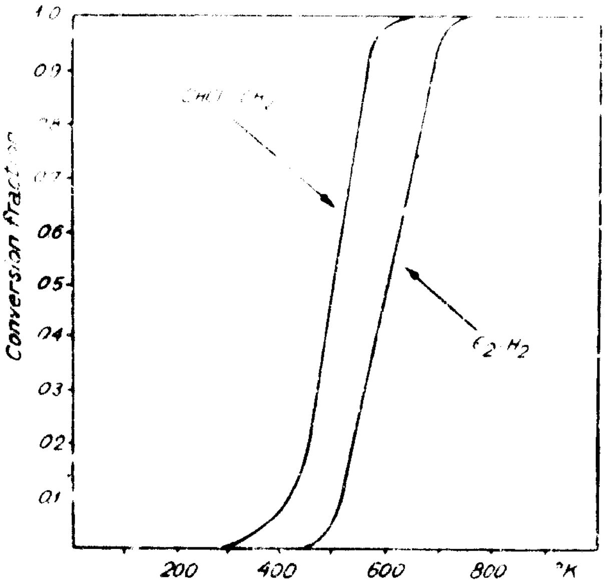


FIGURE 6. THE CONCENTRATION AT EQUILIBRIUM

A comparison of the concentrations at equilibrium for vinyl chloride with those for acetylene (figure 6) under the given conditions, shows that the possibility of both compounds existing in the mixture of reaction products is strong. It follows from this, that selectivity in this dehydrochlorination demands the search for a catalyst which would be distinguishable for its selective action. We have observed that the concentration of vinyl chloride at temperatures from 300 to 350°C and high contact time (low space velocity) was close to the equilibrium value and the maximum yield of vinyl chloride can be expected.

REFERENCES

1. Memoria de labores de Petróleos Mexicanos (1969), México, D.F.
2. Lyle F. Albright, Vinyl chloride Processes, Modern Chemical Technology, (C.E. Refresher) 72—79 (1967).
3. Ibid, manufacture of vinyl chloride, 80—86 (1967).
4. Studies in Petrochemical (volume 1), page 453. Presented at the United National Interregional Conference on the Development of Petrochemical Industries in Developing Countries, Tehran Iran. Nov. 16—30 (1964).
5. A. S. Beucin: Rev. Che. (Bucharest), Technical and Economical aspects of Vinyl chloride production, 16 (11—12), 573—8 (1965).
6. Barton D.H.R. and Howlett K.E., Kinetics of the Dehydrochlorination of Substituted Hydrocarbons, J. Chem. Soc. 148—164 (1949).
7. Kapralova C.A. and Semenov N.N., Study of the Mechanism of 1.2 Dichloroethane Decomposition by the Calorimetric Method Zh, Fiz. Khim,37, 73 (1963).
8. J. Weis., Relations between structure and catalytic properties Z. Anorg, Allg Chem. 354 (3—4) 163—71 (1967).
9. Hiroshi Ozawa, Asahi Garasu..., Preparative methods of Alumina and their effects on its gel structure, Surface, Acidity and Catalytic activity, KenKyu HoKoKu 16, 109—22 (1966).
10. M. Van Tongelen, Determination of the nature of catalyst acid sites by infrared spectroscopy, J. Catalysis 5 (3), 543—7 (1966).

11. Subbotin, A. I. Ellis, V. S. , Kinetic of the thermal chlorination of vinyl chloride, Kinet Kata 1968, 9 (3). 490 – 5.
12. Union Carbide Corp . Vinyl chloride, United States of America 640, 1933 (aug. 30, 1965).
13. Monsanto Co ; Vinyl chloride, United States of America 6515252, (May 25, 1966)
14. Destillers Co., Vinyl chloride, Brit 6600526 (July 20, 1966).
15. Schindler Riegel, Vinyl chloride from 1.2 dichloroethane Ger. Patent 1806547, (May 21, 1970).
16. Konega Fuchi Chem. Ind. Co.; Vinyl chloride France 1556912 (Feb. 7, 1969).
17. Harshow Chemical Co : Catalyst for production of Vinyl halides Brit. 905 241 (July 29, 1964).
18. Société Belge de l'Azote et des Produits Chimiques du Merly, S. A. Vinyl chloride, Ger 1204655 (Nov. 11, 1965).
19. N. F. Nagiev. I. N. Shatchatkluskii and GH. Shick; Vinyl chloride, Union of Soviet Socialist Republics 172767 (July 7, 1965).
20. Instituto Mexicano del Petróleo. Proceso para producción de Cloruro de Vinilo; México (Solicitud de patente abril 27, 1972 en trámite).
21. A. M. Aliev, J. Haspra, ... Conversions of 1,1 and 1,2 dichloroethane over active aluminium oxide. Neftepererabotka i Neftekhim., Nauchn. Tekhn., Sb. 1965 (11), 18–21
22. – Kirk – Othomer; Encyclopedia of Chem. Tech., 2 ed. p. 42.
23. – Belon, Denien, Cosyns; Alumina-Based Catalyst, France 1528570 (Jun 14, 1968).
24. F. Colunga, J. M. Ferreira: Determinación cuantitativa de cloruro de vinilo, 1, 2 dicloroetano y ácido clorhídrico en la reacción de deshidrohalogenación. Rev. Inst. Mex. del Petróleo 1972 (en prensa).
25. Yu. D. Galubev, S. M. Denov..., Composition of impurities in technical vinyl chloride; Plast Massy (1967) (4), 43–7.
26. Mamedov, M. A.; Popova, T. P.., Quantitative determination of the products of high temperature chlorination of Ethylene; Azerb Khim. Zh. 1967 (6), 103–7.
27. P. Maltese, A. Mori, S. Panizzi; Determinazione gascromatografica del cloruro di vinile nel'l acido cloridrico; la Chimie e l'Industria Vol. 50, N–6, 667–668 (1968).
28. Subbotin, A. I. ,Ellis, V.S.. Kinetic of the thermal chlorination of vinyl chloride: Kinet, Katal 1968, 9 (3), 490–5.
29. G. Etienne, F. García Bustos, ... Programa de Computación 835–08, Instituto Mexicano del Petróleo (1971).

RESEARCH AND PRODUCTION OF CATALYSTS[1]

I. V. NICOLESCU*

I. INTRODUCTION

The chemical and petrochemical industry in Romania has developed considerably in the last two decades. Some of the more important products manufactured are: fertilizers, plastics, synthetic fibres, ethylene oxide, glycols, phthalic anhydride, and phenol. Our petroleum refineries produce high octane (90–100) petrol, aromatics hydrocarbons – benzene, xylenes, ethylbenzene, – and other raw materials for the petrochemical industry.

This large and varied production is dependent on catalytical processes and especially, heterogeneous catalysis. For this reason, we have undertaken extensive research in the field of solid catalysts. The relevant branches of science in the universities have also been organized to the personnel necessary for these activities.

In 1950, the year of our first economical plan, the first research groups in the field of heterogeneous catalysis at the University of Bucharest – chair of chemical technology and catalysis – and at the Institute of Petroleum Research (IPR), then functioning in Bucharest, were organized. Today there exist in our country a whole network of research groups, which co-operate and co-ordinate their programmes. Within the Ministry of Education, there are three strong research groups – at the University of Bucharest at the Centre of Physical Chemistry and at the Institute of Petroleum, Gas and Geology. Smaller groups are found at the Universities of Cluj and Timişoara.

The Ministry of Chemical Industry has established a research organization specializing in the technology and engineering at institutes PETROCHIM Ploieşti, I.C.P.T.P.T. Ploieşti and CHIMIGAZ Mediaş. To these one should add the specialized groups which manufacture catalysts (Industrial Central for Chemical Fertilizers Craiova, the Petrochemical Works Borzeşti), as well us those using catalysts, especially at the Industrial Central for Refineries and Petrochemistry Ploieşti and the Petrochemical Works Piteşti.

As catalysis is an interdisciplinary science, recently research in this field was also undertaken in the Institutes of Physics in Bucharest and Cluj. The researchers in these Institutes co-operate with chemists and technologists.

The research activity in the Ministry of the Chemical Industry and the applied research in the Ministry of Education is co-ordinated by the Central Institute of Research in the Ministry of Chemical Industry and by the National Council of Science and Technology.

The structure of the research groups is determined by their research experience and interest, by their material possibilities and especially by guide lines indicated as needed for the development of the industry and by the necessity to ensure a technico-scientific potential for the future.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/27.

* University of Bucharest, Romania.

The research carried out in Romania in the field of catalysts and catalysis may be grouped as follows:

a. The determination of the relationship between chemical composition, conditions of preparation and the physical and chemical properties, with the activity and selectivity of catalysts in specific reactions.

An additional aim in this field of activity is the elaboration of criteria for the prediction of performance and the selection of catalysts.

b. The improvement of existing technologies and the development of new technologies for the use and manufacture of catalysts.

c. The mathematic modelling of catalytic processes and problems of catalytic engineering.

The following is a presentation of the approach used in the development of industrial catalysts and the state of catalytic manufacture in Romania. Examples are chosen from the results of applied research particularly at the universities laboratories and in the Centre of Physical Chemistry.

This activity is dependent on the knowledge, experience, intelligence and inspiration of the researchers and the facilities of the laboratory. Concept research comprises the choice of active components, the conditions and technique of catalyst preparation, the study of the physical, textural and structural properties of catalyst, the analyses of the thermodynamic parameters of the test reaction, the determination of the kinetic parameters with a view to determining catalyst activity and selectivity in test reactions which are pertinent to its use in practice. On the basis of the results obtained in laboratory, there is elaborated a preliminary process outline for the synthesis of the catalysts.

The activity is continued in the pilot installation in two directions – that relating to catalyst properties and that to process development. The following are checked and completed: the macro kinetic parameters (diffusion, mass and heat transfer), there are specified the yields, material balances, the purity of the product as well as other characteristics necessary for the designers.

In the case of catalysts having a functional life of one to two years, many elements of pilot experimentation are eliminated by introducing small reactors in the circuit of an industrial plant. In addition to the economic advantages, this method subjects the catalyst to the various conditions of the industrial process.

II. METHODOLOGY OF STUDY OF INDUSTRIAL CATALYSTS

Our study of industrial catalysts is a multi-faceted program which may be better understood with reference to the diagram in figure 1.

a. We call the first activity **concept research,** the finalization of which is the technologic process at the laboratory level.

b. The transfer of catalyst fabrication technology from the pilot plant (100–150 kg) to the industrial plant is not without its minor difficulties and surprises. However, those concerning the catalysts life, its activity and poisoning, may create more serious problems, requiring a longer time, production cutbacks and consequently great expense.

These difficulties may also arise from a change in dimensions of the reactor which can bring about significant differences in the composition of materials along the length of the catalyst bed, as well as in the efficiency of mass and heat transfer.

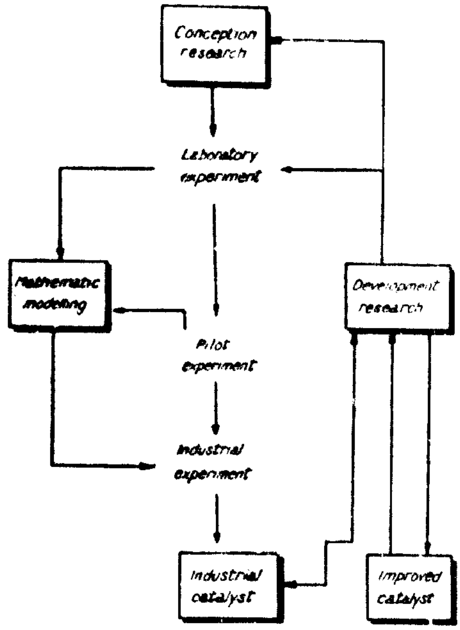


FIGURE 1. METHODOLOGY OF ELABORATION AND IMPROVEMENT OF INDUSTRIAL CATALYSTS

Progress in catalytic engineering and the electric computer have made possible the use of simulation by the transposition of pilot plant or laboratory results directly in the industrial reactor.

c. The catalyst, having succeeded under experimental industrial conditions, may now be considered an "industrial catalyst". From that moment development research begins, a continuous effort aiming at catalyst improvement. Development research can refer back to concept research in the laboratory or the pilot.

The programme in its entirety must take into account all the factors determining catalyst performance according to the scheme of interdependence shown in figure 2.

The chemical composition, the nature of active components and the method preparation determine both the cost of the catalyst, its textural and structural characteristics, its surface geometry and the energy potential of its surface. In our studies, as well as those of others, it has been shown that the structural and textural properties, the physical composition and the valence degree of active components are very different to those of the catalyst under the conditions of the chemical process it promotes.

A significant example of this is shown in the studies of the ammonia synthesis catalyst.

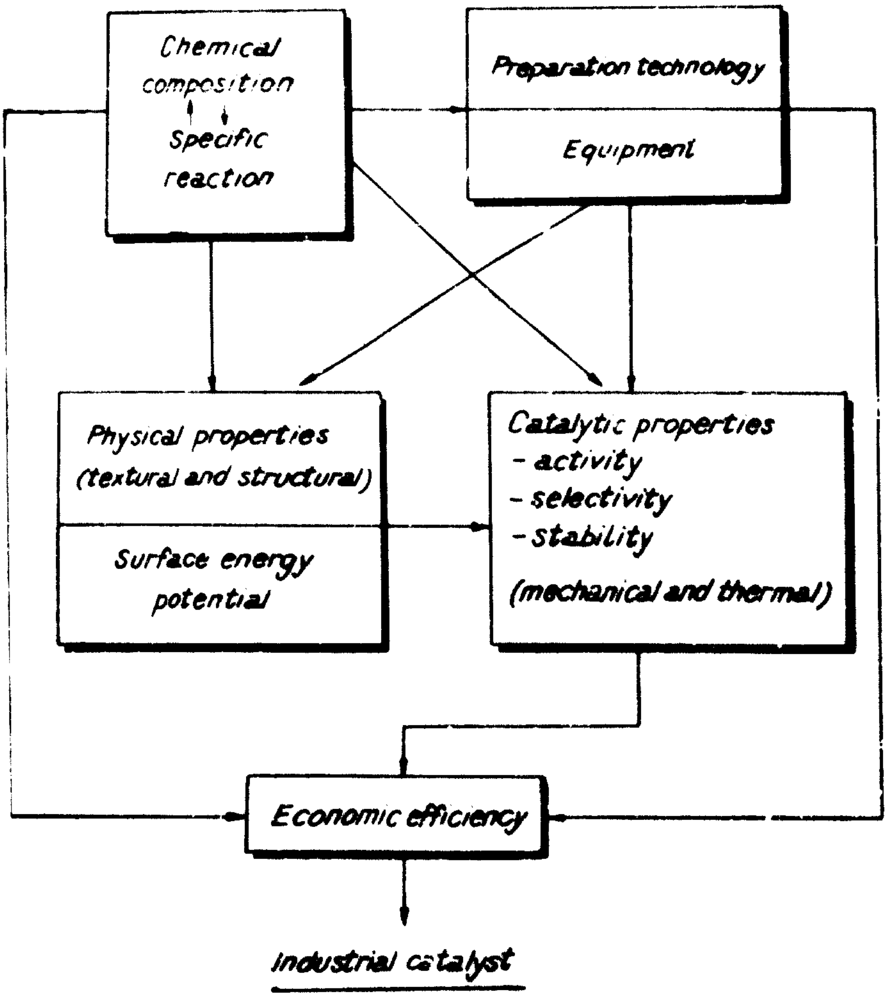


FIGURE 2. THE FACTORS DETERMINING THE QUALITY OF INDUSTRIAL CATALYSTS

In figure 3 is shown the difference between the pore size distribution of an industrial catalyst before (curve 1) and after (curve 2) reduction and reaction. The surface area increases five times in this case.

Figure 4 describes the electrical conductivity isotherms of an industrial catalyst for ammonia synthesis, determined in synthesis gases (N_2+3H_2) and nitrogen media at 500°C. When the initial non-reduced catalyst is in contact with the reactant, the electrical conductivity increases considerably, as a result of the dissociative chemisorption of hydrogen. After twelve hours, ammonia is produced. That time is necessary for the formation of the active centres under the reaction conditions. The electrical conductivity remains practically constant during this period.

At point 2 pure nitrogen is introduced. The electrical conductivity decreases (point 3) and reaches a new constant level.

Here chemisorption of nitrogen is revealed. Again the synthesis gas is introduced (point 4).

The electric conductivity increases and ammonia is produced directly

This method, first initiated in our laboratory, shows the different interactions of the reaction components with the catalyst, the time necessary for the formation of the active centres on the surface and also gives information concerning the reaction mechanism.

The scientific and economic benefits resulting from this university research activity may be appreciated from the following:

- the chemisorption researches concerning the distribution and size of the surface area of the active components Pt, Pd have indicated the preparation conditions required for the preparation of these catalysts, and the character of the activities in aromatization and selective hydrogenation;
- studies in the Mösbauer effect, differential thermal analysis, X-ray, I. R. and E.S.R. spectroscopy have helped to establish criteria for the preparation of catalysts, by defining the phases and active centres on the surface. This has been especially useful for the appreciation of the relationships existing between composition, method of preparation and catalytic activity of catalysts used for the oxidation and synthesis of methanol, hydro-dealkylation of toluene, and the dehydrogenation of butane-butenes.

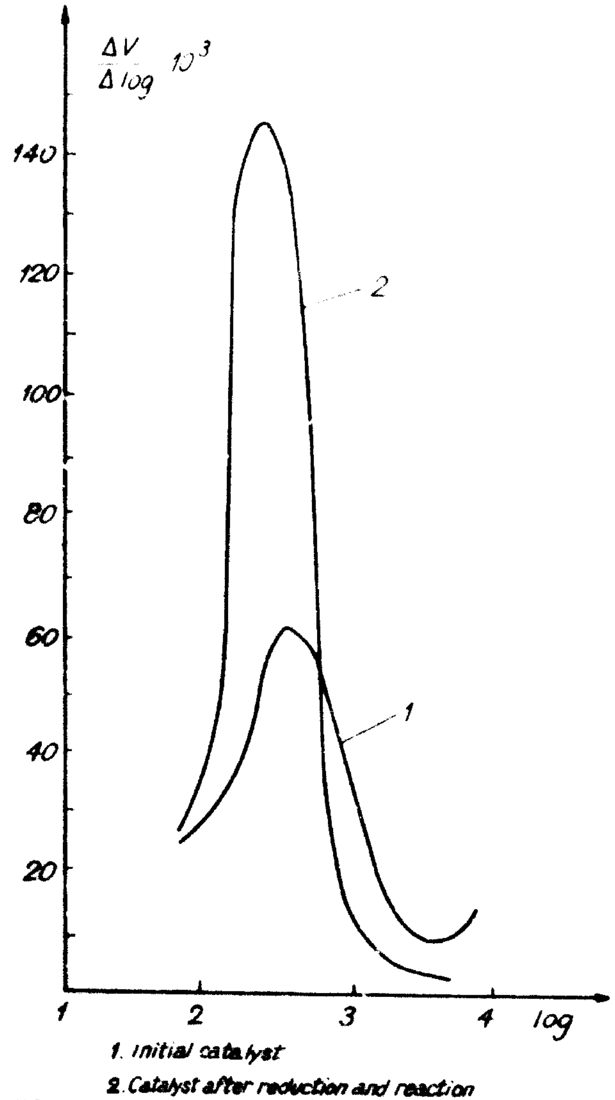


FIGURE 3. CATALYST FOR NH_3 SYNTHESIS. THE PORE DISTRIBUTION BY RADIUM

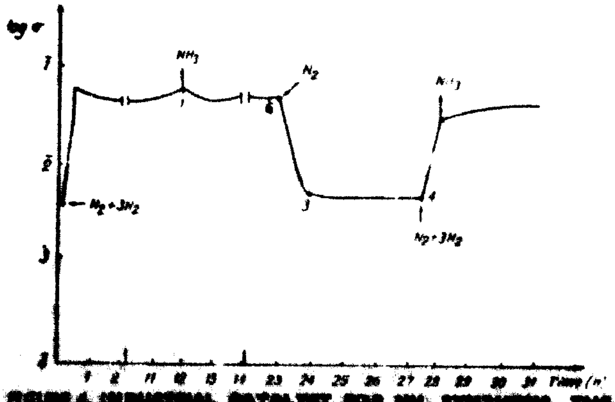


FIGURE 4. INDUSTRIAL CATALYST FOR NH_3 SYNTHESIS. THE [illegible] OF ELECTRIC CONDUCTIVITY IN N_2+3H_2 AND H_2 AT 500°C

Some of the catalysts studied by our research groups, are produced by industry, such as the desulphurization catalyst and the catalyst for the methanation of carbon monoxide present in pyrolysis gases.

These programmes enjoyed the co-operation of the Ministry of Chemical Industry, the Industrial Central for Refineries and Petrochemistry Ploieşti, the PETROCHIM Institute, CHIMIGAZ and the Industrial Central for Chemical Fertilizers Craiova.

III. CATALYSTS MADE IN ROMANIA

Catalysts are manufactured in Romania as a speciality of the Industrial Central for Chemical Fertilizers Craiova, where a plant has been set up for the manufacture of catalysts used in the fertilizer industry and associated manufactures.

Another plant has been set up at Petrochemical Works Borzeşti for the manufacture of catalysts used in the synthesis of monomers, for synthetic rubber and styrene.

The catalysts now manufactured are listed in table I.

TABLE I

INDUSTRY		PROCESS
Ammonia industry	1	first and second reforming
	2	desulphurization
	3	CO conversion high temperature
Synthetic rubber and styrene	4	butane dehydrogenation
	5	butene dehydrogenation
	6	alpha-methylstyrene synthesis
	7	ethylbenzene dehydrogenation
Monomers, petrochemical syntheses	8	vinyl chloride
	9	vinyl acetate
	10	butyl alcohol
	11	CO methanation of pyrolysis gases
	12	fatty acid hydrogenation
	13	alkylation of cumene
	14	diethylbenzene dehydrogenation
	15	2-ethylhexanol synthesis

Research laboratories in the plants, in co-operation with the Institutes of the Ministry of Chemical Industry, carry research to improve the manufacturing processes and to exploit new technologies.

IV. CURRENT RESEARCH

In recent years, our research teams have given special attention to the study of mixed oxidic catalysts used in the oxo-dehydrogenation of hydrocarbons and active aluminas.

Diene production, and particularly, that of butadiene, has increased greatly in the last decade, both using processes for the catalytic dehydrogenation of butans as well as the separation and purification of butadiene which results in the pyrolysis process. However, the transformation ratio butene/butadiene is still unsatisfactory, owing to the low selectivity of the catalysts used. Oxidative dehydrogenation greatly improves selectivity; it Increases the transformation ratio butene/butadiene, as well as the yield of butadiene per pass.

New fabrication technologies have been developed for catalysts, based on Bi-Mo-Fe, of reduced amounts of Bi_2O_3, and which ensure good reproductibility. The method is based on the principle of mechano-topochemical reactions. Increased performance is achieved: selectivity with regard to butenes 92 to 94 per cent, butadiene yield, per pass 60 to 62 per cent at reaction temperature of 420–440°C.

With the purpose of obtaining alumino carriers for catalysts, with predetermined textural, structural and surface properties, research was undertaken in two directions:

– the introduction of tensio-active admixtures in the formation medium of colloidal aluminium hydroxides;

– the preparation of aluminium hydroxides, by solid phase mechano-topochemical reactions, a procedure developed by the author.

In the first procedure, using common raw materials, such as aluminium nitrate solutions, we have shown the influence of adding tensio-active materials to the formation medium on the species of aluminium hydroxide obtained. These hydroxides, upon thermal transformation lead to aluminas of different textural and izomerization properties. Among the tensio-active modifiers used, we mention: polyacrylamide, carboxymethyl cellulose and polyvinylalcohol.

In the second procedure, based on mechano-topochemical reactions, for obtaining aluminas with predetermined properties and isomerization activity, we use various raw materials: aluminium nitrate, chloride or sulphate, and we apply various thermal treatments.

The surface areas of the obtained aluminas vary between 120–320 m^2/g, the greater part of these having bimodal pore distributions, depending also on the ageing conditions and thermal treatment used. These aluminas have been used for preparing industrial catalysts, of satisfactory performance.

Further efforts in these directions should bring new scientific achievements and interesting practical applications.

METHODS FOR THE ESTIMATION OF CRUDE OIL PROCESSING CATALYST ACTIVITY[1]

M. A. BARBUL*, T. M. FILOTTI*, I. BLIDISIL*

I. INTRODUCTION

Research in the development of new catalytic systems as well as the control of catalyst fabrication, life and performance, involves a large volume of work, sophisticated equipment and highly trained specialists in various fields of chemistry and physics. The main criteria in the estimation and selection of catalysts is their activity and selectivity, as well as stability, namely "life" under operating conditions in commercial plants.

The determination of activity and selectivity of catalysts is carried out in micro-reactors or other laboratory equipment, pilot plants and even in commercial plants. To date, experiments carried out in commercial plants are the only ones by which full information can be obtained regarding the performance of catalysts. This is the most severe test which must be passed by a new catalyst. Pilot units are built so as to reproduce as closely as possible the parameters of commercial reactors. Testing of catalysts in such units is carried out under conditions very similar to those encountered in commercial plants, to obtain experimental results for translation to commercial scale. Experiments carried out in commercial plants and pilot units are expensive, requiring large quantities of materials, costly installations, a high degree of automation and much time.

It is evident that economic considerations require that the greater part of the work related to the characterization of catalyst activity should be carried out in the laboratory, while pilot unit experiments should be carried out only with those samples of catalysts previously selected by laboratory tests.

In the following paragraphs, reference will be made only to work regarding the determination of catalyst activity on the laboratory scale. Interest in this approach is twofold:

– the possibility of studying catalytic process kinetics and catalytic functions in the case of complex catalysts;

– the development of standardized and fully tested procedures, which would make possible the correlation of data with those obtained for the same type of catalysts in industrial practice.

II. PROBLEMS IN SOLID CATALYST ACTIVITY DETERMINATION

The determination of catalytic activity means the measurement of the velocity of a given reaction in the presence of the catalyst and the determination of the selectivity for the desired product. The measurement

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG. 122/12.

* Romanian Research and Design Institute for Petroleum Refineries, Ploieşti, Romania.

of reaction velocity under a single set of experimental conditions allows for the selection of catalysts, on condition that experimental conditions remain absolutely unmodified during the entire experimental cycle. By varying reaction conditions, information is obtained on the kinetics of heterogeneous catalytic reactions (activation energy, order of reaction, reaction velocity equation), which is especially useful for a more refined selection of the catalytic system and, in some cases, for the design of commercial catalytic reactors.

It is well known that a reaction catalysed by a porous solid, involves a series of mass and heat transfer effects to and from the solid catalyst. Mass transfer occurs in the following stages:

– transfer of reactant molecules from the fluid stream surrounding the catalyst particles to its outer surface;
– diffusion of reactant molecules within the catalyst pores;
– chemisorption of reactant molecules on pore walls;
– reaction of chemisorbed molecules;
– desorption of reaction products;
– diffusion of reaction product molecules out of pores;
– transfer of reaction product molecules from the catalysts outer surface into the fluid stream.

Heat transfer takes place simultaneously, through a series of analogous stages, which, for an endothermic reaction, may be described as follows:

– heat transfer from the fluid stream to the catalysts outer surface;
– heat transfer from outer surface of catalyst inward;
– heat absorption during chemical reaction.

The complexity of the phenomena associated with a heterogeneously catalysed reaction requires that special care be taken in the interpretation of experimental data obtained from a reactor.

The results obtained may not correctly reflect the activity and selectivity of the catalyst under study. It may be useful to examine some examples.

The distribution of the catalysts pore size may have considerable influence on the experimental data. In most reactions under hydrogen pressure, one of its functions is to avoid the formation and accumulation of precursors that would lead to polymeric substances. These might block the catalyst pores and diminish its active surface and thus, its activity. If the hydrogen does not have total access to the interior of the catalyst, polymerization and degradation processes may occur within the catalyst particles. In such a case the catalyst appears to have a low activity although the nature of its surface is adequate for obtaining high conversion.

The temperature inside the reactor is measured in the reactant stream. In the case of reactions with high thermal effects, the temperature at the surface of the catalyst may differ greatly from that measured and can lead to wrong conclusions.

In view of the above, experiments in laboratory units should be carried out in such a manner as to be influenced as little as possible by mass and heat transfer phenomena. As a rule, this could be achieved by:

– creating a high turbulence in the fluid stream;
– using small particles of catalyst, with large sized pores and high thermal conductivity;
– choosing such operating conditions that low conversions would be obtained (below 10%), far away from the thermodynamic equilibrium corresponding to the reactor temperature.

If the above conditions are achieved, the reactor will operate practically under isothermal conditions, while the partial reactant pressures, or either side of the catalyst layer, will be practically equal. A reactor which operates under these conditions is called a differential reactor.

Most laboratory reactors are not of the differential type, but the so called integral reactor. These have a fixed bed of catalyst, obtain high conversions, are similar to commercial ones and information is obtained quickly regarding the possibility of applying a given catalytic system in the industry. With such reactors it is difficult to estimate the intrinsic activity of the catalysis and to establish the kinetics of a catalytic reaction independent of mass and heat transfer phenomena. Nevertheless, these reactors are still being used to estimate catalyst performances in standard processes used in the crude oil processing industry.

III. TYPES OF LABORATORY REACTORS FOR SOLID CATALYST ACTIVITY DETERMINATION

Laboratory reactors used today may be classified as follows:

- closed reactors
- flow reactors, which in turn may be divided into:
  - impulse reactors, and
  - continuous flow reactors.

In the closed reactors, there is no exchange of materials with the exterior. The catalysts together with the reaction mixture are located in a close volume from which, from time to time, small samples of fluid are taken to determine the degree of chemical transformation.

The impulse reactor consists of a tube in which the catalyst is placed and over which a gas is constantly passed, preferably inert to the chemical changes which are to be achieved. At intervals, small quantities (impulse) of reactants are introduced into the gas stream. The reaction products are analysed with a suitable instrument at the reactor outlet. Such a reactor may also be the column of a gas chromatograph filled with the catalyst being studied.

These two types of reactors are used primarily for preliminary studies, the closed reactors especially for non-catalyzed or homogenously catalyzed reactions, while the impulse reactors are used to elucidate reaction mechanisms or to study the effects of various inhibitors, poisons or promotors.

In laboratory practice, reactors with continuous flow of feedstock are more frequently used. Methods developed between 1930 and 1960, used in the study of crude oil processing technologies, such as gasoline cracking, hydrorefining and reforming, were based on the use of integral reactors. Today, there is a tendency to extend the use of differential reactors in research work to examine new catalysts, or improve existing ones, as well as for the usual control of catalyst fabrication and application.

Differential conditions can be approached in several ways, the main elements referring to:

- achievement of a fast flow over the catalyst layer (Re_p higher than 30), limited by the pressure drop in the catalyst bed;
- use of the smallest possible catalyst particles to avoid internal diffusion, the limitation also being the pressure drop;
- catalyst diluation with an inert material;
- reactant dilution;
- experimenting at low conversions, the only limit being in this case the sensitivity and accuracy of the method of analysis.

Laboratory reactors differ by structural and functional characteristics. One may distinguish the following types:

– fixed bed reactors;
– fixed bed reactors with reactant recirculation;
– reactors with fluidized catalyst;
– rotating catalyst bed reactor.

1. FIXED BED REACTORS

This type of reactor is the most simple to obtain, being composed of a glass or metal tube, partially filled with catalyst, over which the reactant stream is continuously passed. Differential conditions are approached by:

– operation at very low conversions (around $1^{0}/_{0}$);
– dilution of catalyst with an inert material, especially in the case of reactions which occur with significant thermal effects;
– dilution of feedstocks;
– using such a flow that Re_p would be higher than 30.

The achievement of these conditions is seriously limited by the degree of sensitivity and accuracy of the analytical procedures, as well as the pressure drop along the catalyst bed.

In current practice such reactors are of the integral type and only in special cases can experimental conditions be achieved which could be considered as differential.

2. FIXED BED REACTOR WITH REACTANT RECIRCULATION

In such a reactor, the reactants are recycled over the fixed bed of catalyst by means of a pump, at the same time maintaining a continuous feedstock stream and evacuation of reaction products. A high flow rate of reactants is thus achieved over the catalyst bed, conversion being very low in each passage (differential). A ratio between recycle rate and feed rate of between 10 and 15 is sufficient to achieve experimental conditions close to differential ones.

In spite of difficulties in construction, which limit its use, this type of reactor has the following advantages:

– it operates under conditions very similar to those of a differential reactor;
– linear velocities of the fluid stream over the catalyst bed are very similar to those of commercial reactors;
– it does not require an exceptionally sensitive analytical method.

The use of this type of reactor is not recommended when secondary homogeneous reactions can occur.

The circuits through which recirculation is carried out are dead spaces favourable to the development of homogeneous, secondary reactions. Cooling of these circuits in order to minimize secondary reactions makes it difficult to control the temperature within the reactor, reducing the accuracy of the experimental determinations.

3. REACTOR WITH FLUIDIZED CATALYST

This type is rarely used in the laboratory although it has certain advantages, such as:

– temperature can be easily controlled;

- extremely small sized catalyst particles can be used which practically eliminate the resistance to mass and heat transfer within the particles.

Limitations of the gas stream flow rate by those conditions required to obtain fluidization, produces the danger of back-diffusion, which may modify the kinetic data.

4. ROTATING CATALYST BED REACTOR

Such a reactor is composed of an enclosure within which there is a catalyst basket on a shaft, on which are also mounted one or more impellers. The catalyst basket is rotated in the reactant stream at the speed chosen by the experimenter. In such a system, the following is obtained:

– a uniform reactant concentration and temperature within the reactor;

– minimum inter-phase transfer phenomena even at low charge stock rates, because turbulence is produced exclusively by the rotation of the catalyst bed and is thus independent of the feed rate;

conditions to study the influence of physical phenomena on the rate of reaction, simple variation of the speed with which the catalyst basket rotates being sufficient for this purpose.

From the data published to date, it seems that this type of reactor is more appropriate for operating conditions prescribed for differential reactors. Its use is therefore indicated for the study of kinetics in heterogeneous catalyst reactions and to compare the performance of different catalysts. The realization of such a reactor, especially when it is to be operated under pressure, requires high technical skill, thus limiting its use.

IV. TEST REACTIONS TO ESTIMATE CATALYST ACTIVITY FOR PETROLEUM PROCESSING

Optimally, complex feedstocks identical to those used in industry, are submitted to reaction in pilot units under conditions very similar to industrial ones.

The difficulties encountered and the high cost of pilot experiments, as well as the need to individually characterize catalyst parameters, have led to the development of methods for studying the catalysts by test reactions with single compounds.

A test reaction must be so chosen as to be completely characteristic of the catalyst. In other words, the technique used must bring about the same transformations as would be obtained in industry in the presence of the corresponding catalyst. It is recommended that the following considerations be taken into account when choosing a test reaction:

– choose a single reaction and avoid parallel or consecutive reactions;

– the selected reaction should be as near as possible thermodynamically complete;

– the reaction must not alter the catalyst significantly, so that its activity is maintained constant during the reaction cycle;

– reaction products should be analysed as quickly und accurately as possible.

In the crude oil processing industry the main catalytic reactions are cracking, and isomerization, which take place by an acid mechanism, and hydrogenation and dehydrogenation reactions, catalyzed especially by metals, metallic oxides or sulphides. Bi-functional catalysts having both acid and metallic functions, must not be omitted. These catalyze simultaneously cracking, isomerization and hydrogenation-dehydrogenation reactions.

In order to characterize catalyst activity, representative reactions, either acid or metal catalyzed, are selected. A few examples of test reactions, catalyzed by active acid centres are given below.

Non-crystalline or crystalline silica-alumina cracking catalysts are tested by cumene cracking or by conversion of a linear or branched paraffinic hydrocarbon.

Isomerization catalysts are characterized by their activity in paraffinic or alkylaromatic hydrocarbon isomerization (for example n-pentane or xylene isomerization).

Acid supports used for the preparation of different catalysts are also characterized by their capacity to catalyze double bond isomerization or that of some hydrocarbon chains (e. g. isomerization of cyclohexane to methyl cyclopentane).

All these reactions can be chosen for tests to estimate the acid function and specific activity of the above catalysts.

Aromatic hydrocarbon hydrogenation or the dehydrogenation of cycloparaffins, can be used in test reactions for estimating the metallic function of hydrocracking and reforming catalysts.

Finally, the hydrogenolysis reaction of a sulphur compound (such as thiophene) or nitrogen compound (such as pyridine) are tests to estimate desulphurization or denitration activity of the catalysts used for the purification of petroleum fractions by hydrogen treating (hydrorefining).

The test reaction concept, though a simplification of the real case, is of great aid in solving certain problems regarding the selection of catalysts and catalytic systems. In some simple cases (hydrogenolysis reaction of sulphur or nitrogen compounds), it can even be used for scale-up problems. However this concept must be carefully applied when dealing with the characterization of bifunctional catalysts as it may sometimes lead to a misleading over-simplification. Thus, in the presence of hydrocracking or reforming catalysts, composed of a support with an acid function and a metal in elementary form (sometimes as an oxide or sulphate), simultaneous reactions take place, catalyzed by the acid and metallic functions of the catalyst. Reactions, such as paraffin isomerization or aromatization, occur through a mechanism in which the presence of both functions of the catalyst is required. Estimation of the activity of such a catalyst by a test reaction of only one of the functions is not correct. It is also necessary to effect a reaction which would be representative for the catalyst as a whole in order to obtain a correct picture of its activity. For this reason, for bifunctional catalysts, relatively complex test reactions are also used, such as conversion or normal paraffins with more than six carbon atoms. Thus, in the presence of gasoline reforming catalysts, of the Pt on alumina type, and under hydrogen pressure, the heptane is transformed by hydrocracking into low molecular weight hydrocarbons, is isomerized and dehydrocyclized to toluene. Such a test reaction, apparently selected in contradiction to the selection principles mentioned previously, is required to characterize certain catalysts of this type which have complex functions.

V. STANDARD METHODS FOR INDUSTRIAL CATALYST ACTIVITY DETERMINATION

For the purpose of characterizing catalyst activity in the main petroleum refining processes, standard methods have been established which, in many cases, were the basis for commercial implementation or are used in the control of commercial plants.

In the standard methods, the petroleum fractions used as feed are representative with respect to source and composition. These methods are carried out in a continuous system under operating conditions similar to those applied in the industry.

Catalyst activity and selectivity is expressed in terms of technological or commercial interest, such as the yield of the most interesting product or the value of a key characteristic of the process such as a property or composition of the product. In many methods, in order to express the catalyst selectivity at the same time, these characteristics are related to the designed operating conditions or are correlated with the product yields.

To obtain representative data in this manner, deep conversions must be effected, close to thermodynamic equilibrium, as is done in commercial plants. For this purpose the operating conditions of these standard methods place the reactors in the integral group.

Optimally, the behaviour of the catalysts in different sized plants and industrial reactors should be known. Since in the case of catalysts for petroleum refining processes there is such extensive experience, the standard methods are useful and are widely employed. Some of these methods effect determinations in comparison with a known catalyst taken as a standard.

A brief summary is given below of the principle, operating methods and expression of catalyst activity and selectivity by these methods.

A relatively large number of methods have been developed by various companies in different countries to characterize cracking catalysts, using various operating conditions, space velocities, charge stock/catalyst ratio, temperature and cycle time. In all cases heavy distillate cuts, especially atmospherically distilled gas oil obtained from a well known crude (East Texas or Mid-Continent, etc.), are cracked. Fixed bed, as well as fluidized bed catalysts are used, the tendency being to generalize the fluidized bed catalyst procedure.

Activity is expressed by the "activity index" which differs from one method to another. In most cases, the activity index represents the portion of hydrocarbons of boiling temperature below 200°C in the liquid product obtained by cracking under given conditions, plus distillation losses (D+L). In other procedures, the activity index represents the yield of gasoline which distils up to 200 or 210°C compared to that in the feedstock processed. Often this activity index is related to that obtained using a standard catalyst.

For the determination of the activity index of a fresh cracking catalyst, steps are taken to overcome non-characteristic initial catalys. activity. For this purpose the catalyst is brought to a constant activity level, somewhat corresponding to the equilibrium catalyst activity in industrial plants, either by steam treatment or by consecutive reaction-regeneration cycles.

No special methods have been developed for the characterization of catalyst activity and selectivity for gasoline reforming and aromatization catalysts, although the literature is very rich in describing the performance of these catalysts. However, catalyst manufacturers and oil processing companies of various countries have developed their own methods. This state of affairs is partly explained by the high cost of equipment as well as of the work itself. These are prohibitive for activity determination in certain refineries which, in case of need, contact the specialized companies.

Reforming catalyst activity and selectivity are characterized by the reformed product octane number of the gasoline obtained by standard atmospheric distillation, under conditions similar to those used commercially (gasoline stabilized by debutanizing or even depentanizing). Expression of reforming catalyst activity and selectivity also takes into account the stabilized reformed gasoline yield, the content of aromatic hydrocarbons in the resulting product, in correlation to the feedstock and operating conditions (temperature, pressure, space velocity, hydrogen/feedstock ratio, etc.).

Hydrorefining catalyst are tested under hydrogen pressure, in units similar to commercial ones. Hydrorefined products are chemically analysed after removing hydrogen sulphide, water or dissolved ammonia, resulting from hydrogenolysis reactions of S, N and O compounds in the processed oil cut. Catalyst activity is expressed by the degrees of desulphurization, denitration and deoxygenation, which represent the ratio between the respective contents of sulphur, nitrogen and oxygen of the feedstock and product, expressed in percentages. In order to ensure reproducibility of determinations, it is absolutely necessary to work with the same feedstock as the large variety of heterocompounds in the oil cuts and their dissimilar reactivities are well known. Many times it is preferable, as in this case, to compare the performance with that of a standard catalyst. It must also be pointed out that in the estimation of hydrorefining catalyst activity, other commercial characteristics of the product are used, such as colour, colour stability or product odour.

VI. CONCLUSIONS

The present state of knowledge in the characterization of catalyst activity indicates that it would be desirable to test the catalysts in differential reactors if selection is to be based on intrinsic activity. On the other hand, kinetic studies can be carried out from which the rate of the chemical reaction can be determined, excluding the influence of mass and heat transfer phenomena. There is a basis for the application of test reaction studies in the design of commercial units where relatively simple catalytic reactions are concerned. Unfortunately, this is not the case in crude oil processing. In order to obtain design data for oil processing catalytic plants, studies must be carried out in various steps, including pilot units. An exception is the relatively simple hydrorefining process. Data relating to this process obtained by test reactions have been used to design commercial reactors.

On the other hand, despite the empirical character of the so-called standard methods for determining industrial catalyst activity, these procedures are still being used widely, since the techological data are furnished, or are easily accessible to those who use industrial catalysts.

CATALYST TESTING[1]

R. W. BEDFORD[*]

It may seem to be stating the obvious to say that a catalyst tester must be sure he is measuring the property he desires and that the property he is measuring is relevant to the performance of the catalyst in a full scale plant. Testing catalyst is, however, a complex science requiring skill and experience in the catalyst tester and even then it is all too easy for an experienced catalyst tester to make mistakes if he does not maintain a rigid discipline of a clear objective approach to each and every test.

ICI Agricultural Division has been a major centre for research and development of commercial catalysts for over 40 years. During that time, testing techniques have increased in complexity and sophistication in parallel with the development of the chemical plants using the catalyst being developed. Nowadays it is possible to virtually completely characterize new catalyst and predict with reasonable confidence the way it will perform in a commercial plant. It is generally true, however, that the cost and sophistication of the experimental techniques is fairly closely paralleled by their usefulness in predicting plant performance.

This paper will discuss the testing of solid catalysts used in promoting gaseous reactions such as those used in ammonia plants and similar plants based on hydrogen production.

I. INTRODUCTION

Developing a new catalyst requires a lengthy, complex testing programme. There are four groups of characteristics which must be evaluated:

1. Catalytic activity
2. Physical characteristics
3. Mechanical strength
4. Chemical composition.

Of these groups, the fourth one that of analysing a catalyst chemical composition is not particular to catalyst testing and will not be discussed in this paper. In each of the other three, a wide variety of tests may be carried out of varying complexity. These tests may be sorted into three groups which represent three different levels of testing:

1. Simple comparative testing
2. Major catalyst evaluation, including simulated plant operation
3. Fundamental testing in order to completely characterize the catalyst and the reaction it catalyzes.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/20.REV/1

[*] Imperial Chemical Industries Ltd., Billingham, Teesside, United Kingdom of Great Britain and Northern Ireland.

II. CATALYST ACTIVITY

The measurement of catalyst activity is, of course, the whole basis of a catalyst research programme. The steps involved in developing a successful catalyst are set out diagrammatically in figure 1. The procedure is designed to permit the maximum number of variables to be examined in a way which results in all potentially suitable catalysts receiving much more detailed investigation. By this technique, full-scale testing is reserved for those catalysts which have passed the other tests.

A rapid initial screening is carried out at atmospheric pressure, so that those formulations showing promise can then be tested more rigorously under semi-technical and side-stream conditions to obtain basic kinetic and life data. More detailed kinetic and poisoning information can then be obtained under differential operating conditions. Formulations which pass side-stream and semi-technical tests satisfactorily, over an extended period of time, are subsequently submitted to full-scale plant tests.

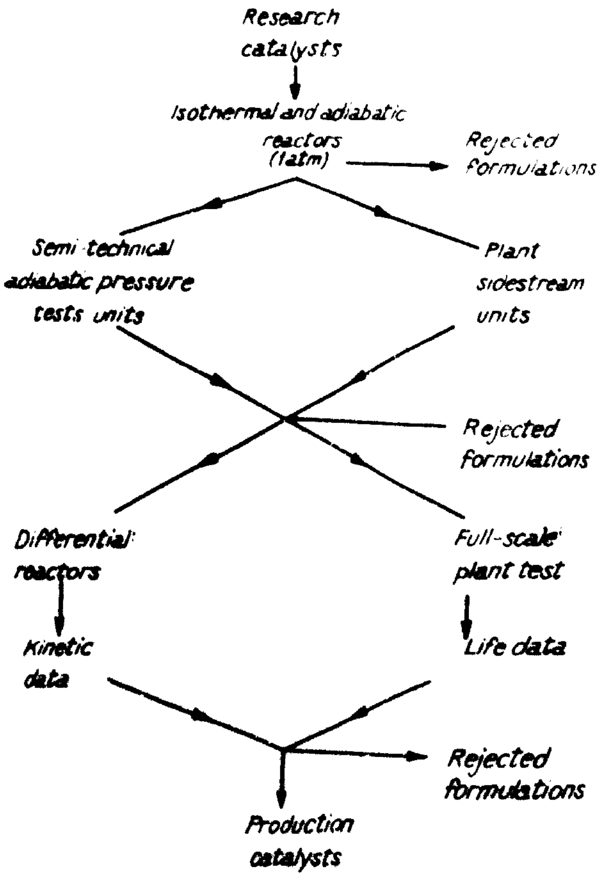


FIGURE 1. STEPS INVOLVED IN DEVELOPING A SUCCESSFUL CATALYST

The rapid screening tests represent the first level of testing defined above, the semi-technical and plant sidestream tests represent the second level while operation in differential reactors represents the third and highest level.

The performance of a catalyst is generally assessed in terms of the rate at which it promotes a desired reaction. It is generally defined by the following equation :

$$\text{reaction rate} = \text{activity} \times e^{-E/RT} f(P, V, X)$$

Under equivalent reaction conditions, i.e. equal temperatures, pressures, reaction volumes, and mole fractions, reaction rate is proportional to catalyst activity.

Before considering how catalyst activity is measured, the properties controlling mass transfer to and from the catalyst surface must be considered. The flow of reactants to the surface of the catalyst can, and usually does, affect the measured activity of the catalyst. Specific activity is the measure of the reaction rate available when there are no external limitations. The observed activity of the catalyst may not be equal to the specific activity because of external limitations.

Unless the mechanism by which reactants are transported to the active surface of the catalyst and the products transported away is fully understood and the rate limiting step or steps are recognized serious errors in catalyst testing may be made. The commonly accepted route by which the reactants reach the active surface of the catalyst in pellet form is shown diagrammatically in figure 2.

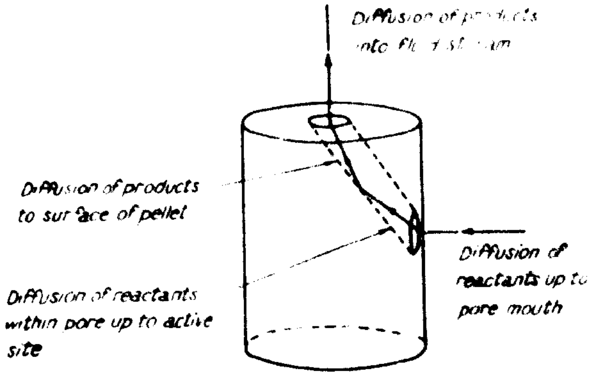


FIGURE 2. DIFFUSION OF REACTANTS AND PRODUCTS WITHIN CATALYST PELLETS

The first stage is normally regarded as the diffusion of reactants to the surface of the pellet through the gas film which surrounds it. Having reached the pellet, the reactants pass through the pellet's internal structure consisting of macro, micro and sub micro pores, before they reach the active surface. The reaction products desorb from the catalyst surface and return to the bulk of the gas stream by the reverse procedure. The behaviour of a catalyst in a commercial plant, depends on the over-all effect and this is often very different from the effect which would be postulated from the catalyst's specific activity. Care must be taken, therefore, in catalyst testing to make sure that the catalyst test accurately reflects the limiting process or processes as found in a commercial unit.

With most catalysts the over-all reaction rate can be considered to depend on three separate processes:

1. The diffusion of one of the reactants from the gas phase to the surface of the catalyst particle.
2. The diffusion of one of the reactants in the pores of the catalyst particle.
3. The rate of reaction at the active surface of the catalyst.

Process 1 is called gas film diffusion and process 2 pore diffusion. Normally the difficulty of mass transfer inside the pellets outweighs that of transfer from the gas stream to the pellet surface. At high reaction rates, and with low gas velocity, however, gas film diffusion may become limiting. It is worth remembering that this type of limitation is more likely to occur at gas velocities used for catalyst testing than under plant conditions, where reactor height usually ensures that velocities are also high. Care must be taken therefore, to find out if testing is being carried out in this region and, if so, steps must be taken to avoid it.

If pore diffusion is a contributing limitation, the rate of reaction is dependent on the properties of the catalyst particles, for example, size, voidage, and surface area. It is therefore important, that catalyst testing should, wherever possible, be carried out on the full size catalyst pellets.

Serious errors may be made in determining the catalyst activity if different sizes of catalyst particle are used during the test. The best experimental method for assessing the importance of pore diffusion is to measure the rate of reaction with varying particle size. In the absence of pore diffusion limitations, the reaction rate will remain unchanged. It should also be borne in mind that pore diffusion limitation increase with temperature and pressure and catalyst activity measured at moderate temperatures and at atmospheric pressure will not usually be applicable for full scale plant operation at higher pressures.

While considering possible physical limitations in testing methods, it is worth while to point out the danger of so called "edge effects" in small scale reactors. Where catalyst particles are in contact with the walls of a tubular reactor, the voidage is much higher than that in the centre of the catalyst bed. Because of this, there is a preferential flow route for the gas along the edge of the catalyst bed. In a full scale reactor this uneveness of flow is negligible in relation to the total flow through the catalyst bed, but in small-scale reactors the amount of catalyst in contact with the reactor wall is much greater in proportion and can result in errors in the measurement of catalyst activity. This is especially true for reactions where high conversions are obtained, such as during methanation. If slip is occurring under these circumstances, not only will the catalyst activity be underestimated, but the difference between differing catalysts will be minimized. A poor catalyst of smaller particle size may well compare favourably with a better catalyst of larger particle size, not only because of the smaller pore diffusion limitation but also because of the smaller edge effect which will be obtained.

III. REACTOR TYPES

The simplest type of reactor is one which consists of a tube, made of glass or metal, containing the catalyst through which reactant gas is passed. This basic design can be developed for use in either of the three levels of catalyst testing. It is the type of reactor most widely used in ICI's catalyst testing programme.

There are two fundamental types of continuous test reactor, the integral reactor and the differential reactor. The simple tubular reactor is the type used for integral reactor systems. With an integral reactor a reactant concentration profile will develop along the length of the catalyst bed, and the rate of reaction along the length of the converter will change. With a differential reactor the reactant concentration in contact with all parts of the catalyst bed will ideally be the same, and the rate of reaction will therefore be the same at all points in the converter. This is why the differential reactor is potentially the more suitable for the derivation of kinetic data, because the reaction rate can be calculated directly from the flow rate and the inlet and exit reactant concentrations. In the case of an integral reactor, an integration, which may be impossible to carry out algebraically, is often required. Integral reactors are, however, much simpler to operate, and this is the type normally used for the bulk of catalyst testing.

Integral tubular reactors can be operated in three different ways: isothermally, adiabatically or pseudo-adiabatically (that is neither isothermally nor adiabatically). In practice isothermal operation is rarely possible, particularly with reactions having a high heat of reaction, because of heat transfer limitations. These limitations are important because poor heat flow control, leading to small temperature difference in the bed, can have a very severe effect, since the rate of reaction is exponentially dependent on temperature.

With exothermic reactions, tubular adiabatic reactors are commonly employed in order to overcome this problem. The temperature control system is arranged in such a way as to prevent heat flowing either in or out of the reactor through the walls. Consequently a temperature profile similar to that found in operating plants develops along the length of the reactor, the extent and shape of the latter depending on the heat of reaction, the specific heat of the gas and the reaction kinetics. Small-scale adiabatic converters are therefore useful for life tests or for simulation of full scale plant operation where adiabatic operation is normal.

In the first level of testing, perhaps 100 to 1,000 formulations are tested in a catalyst research programme. It is often convenient to do a quick screening operation using even simpler reactors operating pseudo-adiabatically. In this case, the reactor is surrounded by a heating jacket as in the small-scale adiabatic reactor, but no attempt is made to balance the heat flow in or out of the reactor. In this case it is essential that the test conditions for each catalyst be as near identical as possible, so that a true comparative test is obtained. The test is essentially qualitative and can sort good catalyst from moderate catalyst from bad catalyst but it cannot sort out good catalyst into very good and not so good. In all comparative testing it is essential that a standard catalyst size is used, together with a standard catalyst volume, standard temperature conditions and standard gas composition. The simpler the test the more standard the conditions must be if meaningful results are to be obtained.

In addition in choosing the operating conditions it should be borne in mind that it is much more difficult to differentiate between catalysts under conditions of high conversion or conditions which result in a product gas being close to equilibrium.

When more advanced testing is required it is necessary to have much more complicated apparatus. Whether the testing unit is a semi-technical laboratory unit or a plant sidestream unit, great care must be taken in its design. Whereas fairly simple control and measurement systems may be used at the first level of catalyst activity testing, much more precise methods must be used at this level. These units are essentially miniature versions of full-scale plant units and so require miniature versions of all the control and measurement devices which are used in a full-scale plant. In addition, equipment is required to maintain adiabatic operation and to provide further information, such as temperature profiles, on the behaviour of the catalyst which is not normally required in a full-scale plant. In order to obtain as much precise information as possible, attention must be paid to the detail design. The edge effect caused by miniaturization of equipment has been mentioned earlier. A similar effect is that of conduction of heat from the exit of the catalyst bed to the inlet along the reactor itself. The reactor material must therefore be chosen so as to minimize this effect. The location of measuring devices for the control circuits is also important and the position of them must be chosen so as to give quick response to changes in operating conditions. This is particularly true of those thermocouples controlling the adiabatic operation of the converter. They must be located so as to minimize the fluctuations of heat inflow to heat outflow if the system controlling the adiabatic function is sluggish in its response. Under these conditions, extremely good results can be obtained and catalyst can be sorted with great accuracy. Life testing over several months can be carried out and the effects of poison measured on sidestream units. The optimum catalyst may then be developed by balancing the requirements of a good life, high initial activity and poison resistance.

Although it is generally more difficult to derive a kinetic equation from integral data than from differential data it is nevertheless possible to obtain a large amount of information from a relatively small number of experiments and often it is possible to derive design equations predicting full-scale plant operations from adiabatic integral experiments. In any case, a design equation obtained from differential data must be cross checked against integral data obtained both on the small scale and the full scale before it can be used with any degree of confidence.

In a normal research programme one might think in terms of testing 20 to 30 catalysts on semi-technical units and about 10 to 20 on plant sidestream units before choosing the two or three formulations to be investigated more fully in differential reactors and in full-scale plant tests.

IV. DIFFERENTIAL REACTORS

In differential reactors the reaction rate is the same for all the catalysts being tested and changes in reaction rate caused by changes in each variable can be studied separately. The procedure can be very time consuming because a very large number of experimental results over a wide range of conditions may be needed before a design equation can be produced. The exercise is therefore very expensive, but is worth while for a catalyst researcher because the very accurate results obtained are extremely useful in plant designs.

Single pass tubular reactors may be used under differential conditions. Here the conditions are chosen so that the amount of reaction over the catalyst is very small and thus the change of concentration of reactants in the gas phase and the change in temperature due to the reaction may be ignored. The use of single pass tubular reactors, however, suffers from the disadvantage that very accurate composition analyses are required if an accurate reaction rate is to be calculated from the small differences between inlet and exit concentration. With modern methods of analysis this can be done for many reactions, but it is often better to use other methods if very accurate results are required.

This analytical requirement is removed when a recirculating system is used. With this system, part of the exit gas is recycled and mixed with a small amount of fresh gas. After some initial changes, the system will reach a steady state and the composition of the make-up gas and exit gas are then measured together with the exit flow rate. Since the pass conversion depends on the recycle rate, which can be very large, the system can be made to approach very closely to true differential operation.

The over-all concentration difference between the feed gas and the exit gas can be very different, even though the converter is operating differentially, which decreases the importance of analytical error. A major disadvantage of this system, however, is the potential for build-up of by-products or impurity concentrations. For this reason it cannot be used for reactions in which there are likely to be by-product formations but it has been used very successfully to study the kinetics of ammonia synthesis from nitrogen and hydrogen (see later).

A type of differential reactor which is being widely used within ICI, is the continuous stirred tank reactor. In this system, the reactants are fed continuously into a tank where they are perfectly mixed and brought into contact with the catalyst by a stirrer. In order to balance the inflow of reactants, gas which contains both the reactants and the products is continuously removed from the system. Within ICI it has been found convenient to contain the catalyst in baskets which form the blades of the stirrer and it has been found particularly suitable for the differential study of poisoning reactants since all the catalyst is exposed simultaneously to the same concentration of poison.

The simplifying assumption of perfect gas mixing is necessary if continuous stirred tank reactors are to be used for the derivation of kinetic data, so the occurrence of such mixing must be checked before carrying out experimental work. If any deviations from ideal behaviour are discovered, their causes should be traced and the situation corrected, because the experimental data resulting from a combination of the effects of both imperfect mixing and the chemical reaction are usually too complex for accurate interpretation.

V. STRENGTH TESTING

Catalyst particles must be strong enough to withstand four different forms of stress:

1. Abrasion during transit
2. Impact when loaded into the converter
3. Internal stresses, especially those occuring during reduction or being brought on line
4. External stressing caused by pressure drop, catalyst weight and possibly thermal cycling.

It is generally difficult to subject catalysts to a simulation of the conditions which affect their strength during life while measuring the reaction of the catalyst to those conditions. ICI uses two types of general tests which may be applied to both new catalyst and to catalyst subjected to operating conditions. One test is to measure the crushing strength of the catalyst and the other test involves tumbling the catalyst.

The equipment used for the crushing strength is manually operated and consists of two flat polished platens one set above the other. The pellet is placed on the lower platen and the platen is raised manually until it comes into contact with the upper platen. The pressure generated by compressing the pellet between the platens actuates a piston which hydraulically activates a pressure gauge. The piston has a cross section of exactly one square inch so the pressure gauge measures the load on the catalyst particle in pounds weight. The load at which the catalyst particle breaks is then noted. This test is carried out on at least 20 particles and the mean taken. For solid pellets it is usual to measure the crushing strength with the catalyst pellet set vertically so the platens come in contact with the flat ends of the pellet. For extrusions and rings the particles have to be laid horizontal, and in the case of rings, it is normal to replace the bottom platen with a bar shaped one. Some care must be taken in the operation of the machine as the crushing strength obtained does vary with the speed of compression, but it has been found better to use a simple manually operated machine than to complicate it with a mechanical drive.

In the tumbling test a fixed volume of catalyst (normally 25 mls) is placed in a steel tube which is rotated end over end at a speed of 40 rpm for 45 minutes (3,600 falls). After the test catalyst is sieved to remove dust and catalyst chips and the percent weight loss is measured.

In establishing these tests as standards, ICI carried out extensive investigations into the parameters measured in the tests and their relationship to the strength requirements outlined above. Most of this work was once and for all project relating the pressures involved in a catalyst bed with the bed size and shape and involved analysing the way catalyst forming methods affected the final strength. For each new catalyst, however, the relationship between strength as new and strength under operating conditions has to be determined so as to establish parameters for production control.

One interesting outcome of ICI's work on catalyst strength, was that the most important requirement for high strength in a catalyst was resistance to the forms of stress outlined under 1 and 2 above and that the actual strength required during operation was much less than that required for handling the catalyst before operation.

VI. PHYSICAL CHARACTERISTICS

When deciding on the required strength of a new catalyst, it is often necessary to arrive at a compromise between the strength of the catalyst and other factors. The other major factors which are affected are the density of the catalyst and thus its pore structure and surface area. Generally speaking, because of the pore diffusion limitation which exists for most catalysts, it would be advantageous to make lower density, more porous catalyst with higher surface areas. The requirement of sufficient strength to withstand handling of the catalyst, however, often results in a catalyst being denser than otherwise would be required.

Density, pore structure, and surface area measurements are usually made at both the first and second level of catalyst testing and are done by the normal techniques of mercury density, helium density, and BET surface area measurement. In ICI we now use Krypton as the absorbent gas in our BET experiments. At the highest level of testing information can be obtained by measuring the pore size distribution using a mercury porosimeter or adsorption desorption techniques.

ICI has also developed a method for measuring the surface area of the active species in the catalyst rather than the total surface area. This is done by using a gas which is chemisorbed only on the active species and the diagram below (figure 3) shows a correlation between the surface area of the active species in low temperature CO shift catalyst with the catalyst activity.

This was very useful in defining the mode of operation of the catalyst. At the fundamental level of testing it is possible to engage the whole range of physical measurement and testing techniques now available to research chemists to assist in understanding the mechanism of the reaction, the way the catalyst entered into the reaction, and the way the active species are produced during the preparation of the catalyst. ICI has found X-ray diffraction particularly useful in this respect and has used it both to follow the various steps in catalyst manufacture and also to measure the crystallite sizes existing in the final catalyst product.

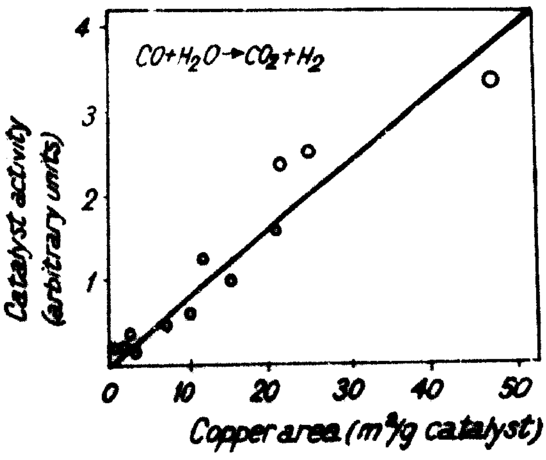


FIGURE 3. RELATIONSHIP OF CATALYST GEOMETRY TO CATALYTIC ACTIVITY. COPPER CRYSTAL SIZES AND EXPOSED SURFACE AREAS MEASURED BY X-RAY DIFFRACTION AND OXYGEN CHEMISORPTION

VII. APPLICATION TO PARTICULAR CATALYSTS

The above discussion is relevant to almost all catalyst testing but each catalyst used in a modern ammonia plant has certain points which need to be borne in mind when testing is carried out. These points are outlined in the following paragraphs.

VIII. HYDRODESULPHURIZATION CATALYST

Generally speaking one uses the standard series of tests to test hydrodesulphurization catalysts but it is better to use standardized feedstocks, whether gaseous or liquid hydrocarbons, because of the complication of the different reaction rates obtained with different types of sulphur compounds. When comparing different catalysts or different batches of the same catalyst it is essential that exactly similar feedstocks are used so that synthetic feedstocks which can be reproduced time and time again are most convenient. In ICI, a useful standard test involves the use of thiophene doped heptane.

IX. ZINC OXIDE

When comparing zinc oxide catalyst, the total sulphur pick-up possible with the catalyst is meaningless, because this is merely a measure of the available zinc oxide in the catalyst. What is important is the measure of the amount of sulphur which may be picked up under normal operating conditions before significant quantities of sulphur break through the catalyst. Besides the standard series of tests, and again one must bear in mind the question of the complication of different sulphur types, ICI use a standard test to measure the absorption capabilities of zinc oxide catalyst. The test uses 5 per cent hydrogen sulphide in a hydrogen stream which is passed through the zinc oxide catalyst in a pseudo-isotehrmal reactor at 370°C. When the first minute trace of hydrogen sulphide breaks through, as measured in lead acetate solution, the test is stopped and the average sulphur content of the catalyst bed measured. This is only a simple, semi-quantitative test with an accuracy of plus or minus 5 to 10 per cent but is a useful accelerated life test for differentiating between good catalyst and those which are second rate.

Because ICI catalyst 32–4 is in the form of granules, the crushing strength tests are meaningless and the standard strength test is the tumbling test.

An interesting example of the use of sophisticated techniques is the use of electron beam scanning in the study of the absorption of hydrogen sulphide by ICI catalyst 32–4. In this case the sulphur profile across a cross section of a catalyst granule is measured after varying degrees of sulphur absorption. The granule cross section forms the target in an X ray tube and the sulphur concentration is measured by the amplitude of the characteristic fluorescence given off by the sulphur atoms. This work shows that the controlling rate in the absorption is diffusion of the reactants through the sulphided layer.

X. REFORMING

Unfortunately there appears to be no short cut to accurate testing of reforming catalyst. A simple test had been found to be of very little use in evaluating primary reforming catalyst. For a long time full size tube tests were the only way in which reliable information could be found, and this proved very costly. ICI have, however, developed small tubular reactors with a complex heating system to simulate the heat input in a reformer tube. These units have proved very successful for tests in the first and second level of catalyst testing but have proved a little less than 100 per cent in simulation of full scale plant operation, not least because the catalyst has to be in smaller granules than full size rings. The ultimate test remains, therefore, a full scale trial in a full size tube in a semi-technical reformer.

ICI have also carried out strength tests under operating conditions but it was generally found that tests on the strength of the catalyst discharged after operation in a full size tube were sufficient indication of the strength during operation.

Tests of a secondary reformer catalyst are similar to those for a primary reformer, except that the temperatures which the catalyst must withstand are much higher. In this context it may be pointed out that thermal shock tests on these types of catalyst are more or less meaningless. If the high temperature strength of the catalyst is to be determined, it must be taken using a standard strength test while under simulated operating conditions.

XI. CO-CONVERSION CATALYSTS

Whereas the high temperature conversion catalyst has been manufactured for many years, low temperature conversion catalyst are a recent addition to the ammonia plant scene. In developing their present catalysts, ICI catalyst 52-1, ICI followed the process steps outlined in figure 1. Special catalyst test units were built for the programme, both in the laboratory and on a semi-technical scale. All the units were truly adiabatic and were designed for sorting tests both for initial activity and life and run continuously under full automatic control for periods of up to several months. The laboratory units consist of two reactors in series so that two different catalysts may be tested on each one at any one time. A continuous on line gas chromatograph measures the inlet and exit concentrations to each reactor and the dry inlet gas of the correct composition is obtained by mixing the purified constituent gases in a mixer/preheater/final purifier. The water is added by a metering pump via a vaporizer. The pressure units are exactly similar but are built to withstand the normal elevated pressures found in ammonia plants. Studies of the kinetics of the process and the effects of poisoning were carried out using a stirred tank reactor technique as outlined above. Under these conditions the units are also used for high temperature conversion and methanation testing.

Methanation presents a specially difficult problem because of the that still measure the correct apparent activity, where differentiation may conditions. One, therefore, has to choose a different set of conditions which makes differentiation between catalysts difficult under simulation high conversion to low carbon oxide levels normal in ammonia plants normal adiabatic reactors were substituted by a stirred tank reactor. These be made. In ICI use is mainly made of high space velocity tests for these sorting tests. Even so a special analytical technique and apparatus were developed to enable the accurate analysis required to be made.

XII. AMMONIA SYNTHESIS

For studies on ammonia synthesis catalysts very similar reactors to those used for CO conversion are used but, of course, only pressure units can be used because equilibrium ammonia concentrations at atmospheric pressure are negligible. Because of the large volume of gas required ICI uses an ammonia cracker to produce the feed gas to its small-scale ammonia units. The differential reactor used for ammonia kinetics and poisoning studies was a recirculatory type similar to that developed by Professor G. K. Boreskov and mentioned above. To maintain isothermal operation, the reactor is immersed in a heated, fluidized sand bath.

XIII. THE CATALYST MANUFACTURER

Once the manufacturing method has been established, further use of the more sophisticated testing techniques are unnecessary. If the manufacturing technique is applied rigorously, good catalyst should always be produced but the catalyst manufacturer has to carry out enough tests to measure critical parameters which directly or indirectly identify the catalyst he is producing. He must determine that it is similar to that originally developed under laboratory conditions. These tests must, however, be simple so as to allow them to be carried out quickly on a regular basis to control production.

Besides chemical analysis, strength tests are also routine on all catalysts. Also routine are pellet density, bulk density and size measurements because these infer the catalyst has the requisite internal pore structure.

Catalyst activity measurement is avoided unless absolutely necessary because of its time consuming nature and this is especially true for those catalysts where activity measurement must be measured under elevated pressure. If initial activity must be measured then simple pseudo-adiabatic or pseudo-isothermal units are preferred to simplify the procedure. Activity measurements are, of course, required when other characteristics do not infer that a catalyst must have good or bad activity. Similarly surface area or pore volume measurements must be made on some catalysts if measurement of density and other characteristics do not enable one to infer that an adequate pore structure is present.

Besides tests on the finished product it is normal to carry out tests on intermediates and vital stages in the production strength.

XIV. THE CATALYST USER

It is unrealistic for a catalyst user to envisage becoming a full scale catalyst tester. He is only interested in testing his catalyst outside of his plant every 2 to 5 years as they require changing and this is hardly sufficient opportunity for him to build up the required expertise in his organization. Nor is it likely that he would be in a position to spend the required amount of money. Most fertilizer producers who are not involved in catalyst manufacture do not test catalyst themselves but leave it to the catalyst suppliers. They rely on building up a relationship of mutual trust between them and their suppliers. Many fertilizer producers find they need to concentrate all their resources on the running of their plants and this leaves little opportunity for them to develop their technical abilities as catalyst testers. Some simple tests can be carried out by a catalyst user, if he so desires. Tests which lend themselves to be done by a catalyst user are chemical analysis, density and strength measurement. There is, however, really no possibility of fully checking on the catalyst supplier. Because of this there is no substitute for the relationship of mutual trust mentioned above and the competence and reliability of the catalyst supplier should play a major role in the catalyst choice.

THE PHYSICAL AND MATHEMATICAL MODELLING OF A PROCESS FOR ALKYLAROMATIC DEHYDROGENATION IN ADIABATIC SYSTEMS[1]

V. MOCEAROV[*], G. CSOMONTANYI[*], S. POPA[*], G. PANAITESCU[*],
A. PANOVICI[*]

Modern trends in the transfer of laboratory research results to pilot or commercial scales involve physical and especially mathematical modelling.

In physical modelling, the nature of the phenomenon is identical in the model and apparatus, the totality of the individual stages being seen as a single phenomenon. From the given equations with one variable one deduces similar criteria, and the relationships between them are established in an experimental way.

In mathematical modelling it is necessary to compute the material and heat balance equations for the initial and local conditions of temperature, reactant concentration and the geometric features. Mathematical modelling contains three stages: the elaboration of the equations describing the process, the elaboration of the algorithm for the solution of these equations and the check of the reliability of the mathematical model on the studied plant.

Our group studied the optimization of the process used in obtaining styrene, for implementation on a commercial scale. The programme aimed to scale down a commercial ethylbenzene adiabatic dehydrogenation reactor and to elaborate the mathematical model describing the industrial process for obtaining styrene.

PHYSICAL MODELLING

In order to test the various improved versions of the dehydrogenation catalyst recommended for use in the styrene process, it was necessary to construct the physical model of the commercial reactor. To ensure the plug flow through the reactor the following conditions must be fulfilled: $\frac{D}{d_p} > 30$ where D is the diameter of the catalytic bed and d_p the diameter of the pellet and $Pé_R$ (radial mass transport factor) must be one order of magnitude greater than $Pé_L$ (axial mass transport factor) (1, 2, 3).

In a commercial adiabatic plant used for alkylbenzene dehydrogenation, these conditions are fulfilled because $D/d_p \gg 30$, and for $Re_{pellet} = 80.5$.

$$Pé_L = 0.95 \text{ and } \quad Pé_R = 8.5$$

The variation of the values of both Péclet numbers as a function of the modified Reynolds number is represented on a logarithmic plot in figure 1.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/14.

[*] Romanian Research Institute for Petrochemistry — PETROCHIM, Ploieşti, Romania.

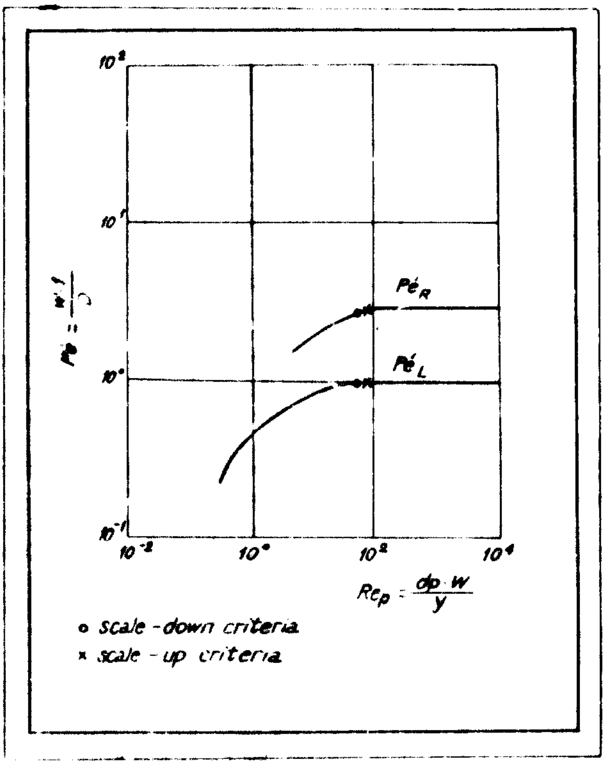


FIGURE 1. VARIATION OF $Pé_L$ AND $Pé_R$ AS A FUNCTION OF Re_p

The scale-down approach, based on maintaining the geometry of the commercial reactor, namely the D/H ratio (diameter of the catalytic bed to the height of the catalytic bed), led to a physical model in which the values of $Pé_R$ and $Pé_L$ corresponding to Re_p=8.2 are the same. Therefore the axial mixing of reactants cannot be avoided.

By scaling-down, maintaining the hydrodynamic conditions similar to those of the industrial reactor (D/dp ratio above 30), the model fulfills the condition of the commercial apparatus. The difference between $Pé_R$ and $Pé_L$ is near to that of a commercial reactor at an Re_p number of 50.2. Therefore there is no danger of axial mixing of the reactants, and the flow approaches plug type.

Based on these considerations, an adiabatic reference device with a capacity of 10 litres of catalyst was designed and constructed. It was used for comparative tests in an adiabatic system using catalysts which were previously tested in the laboratory isothermal system with the view of recommending the best plant conditions to apply in the commercial plant.

MATHEMATICAL MODELLING

Mathematical modelling for the catalytic dehydrogenation of ethylbenzene to styrene was applied on the reference adiabatic reactor which represents the scale-down of the industrial reactor.

Six catalytic reactions (I—VI) were proposed to describe the process. These account for the presence in the resulting gas effluent of ethylbenzene (1), styrene (2), hydrogen (3), toluene (4), methane (5), benzene (6), ethylene (7), carbon dioxide (8), water (9) and carbon (10). Reactions I—IV are considered in a number of papers concerned with the modelling of this process as plausible and consistent for describing the process in an adiabatic system (4, 5, 6).

Reaction XV was considered by us in a kinetic study of catalyst fouling, and reaction VI results from a study of catalyst regeneration (7, 8).

1. Styrene generation:

$$C_6H_5—C_2H_5 \rightleftharpoons C_6H_5—C_2H_3+H_2 \qquad (I)$$

2. Toluene generation:

$$C_6H_5{-}C_2H_5+H_2 \rightarrow C_6H_5{-}CH_3+CH_4 \qquad (II)$$

3. Benzene generation:

$$C_6H_5{-}C_2H_5 \rightarrow C_6H_6+C_2H_4 \qquad (III)$$

$$C_6H_5{-}CH_3+H_2 \rightarrow C_6H_6+CH_4 \qquad (IV)$$

Coke generation:

$$C_6H_5{-}C_2H_5 \rightarrow 3H_2+CH_4+7C \qquad (V)$$

Coke regeneration:

$$C+2H_2O \rightarrow CO_2+2H_2 \qquad (VI)$$

In elaborating the mathematical model, the following simplifying assumptions and calculation formula were used:

(a) It was assumed that axial and radial mass and heat transfer phenomena have no influence on the kinetics of the studied reactions and as a result, the therms representing mass and heat transfer from the materials and the heat balance equations were considered negligible.

(b) It was assumed that the hydrogenation reactor proposed for the mathematic modelling is perfectly adiabatic, i.e. there is no heat exchange with the outside.

(c) It was assumed that the pressure variations are negligible in the catalyst bed; in the calculations, a mean pressure value of 1.10 atmosphere was used.

(d) In calculating the molal specific heats, a simplified formula was used (4):

$$Cp_i = A_i + B_i T + C_i T^2 \qquad (VII)$$

where A_i, B_i, C_i are constants, defined in Table I for each component of the gas phase (1–10).

TABLE I

VALUES OF COEFFICIENTS A_i, B_i, C_i FROM MOLAL SPECIFIC HEAT EXPRESSIONS, Cp (VII)

Component	A_i	B_i	C_i
1	$-0.9289 \cdot 10^{0}$	$0.3500 \cdot 10^{0}$	$-0.1988 \cdot 10^{-3}$
2	$0.9100 \cdot 10^{1}$	$0.9140 \cdot 10^{-1}$	$-0.3200 \cdot 10^{-4}$
3	$0.6880 \cdot 10^{1}$	$0.6600 \cdot 10^{-4}$	$0.2790 \cdot 10^{-6}$
4	$-0.7598 \cdot 10^{0}$	$0.2935 \cdot 10^{0}$	$-0.1591 \cdot 10^{-3}$
5	$0.3422 \cdot 10^{1}$	$0.1784 \cdot 10^{-1}$	$-0.4170 \cdot 10^{-4}$
6	$-0.7405 \cdot 10^{0}$	$0.2702 \cdot 10^{0}$	$-0.1405 \cdot 10^{-3}$
7	$0.2706 \cdot 10^{1}$	$0.2916 \cdot 10^{-1}$	$-0.9060 \cdot 10^{-5}$
8	$0.6850 \cdot 10^{1}$	$0.8533 \cdot 10^{-4}$	$0.2475 \cdot 10^{-6}$
9	$0.6890 \cdot 10^{1}$	$0.3283 \cdot 10^{-2}$	$-0.3400 \cdot 10^{-6}$
10	$-0.1097 \cdot 10^{0}$	$0.3692 \cdot 10^{-1}$	$-0.2134 \cdot 10^{-4}$

(e) In calculating the heats of the reaction − Hr_i (cal/mol) there was used the simplified relation (4)

$$\Delta Hr_i - A_i + B_i T \qquad (VIII)$$

where A_i, B_i are constants which characterize the reactions (I–VI), as shown in table II.

(f) Values of the equilibrium constant for obtaining styrene as a function of temperature were calculated using the relationship derived

TABLE II

VALUES OF COEFFICIENTS A_i, B_i, FROM THE RELATION $\Delta Hr_i = A_i + B_i T$ (cal/mol)

Reaction	A_i	B_i
I	28.843	1.090
II	−12.702	−3.150
III	25.992	−1.900
IV	− 9.568	−2.665
V	23.653	−2.490
VI	22.320	−2.604

from literature data (10).

$$K_p = 0.483 . 10^{6} \exp(-29.685/RT) \tag{IX}$$

The differential equation system which describes mass and heat balances can be expressed in a condensed form when defining the matrices of the following terms: the stoichiometric coefficients (S), reaction rates (R) heat capacities (C), heats of formation for reaction products (H) and molal concentrations (X).

$$S = \begin{vmatrix} -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & -1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 3 & 0 & 1 & 0 & 0 & 0 & 0 & 7 \\ 0 & 0 & 2 & 0 & 0 & 0 & 0 & 1 & -2 & -1 \end{vmatrix}$$

The horizontal rows of this matrix represent the stoichiometric coefficients which interact in the six reactions (I–VI) and the columns of the matrix represent reactions stoichiometric coefficients, namely those of the reaction products (1–10). Stoichiometric coefficients of compounds which are consumed in one of the studied reactions are marked with a minus, and those of compounds which are produced, with a plus.

R, C, H and X matrices are shown under the form of multi-dimensional vectors.

$$R = \begin{vmatrix} r_1 \\ \vdots \\ r_6 \end{vmatrix} \quad C = \begin{vmatrix} C_{p_1} \\ \vdots \\ C_{p_{10}} \end{vmatrix} \quad H = \begin{vmatrix} H_1 \\ \vdots \\ H_6 \end{vmatrix} \quad X = \begin{vmatrix} x_1 \\ \vdots \\ x_{10} \end{vmatrix}$$

Mass and heat balance equations expressed in finite differences have the following form:

$$\Delta X = R^{o} \cdot S \tag{X}$$

$$\Delta T = \frac{R^{o} \cdot H}{[illegible]} \tag{XI}$$

where:

R^* — reaction rates transposed matrix,
X^* — molal concentrations transposed matrix,
ΔX, ΔT — finite variations for concentration and temperature on the increment of the catalytic bed height,
F — molal effluent flow (raw material + diluent).

The knowledge of the finite differences X and T makes possible the calculation of concentrations and temperatures values, successively, for each increment of the catalytic bed.

It is obvious that:

$$X_{i+1}=X_i+\Delta X \tag{XII}$$

$$T_{i+1}=T_i-\Delta T \tag{XIII}$$

The development of relation (X) gives:

$$\Delta X_1=-r_1-r_2-r_3-r_5 \tag{X.1}$$

$$\Delta X_2=r_1 \tag{X.2}$$

$$\Delta X_3=r_1-r_2-r_4+3r_5+2r_6 \tag{X.3}$$

$$\Delta X_4=r_2-r_4 \tag{X.4}$$

$$\Delta X_5=r_3+r_4+r_5 \tag{X.5}$$

$$\Delta X_6=r_3+r_4 \tag{X.6}$$

$$\Delta X_7=r_3 \tag{X.7}$$

$$\Delta X_8=r_6 \tag{X.8}$$

$$\Delta X_9=-2r_6 \tag{X.9}$$

$$\Delta X_{10}=7r_5-r_6 \tag{X.10}$$

and from relation (XI), ΔT takes the form of:

$$\Delta T=\frac{r_1 H_1+r_2 H_2+\cdots\cdots+r_6 H_6}{F(x_1 C_{p1}+x_2 C_{p2}\cdots\cdots+x_{10} C_{p10})} \tag{XI.1}$$

Simplified forms for the expression of the reaction rates ($r_1, \ldots, r_6$) were used, in compliance with some literature sources (4, 5, 6, 9); the studied reactions (I–VI) were considered as first order and pseudo-homogeneous, each reaction being taken separately.

$$r'_1=k_1\left(p_1-\frac{p_2\cdot p_3}{k_p}\right) \tag{XIV}$$

$$r'_2=k_2\cdot p_1\cdot p_2 \tag{XV}$$

$$r'_3=k_3\cdot p_1 \tag{XVI}$$

$$r'_4=k_4\cdot p_3\cdot p_4 \tag{XVII}$$

$$r'_5=k_5\cdot p_1 \tag{XVIII}$$

$$r'_6=k_6\cdot p_{10}\cdot p_9^2 \tag{XIX}$$

where:

$p_{i(i=1,2,\ldots\ldots,10)}$ — partial pressures calculated by the multiplication of the molal concentration vectors with the average pressure of the system

$k_{i(i=1,2,\ldots,6)}$ — rate constant

$r_{i(i=1,2,\ldots,6)}$ — reaction rate, mole/gr.cat.H

In a kinetic study made by us on integral laboratory reactors, under pseudo-isothermal conditions, the values of the rate constants $k_1, k_2, \ldots, k_6$ were determined for the six reactions. The results obtained are shown in table III.

TABLE III

VALUES OF THE KINETIC CONSTANTS K_{oi}, E_i, FOR REACTIONS I-VI

Reaction	k_{oi} mol/gr. cat. H	E_i cal/mol
I	$0.120 \cdot 10^7$	30.000
II	$0.990 \cdot 10^7$	30.900
III	$0.190 \cdot 10^{10}$	47.600
IV	$0.720 \cdot 10^9$	45.000
V	$0.175 \cdot 10^6$	30.400
VI	$0.194 \cdot 10^6$	30.800

These values were adjusted in a computer in order to correspond to the macrokinetic conditions of the modelled adiabatic reactor.

With the help of the values $k_1, k_2, \ldots, k_6$, using relations XIV–XIX, the values $r_1, r_2, \ldots r_6$ were calculated and these were multiplied by $\rho . A . \Delta z$.

Where:

ρ — catalyst bulk density, gr/cm^3

A — area of the catalytic bed section, cm^2

$z = \frac{Z}{n}$ = increment of heigt, where Z=the height of catalytic bed, n=the number of increments. This yielded the values $r_1, r_2 \ldots r_6$ which interact in vector R.

The mathematical model for the styrene process was thus developed. The calculations were accomplished with the I.B.M. Disk Monitor System, Version 2 using the Euler integration method and Fortran language. Figure 2 depicts temperatures profiles calculated in accordance with the model on z increments from Z—the heigt of the catalytic bed for the case when effluent enters at 630°C. Tem-

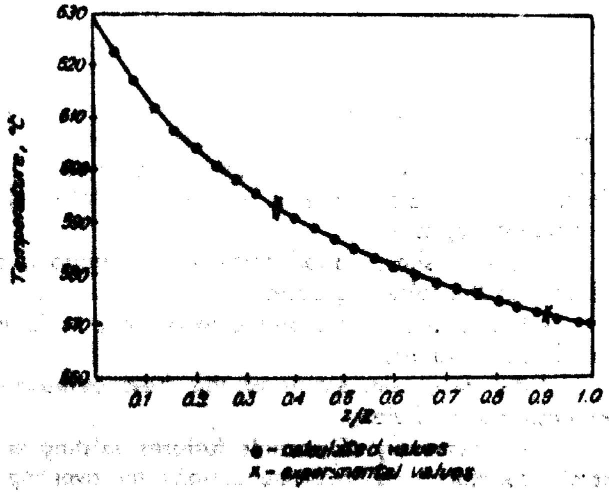


FIGURE 2. TEMPERATURE VARIATION ALONG THE LENGTH OF THE CATALYTIC BED FOR ADIABATIC STYRENE REACTOR [illegible]

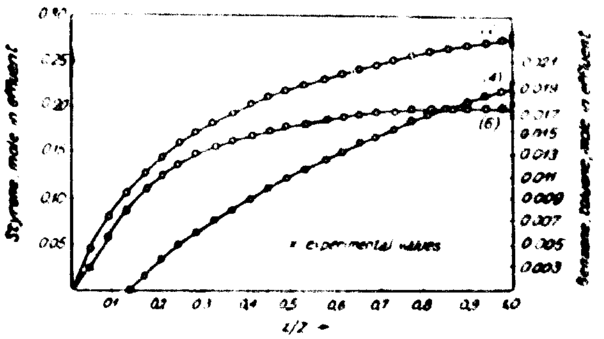


FIGURE 3 THE VARIATION OF ETHYLBENZENE CONVERSION TO STYRENE (1), TOLUENE (4), BENZENE (6) AS A FUNCTION OF UNIDIMENSIONAL LENGTH z/Z AT 630°C

perature values measured experimentally at three positions along the height of the catalytic bed of the adiabatic reactor (also marked in figure 2) confirm the fact that the model developed satisfactorily follows temperature changes in the chemical process.

Good agreement between the values calculated with the help of the model and experimental can be seen in figure 3 which shows the variatian for ethylbenzene conversion ta styrene, toluene and benzene, calculated on z increments, from Z – the height of the catalytic bed (effluent inlet temperature assumed to be 630°C), the experimental values (marked with X in figure 3) are practically superimposed on those calculated from the madel.

CONCLUSIONS

We have presented one of the methods currently used in our research work on hetero-catalytic processes. The method consists of:

– characterizatian of catalyst kinetics in a dynamic isothermal system using an integral laboratory reactor,

– the thermodynamic characterization of the principal reactions studied,

– the scale-down of the commercial reactor,

– the formulation of the analytically balanced equations for heat and materials from experimental laboratory data,

– subsequent adjustment of the kinetic data which characterize the catalyst in an isothermal system to correspond to the microkinetic conditions of the adiabatic reactor.

With such a system of differential balanced equations, one proceeds to the optimization of the system based on economic criteria. The optimal conditions obtained by calculations are checked in an adiabatic pilot plant, which is also used to establish catalyst operating conditions in an adiabatic system.

In a very short period of time, our group is able to give optimum solutions in the following cases:

– the choice of the best catalyst in a wide variety of processes in an adiabatic system,

– the recommendation of the best operating conditions from an economic point of view,

– the discovery of possible failures existing in some adiabatic commercial reactors and recommendations for avoiding them.

We also offer our technical aid in organizing such activities in other countries and the training of technical staff.

REFERENCES

1. Olah A. Hougon Ind. Eng. Chem., 53, 7 (1961).
2. G. Roemer et al. Ind. Eng. Chem. 1, 4, (1962).
3. J. J. Carberry Ind. Eng. Chem. 65, 11, (1964).
4. B. Davidson, J. Ros. Delop., 9, 5—6, (1965).
5. J.G.P. Shell, Canad., Soc. Eng., 47, 2, (1969).
6. J. Smith, Chem. Eng. Series, Mc. Grew-Hill, (1956).
7. C. Coricluc, G. Csomontanyi, S. Popa, Rev. Roumaine Chim. 3, (1972).
8. V. Macearov et al., Unpubl. Petrochim paper, (1970).
9. O. Levenspiel, Chemical Reaction Engineering, New-York (1962).
10. Ray H. Boundy, Raymond F. Boyer, Styren its Polymers, Copolymers and Derivatives, New York, (1952).

NEW TECHNIQUES IN ECONOMIC EVALUATIONS OF CATALYST EFFICIENCY[1]

SECRETARIAT OF UNIDO

INTRODUCTION

The problem of examining the efficiency of catalysts is encountered in several cases:

a) **in usage of catalysts for technical processes or laboratory scale experiments**

Usually, there is no need for new techniques in evaluating a catalyst during its usage as the yield pattern of a catalyzed reaction and its change due to the operating conditions or ageing of the catalyst show directly its efficiency.

b) **in planning a specific catalytic process**

Relying upon the experience of the vendor or other users the planner will select the most convenient among different catalysts with *guaranteed efficiency* without testing the catalyst itself.

c) **before, during and after production** runs catalysts are tested carefully on a commercial scale with regard to the requested guarantee. These final tests are expensive as the equipment used must allow the catalyst to be tested under normal process conditions regarding temperature, pressure, heat exchange, space velocity, catalyst to reactants ratio, and quality of the catalyst and feed stock.

d) **in search and development of suitable catalysts**

Most techniques for testing catalysts efficiency had been developed for this area of activities. There is a wide range from micro-catalytic scale up to pilot plant tests.

All these techniques attempt to predict catalyst activities desired for specific reactions.

The properties normally used for such predictions are:

surface area
pore volume
pore size
pore size distribution, and
reactivity

All techniques allowing the determination of one or more of these properties, as well as those techniques which deal with the determination of the interactions of reactants with a catalyst based on the mentioned properties, may serve as a tool for the evaluation of catalysts efficiency.

NEW TECHNIQUES IN ECONOMIC EVALUATIONS OF HETEROGENEOUS CATALYST EFFICIENCY

FIELD IONIZATION MASS SPECTROMETRY

This technique offers the possibility of ionizing the molecules of the gas phase, at a pressure of about 10^{-4} torr, which are in interaction with

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/24.

a catalyst by means of high electric fields and to analyze them by mass spectrometry.

Although not new as a technique, its application to catalyst evaluation has been described by W. A. Schmidt in 1968 (1, 2) with regard to the NH_3 synthesis and its possible intermediate products.

Table I shows various ion types and their relative intensities obtained by field ion mass spectrometry of NH_3 on iron.

TABLE I

ION TYPES IN THE FIELD ION MASS SPECTRUM OF NH_3 ON AN IRON TYPE (FIELD STRENGTH 10^7 V/cm)

Ion type	Relative intensity	Ion type	Relative intensity
N_2^+	1.0	NH_3^+	2.3×10^4
N_2H^+	5.0×10^0	NH_4^+	1.0×10^6
$N_2H_2^+$	3.5×10^1	$NH_4^+ NH_3$	2.85×10^3
$N_2H_3^+$	1.0×10^2	N_4^+	1.2
$N_2H_4^+$	1.0×10^1	N_4H^+	1.0
$N_2H_5^+$	3.3×10^1	FeN_4Hn^+	1.0 – 10.0
$FeN_2H_n^+$		$0 \leqslant n \leqslant 12$	
$0 \leqslant n \leqslant 6$			
N_3^+	3.5		
N_3H^+	2.5		
$N_3H_2^+$	6.5		
$N_3H_4^+$	1.5		
$N_3H_5^+$	1.0		
FeN_3Hn^+	1.0 – 10.0		
$0 \leqslant n \leqslant 9$			

The high intensities of the NH_3^+ and NH_4^+ ions and the absence of NH_2^+, NH^+ and N^+ ions are significant. Schmidt investigated the field ion mass spectrum of NH_3 on platinum, too. Under similar conditions only ion structures of $PtNx^+$ ($0 \leqslant n \leqslant 6$) and PtN^+ were found. No hydrogen was present in these ions.

The high efficiency of iron in this experiment is evident.

INFRA-RED SPECTROSCOPY

This well known technique was also used by Nakata and Matsushita (3) who found only NH and NH_2 surface complexes after adsorption of N_2–H_2 mixtures and NH_3 on a Fe–SiO_2 catalyst at higher temperatures. According to Jiru (4), better results are obtained by replacing the SiO_2 carrier by an MgO carrier, where by the strong bandes of SiO_2 between 1900 and 1400 cm^{-1} are avoided. With the MgO carrier, the infra-red spectra of surface complexes may be measured in the range of 4000 cm^{-1} to 300 cm^{-1}.

ELECTRON SPECTROSCOPY

This promising technique has been known for 25 years since Siegbahn and co-workers analysed photo ejected electrons with a double focusing spectrometer (5, 6, 7). But its general utilisation dates only from 1962. Turner reported instrumentation and studies using high resolution electron spectroscopy to determine the vibrational states of molecular ions (8). [illegible] But electron spectroscopy is mainly a surface technique as the average penetration of a photoelectron is approximately 50 Å (9).

The basic processes common to all electron spectroscopy techniques are shown in figure 1. Ionizing radiation causes the ejection of sample electrons. The electrons go into an electron monochromator and the energy of the photo-ejected electrons is determined. After energy resolution by the monochromator, a signal proportional to electron intensity is read out on the detector.

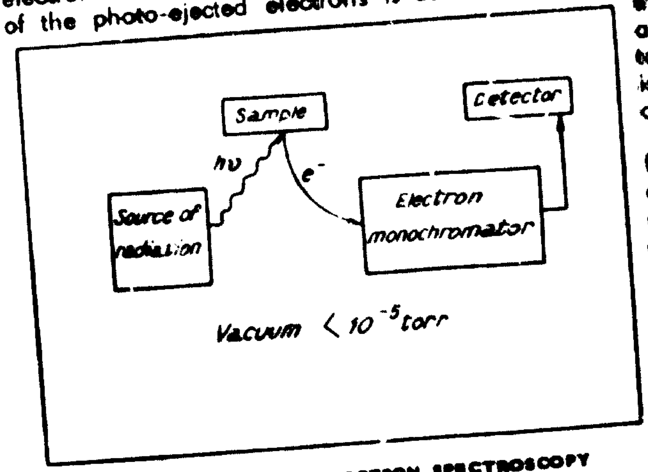


FIGURE 1. SCHEME OF ELECTRON SPECTROSCOPY

The kind of information obtained depends upon the energy of the ionizing radiation and the resolution of the monochromator. With high energy radiation, such as X-rays or γ-rays, core electrons may be ejected and their binding energies determined. With low energy radiation, such as ultraviolet radiation, valence shell electrons will be ejected and their ionization potential determined.

This qualitative flexibility and the possibility of quantitative measurement make this technique attractive in chemical and structural analysis. In particular, electron spectroscopy is suitable for surface studies even though the surface may be covered by a layer of material. The surface and the layer can be studied simultaneously. This is particularly interesting for catalyst studies, as the nature of changes occurring at active centres on the catalysts, as well as changes in the material being adsorbed onto the catalyst, may be determined simultaneously.

GAS CHROMATOGRAPHY

Gas-solid chromatography may be used in two different ways for the evaluation of catalyst efficiency. These are described below.

a) **Catalytic pulse methods**, developed in 1955 by Emmett (10, 11) differ in the way reactants are introduced into the reactor and the gas flow system.

These techniques – the static pulse method,
the flow pulse method,
the continuous flow method, and
the circulational flow method

have in common a reactor containing the catalyst to be examined,
an analytical column and
supplementary equipment.

The reactor and supplementary equipment is attached to a gas-chromatograph which serves as an analytical tool for the determination of reaction products. In principle, an inert gas is passed through a short catalytic bed and small pulses of reacting substances are metered into it under selected reaction conditions. The column and a detector are used for the qualitative and quantitative analysis of the reaction products and unchanged starting reactants (10, 11).

A simple example, figure 2, may illustrate the method and its evaluation (12):

Catalytic oxidation of methanol at 270°C,

I. CH_2O formed after a pulse of methanol,

II. O_2 consumed after a pulse of oxygen.

This example shows a two-step oxidation — catalyst regeneration process which may be describ as follows:

$$
\begin{array}{l}
\text{I. } CH_3OH(g)+KAT-O(s)=CH_2O(g)+KAT(s)+H_2O(g)\\
\underline{\text{II. } KAT(s)+{}^1/_2O_2(g)=KAT-O(s)}\\
\hline
CH_3OH(g)+{}^1/_2O_2(g)=CH_2O(g)+H_2O(g)
\end{array}
$$

b) In the microactivity method, the catalyst itself is loaded into the chromatographic column, and its catalytic properties are evaluated under experimental conditions approximating those of the process in question. This technique may be applied only for routine evaluations. However, the activity of the catalyst may be a function of component retention volumes, and corresponding corrections may be required. Studies of this kind have been made with $Fe_2O_3/Cr_2O_3/Na_2O$ conversion catalysts for CO and a methane converting Ni catalyst (13).

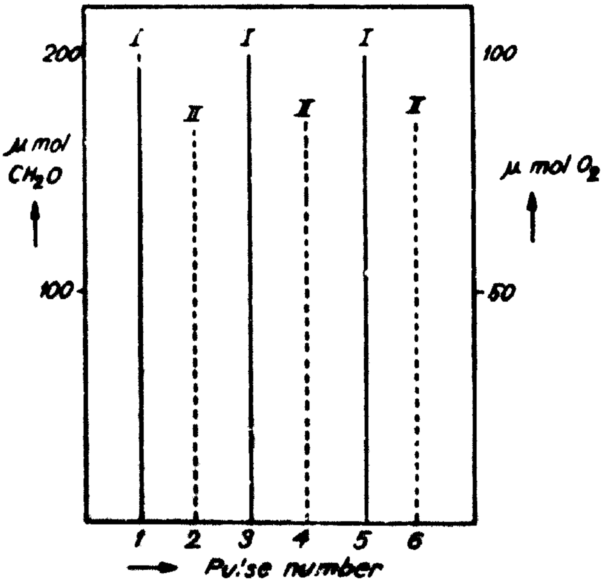


FIGURE 2. PULSE METHOD, CATALYST Fe-Mo-O

CATALYST SELECTION RATIONAL

Conventional methods used to estimate the efficiency of catalysts are very expensive and time consuming. Great efforts have been made to develop new, more rapid and less expensive techniques. Twenty thousand catalyst formulations were tried by German researchers (17) in developing a suitable catalyst for the synthesis of ammonia. To simplify the problem, attempts have been made to correlate catalyst efficiency for a number of parallel reactions (15, 16, 17).

As an example, an oxidation reaction model is described (table II). First the available activity sequence of various oxide catalysts is taken. F. E. Stone established the pattern for nitrous oxide decomposition, for the same catalysts (18). Apparently, the activities of the various catalysts may be divided into three groups:

The p-type oxides are clearly the best catalysts,
the n-type oxides are the least effective and
the MgO and CaO show an intermediate behaviour.

The other reactions chosen, namely carbon-monoxide oxidation, isotopic oxygen exchange, and the recombination of oxygen, show a similar

TABLE II

METAL OXIDE CATALYSTS IN THE ORDER OF DECREASING ACTIVITY

N_2O Decomposition (18)	CO Oxidation (19)	O_2 Isotopic exchange (20)	O Atom recombination (21)
Cu_2O	CoO	Co_3O_4	CuO
CoO	Cu_2O	MnO_2	MgO
Mn_2O_3	NiO	NiO	Fe_2O_3
NiO	MnO_2	CuO	Co_3O_4
CuO	CuO	Fe_2O_3	Mn_2O_3
MgO	Fe_2O_3	ZnO	CdO
CaO	ZnO	Cr_2O_3	NiO
Al_2O_3	TiO_2	V_2O_5	ZnO
ZnO	Cr_2O_3	TiO_2	SiO_2
CdO	V_2O_5		Cr_2O_3
TiO_2	Al_2O_3		
Cr_2O_3			
Fe_2O_3			

trend (14). We recognize that the most active catalysts are those having cations with unpaired d-electrons. The behaviour of chromium oxide is anomalous. Hydrogen is absent in all of these systems.

In parallel, one may examine hydrogen containing reactants with the same catalysts (table III).

TABLE III

METAL OXIDE CATALYSTS IN THE ORDER OF DECREASING ACTIVITY (REACTIONS WITH HYDROGEN CONTAINING COMPOUNDS)

C_2H_2 Oxidation (22)	CH_4 Oxidation (23)	Hydrocarbon Oxidation (24)	NH_3 Oxidation (25)	H_2 Oxidation (26)
Co_3O_4		Co_3O_4	Co_3O_4	Co_3O_4
Cr_2O_3	Cr_2O_3	Cr_2O_3	Cr_2O_3	
Ag_2O			CuO	CuO
Mn_2O_3	Mn_2O_3	Mn_2O_3	Mn_2O_3	MnO_2
CuO	CuO	NiO	NiO	NiO
NiO	Co_3O_4	Fe_2O_3	Fe_2O_3	Fe_2O_3
V_2O_5		TiO_2	V_2O_5	
CdO		Al_2O_3	ZnO	ZnO
Fe_2O_3	Fe_2O_3	CuO	TiO_2	Cr_2O_3
TiO_2	NiO	MgO	Al_2O_3	V_2O_5
ZnO	Ag_2O	V_2O_5		TiO_2

This set of reactions produces the same activity pattern. Chromium oxide appears in its expected position.

In spite of such correlations catalysis is a very complex phenomenon and cannot be explained in terms of a single criterion. However, this observed activity pattern can be of help in the selection of oxidation catalysts. The extension of this approach to include other, physico-chemical properties of catalysts might be equally rewarding.

REFERENCES

1. W. A. Schmidt, Angew. Chem. 80, 151 (1968)
2. W. A. Schmidt, Vortrag, Gesellschaft Deutscher Chemiker, Hauptversammlung Berlin (1967)

3. T. Nakata, S. Matsushita, J. Phys. Chem. 72, 458 (1968)
4. P. Jiru, La Chimica e L'Industria, 52, (2), 1970
5. N. Svartholm and K. Siegbahn,
   Arkiv. Mat. Astron. Fys., 33A, 21 (1946)
6. K. Siegbahn and K. Edvarson,
   Nucl. Phys., 1, 137 (1956)
7. C. Nordling, E. Sokolowski, and K. Siegbahn,
   Arkiv. Fys., 13, 483 (1958)
8. D.W. Turner and M. I. Al-Joboury,
   J. Chem. Phys., 37, 3007 (1962)
9. K. Siegbahn at al., ESCA „Atomic, Molecular and Solid State
   Structure Studied by Means of Electron
   Spectroscopy", Almquist and Wiksells,
   Uppsala, 1967.
10. R. J. Kokes, H. Tobin, P. H. Emmett,
    Ind. Eng. Chem. 77, 5860 (1955)
11. B. Wichterlova, P. Jiru,
    Chem. Listy 59, 1451 (1965)
12. P. Jiru, B. Wicuterlova, J. Ticui,
    Proc. 3rd Int. Congr. Catalysis,
    Amsterdam, p. 199 (1964)
13. A. Tcheknavorian-Asenbauer,
    Dissertation Technische Hochschule
    Wien (1968)
14. N. Giordano, La Chimica e L'Industria 51, (11),
    1189—1199 (1969)
15. O. Grubner, „Advances in Chromatography"; Ed. by
    J. C. Giddings etc. Vol. 6., p. 173 (1968)
16. O. Gruber, H. Struppe, P. Jiru,
    „Gas Chromatography" Proc. 6th Int. Sym. on Gas Chromatography, Rome, p. 424 (1966)
17. A. A. Balandin, „Present State of the Catalysis Problem and the Theoretical Basis of the Search for Catalysts". Div. Chem. Sciences, Acad. Sci. USSR, 1955 (Engl. Trans.)
18. F. S. Stone,
    Advances in catalysis 13, 1 (1962)
19. F. S. Stone, in „Chemistry of the Solid State",
    p. 367, Academic Press, New York, 1955.
20. G. K. Azlasiak, Boreskov, Kasatrina,
    Kinetica i Kataliz 3, 81 (1962)
21. P. G. Dickens, M. B. Sutcliffe,
    Trans. Faraday Soc. 60, 1272 (1964)
22. B. Dmuchovsky, M. C. Freerk, F. B. Zienty,
    J. Catalysis 4, 577 (1965)
23. R. B. Anderson, C. K. Stein, J. J. Feenan, L. J. E. Hofer,
    Ind. Eng. Chem. 53, 809 (1961)
24. K. C. Stein, J. J. Feenan, L. J. E. Hofer,
    Ind. Eng. Chem. 52, 671 ([illegible]
25. N. Giordano, E. Cavaterr[illegible]ams,
    Chimica e Industria 45, 15 (1963)
26. V. Y. Popovsky, G. K. Boreskov,
    Kinetica i Kataliz 1, 566 (1960).

Let us consider the manufacture of a reforming catalyst for a capacity of 2 million tons/year reformed gasoline of octane number 90. At a yield reduction of 2 per cent for the same quality, a loss of 20 million lei/year would be sustained, considering the difference in value between the gasoline of quality shown and gases formed in lieu of gasoline.

TABLE I

STAGES IN THE PREPARATION OF AN INDUSTRIAL CATALYST

Nature of catalytic constituents	Process steps and method of separation from reaction medium	Shaping	Thermal treatments	Special chemical treatments	Regenerating and reactivating possibilities
Elements or combinations	Precipitation, coprecipitation (temperature, concentration, time, pH)	Forcing Tableting Atomization	Controlled atmosphere (air, inert gas, reducers, etc), temperature and time control	With: Cl, H_2S, O_2H_2, H_2O, etc. to introduce special features	Methods vary
Crystalline, non-crystalline, gels, solutions	Solid-solid reactions Separation, intermediate washing, transport				
Supported, unsupported	Ageing (specified medium, pH, temperature, time)				

TABLE II

PROBLEMS IN THE FABRICATION OF A CATALYST FOR GASOLINE REFORMING AND AROMATIZATION

Development problems	Physico-chemical properties to be defined	Measurements of catalyst properties	Catalytic properties of major interest
Nature of alumina used as support and preparation procedure Alumina activation procedure	Surface area and purity	Adsorption methods (BET etc.), impurity dosage Selective adsorption, arbitrary method	Activity by test reactions to establish supporting qualities
Active component integration procedure	Platinum dispersion Crystal stability	CO, H_2, etc. chemisorption X-ray diffraction Electronic microscopy	Activity by test reactions for hydrogenation and dehydrogenation.
Special suport treatments, for acid treatment (Cl, F, SiO_2) in catalyst finishing	Acid and hydrogenation-dehydrogenation balance Nature of acid centre	Gas adsorptions measurable by: ●colourimetry ●thermo-dif. anal ●I. R. and NMR ●special titrations	Activity for dehydrocyclization and isomerization reactions Activity under special conditions for the control of catalyst stability

Several examples of the fabrication of a catalyst, using active alumina as a support, obtained by the precipitation procedure, elucidate some of the above aspects.

a) PRECIPITATION OF ALUMINIUM HYDROXIDE GEL FROM AN ALUMINIUM SALT SOLUTION

Usually the hydrogel is filtered, but filtrability is very poor. Generally, at least two filtrations are required, one for the formed precipitate and the other, or others, for the washed precipitate. In sizing the filtering equipment, suspension filterability must be taken into account for each filtering operation since filterability changes during gel washing. It has been determined experimentally that filtering rates are reduced 3 to 4 times by the washing operations. However, certain preliminary preparations of the suspension may increase filtering efficiency several, times, thus reducing investment costs. These must be utilized.

A second example, in the case of alumina gel precipitation can demonstrate what could happen if a designer does not respect conclusions deriving from research work. Two reactants, one with basic and the other with acid properties, and rates in the order of 100/1, are contacted to obtain alumina hydrates. The influence of pH on the quality of the catalytic support is known as is the effect of contacting mode and temperature. If uncontrolled contacting be practiced or the reaction temperature controlled by regulating feed rates instead of providing adequate cooling equipment, nonreproductibility of hydrate properties is ensured.

In figures 1 and 2 are shown the effect of pH and reac-

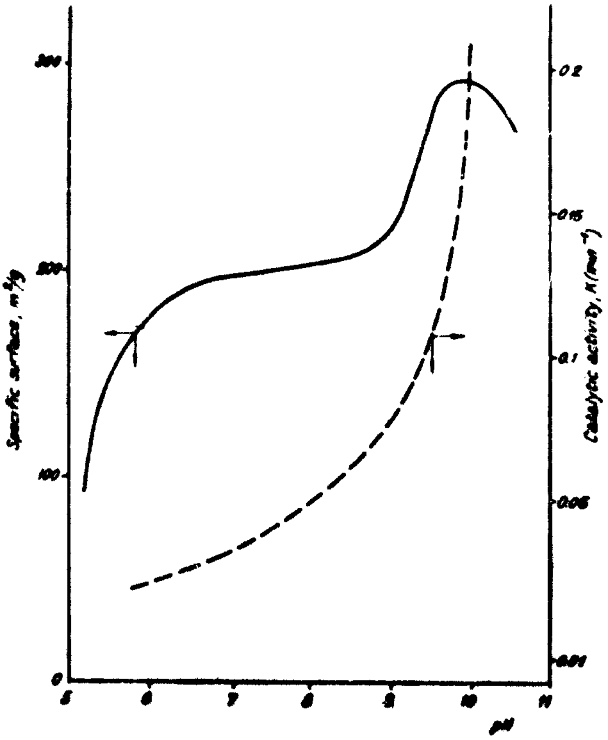


FIGURE 1. THE INFLUENCE OF PRECIPITATION pH ON THE SPECIFIC SURFACE AREA AND THE CATALYTIC ACTIVITY OF ACTIVATED ALUMINA IN ISOPROPANOL DECOMPOSITION

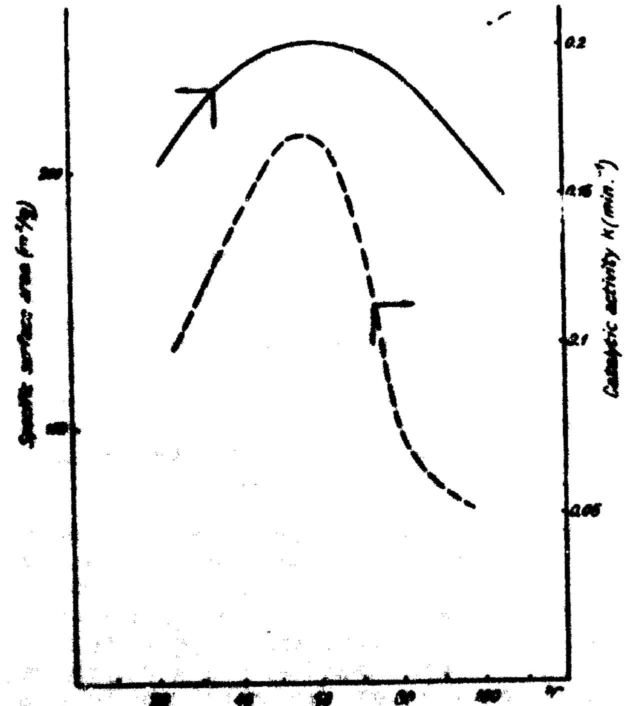


FIGURE 2. THE INFLUENCE OF PRECIPITATION TEMPERATURE ON THE SPECIFIC SURFACE AREA AND CATALYTIC ACTIVITY OF ACTIVATED ALUMINA IN ISOPROPANOL DECOMPOSITION

tion temperature on the structural properties of alumina hydrates (2, 3). It is observed that hydrate properties are sensitive to even slight variations of the parameters shown, affecting the support or catalyst structure at later stages.

Automation of the precipitation step must be considered not for the sake of a reduction in manpower but as a means to achieve process control. In addition, the control instrument must be placed in the weakest point of the operation and not some place where it shall detect average values of the parameters required.

The chemical engineering aspects are difficult since the reaction is practically instantaneous and the products are solids and solutions with a strong reciprocal influence.

b) OBTAINING HYDRATED ALUMINA BY ELIMINATING INTERPARTICLE LIQUID

This is another production step which impresses its character on the properties of the finished catalyst strongly. As a function of the precipitation conditions used, tri- and mono-hydrates are obtained which, in the dehydrating treatments, successively pass through a series of species into α-alumina (3). The transformation procedure is a function of initial structure, temperature, drying medium, calcination, etc.

It is sufficient to present only one variant of this transformation in order to see the importance of control in this stage. Table III shows the decomposition stages of aluminium hydrates by heating in dry air (4). It can be observed that although the final decomposition structure of any hydrate is alpha-alumina, the intermediate stages depend upon the initial hydrate structure as well as the temperature at which the transformation occured. As regards the gamma and eta forms, which are more frequently employed as catalytic supports, it is observed that these require that the initial structure be either trihydrates or alpha-monohydrates, but in no case beta-monohydrates which lead directly to the alpha form. It is understood that in some cases alpha-alumina is the one required, but only when special structural properties are not required in a catalytic support.

TABLE II

DECOMPOSITION STAGES OF SOME ALUMINIUM HYDRATES

$$\text{Alpha-trihydrate} \xrightarrow[260^\circ]{140^\circ} \text{Alpha-monohydrate} \xrightarrow[450^\circ]{280^\circ} \text{Chi} \xrightarrow[950^\circ]{500^\circ} \text{Gamma} \xrightarrow[1050^\circ]{1020^\circ} \text{Kapa} \xrightarrow[1120^\circ]{1080^\circ} \text{Theta} \xrightarrow[1180^\circ]{1150^\circ} \text{Alph}$$

$$\text{Beta-trihydrate} \xrightarrow[240^\circ]{140^\circ} \text{Alpha-monohydrate} \xrightarrow[450^\circ]{250^\circ} \text{Eta} \xrightarrow[850^\circ]{800^\circ} \text{Theta} \xrightarrow[1250^\circ]{1180^\circ} \text{Alph}$$

$$\text{Alpha-monohydrate} \xrightarrow[450^\circ]{400^\circ} \text{Gamma} \xrightarrow[1050^\circ]{850^\circ} \text{Delta} \xrightarrow[1120^\circ]{1080^\circ} \text{Theta} \xrightarrow[1200^\circ]{1150^\circ} \text{Alpha}$$

$$\text{Beta-monohydrate} \xrightarrow[490^\circ]{400^\circ} \text{Alph}$$

- Transformation conditions: one hour heating in dry air
- Above arrows: temperature at which phase transition sets in (°C)
- Below arrows: temperature at which transformation is complete (°C)

The specific area of the alumina obtained by the decomposition of alpha-trihydrate and alpha-monohydrate as a function of temperature and dehydrating medium (4) are shown in figure 3. It can be observed that while the specific area of the alpha-monohydrate practically does not undergo any modification up to 400°C, the specific area of alpha-trihydrate undergoes a maximum modification in the interval shown. Thus the hydrate's initial structure influence the properties of the support obtained. In tables IV and V are shown other structural modifications of the above mentioned hydrates, indicating essential differences between the behaviour of mono- and trihydrates (4).

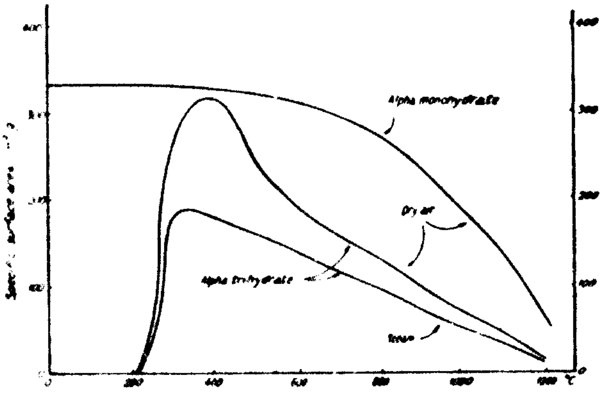


FIGURE 3. THE INFLUENCE OF TEMPERATURE AND MEDIUM ON ALUMINA SPECIFIC SURFACE IN THE DEHYDRATION OF SOME ALUMINA HYDRATES

From the above it can be seen that it is absolutely necessary that the procedure for obtaining hydrogels, hydrate or hydrates, must be clearly defined in all details.

It is the researcher's duty to establish the basic parameters for the industrial plant. The laboratory studies must be considered only as a preliminary phase proving the feasibility of such a product but not the manner in which it should be obtained on an industrial scale. Arbitrary

TABLE IV

ALPHA-TRIHYDRATE TRANSFORMATIONS

Characteristics	Initial value	Value after 20 hour calcination at:					
		200°C	205°C	290°C	310°C	350°C	400°C
H_2O/Al_2O_3 ratio	3.0	2.5	2.0	1.5	1.0	0.5	0.1
Density, with He, g/ml	2.4	2.4	2.4	2.5	2.6	2.7	3.0
Density, with Hg, g/ml	2.3	1.9	1.7	1.6	1.6	1.7	1.9
Pore volume, ml/g	0.025	0.114	0.175	0.222	0.248	0.244	0.203
Specific area, m²/g	negligible	5	50	125	250	325	225
Pore radius, Å	...	400	70	36	20	15	18

TABLE V.

ALPHA-MONOHYDRATE TRANSFORMATIONS

Characteristics	Initial value	Value after 20 hour calcination at:		
		265°C	355°C	450°C
H_2O/Al_2O_3 ratio	1.5	1.0	0.5	0.1
Density, with He, g/ml	2.4	2.4	2.4	2.5
Density, with Hg, g/ml	0.9	0.8	0.8	0.85
Pore volume, ml/g	0.71	0.83	0.83	0.79
Specific area, m²/g	310	310	310	285
Pore radius, Å	41	54	54	55

repetition of the process on a pilot scale will not give more information. On the contrary, in many cases, the pilot units are so constructed that more problems are raised by they than they solve and, in the end, the industrial plant is designed without having the necessary data in spite of having had a process pilot unit.

c) INTEGRATION OF ACTIVE COMPONENTS AND CATALYST FINISHING

Due to the numerous problems relating to the preparation of the support, in many cases, researchers are tempted to limit their attention to the subsequent steps of active component integration and catalyst finishing. If the proportion of the active components with respect to the support is high, this aspect may be less important. The situation changes when the active component concentration is low. In this case, it is the interdependence of support and active components which plays a decisive role in catalyst performance.

As an example, a bifunctional catalyst may be considered which contains platinum or platinum associated with other elements where the active metal content is in the order of 0.3 to 0.6 per cent.

When using the impregnation method, complications arise in extrapolating laboratory results to an industrial scale, especially due to the strong adsorbant properties of the support resulting in an uneven distribution of the platinum in the catalyst. Absorption and diffusion phenomena, as well as intergranular flow must be thoroughly studied in order to design and size the equipment properly. There is no information given in literature regarding impregnation process engineering. Moreover, this problem must be solved specifically for the type of support and catalyst finishing method (forcing, tableting, atomization).

Usually, in order to ensure an even impregnation, a so-called "competitor" is used. This consists of another solute, which, in certain concentration, reduces the relative adsorption of the platinic compound on the support surface, promoting its penetration into the granule. Determination of adsorption coefficients with respect to the given support, for both the platinic compound and competitor solute (acid, salt, etc.) represents the first step in elaborating the data required for designing the industrial equipment.

In figure 4, the influence of several competitors on the activity of a platinum catalyst in the dehydrogenation of cyclohexane to benzene is shown (5). The effect of the competitors depends on their nature as well as on the content of the active component, in this case platinum. They can stimulate or inhibit catalyst activity. Under all circumstances compounds which might potentially endanger catalyst stability must be avoided, even though they seem to present advantages. Thus, in the example quoted, it has been shown that sodium nitrate can be a good competitor although it is known that alkaline elements are not desired in platinic type catalysts for gasoline reforming. A premature conclusion in this respect may be very detrimental to the catalyst's performance during operation.

The above conclusions are also valid for tableted catalysts. In this case, impregnation is done before the tableting operation in certain grained powders. Although problems relating to the absorption of active components is simplified, other complications arise due to the use of additives before and during the tableting operation. In some cases, these strongly influence catalyst properties.

As an example, figure 5 shows schematically the relative distribution of density in the mass of a cylindrical tablet (6). The distribution of density

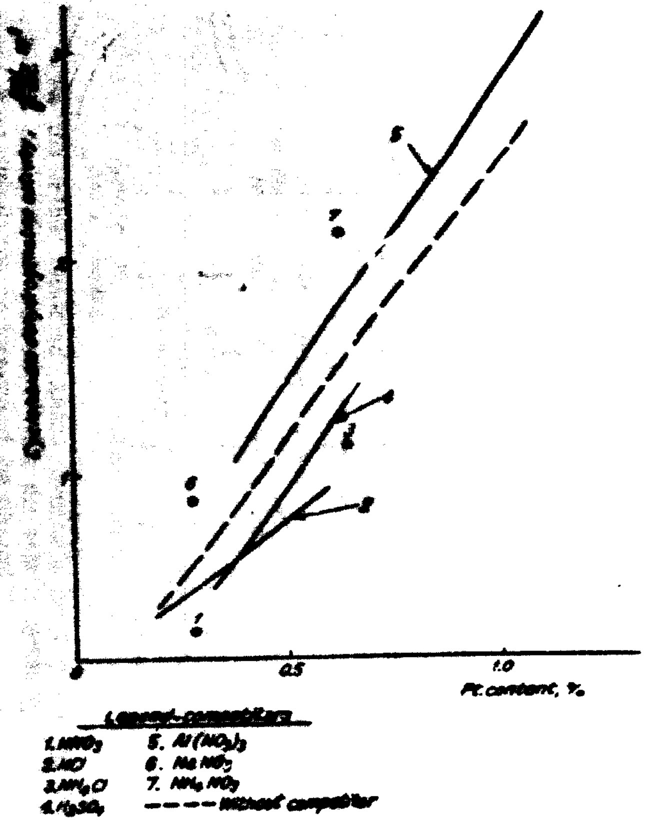


FIGURE 4. THE INFLUENCE OF IMPREGNATING COMPETITORS ON THE CYCLOHEXANE DEHYDROGENATION ACTIVITY OF A PLATINUM CATALYST

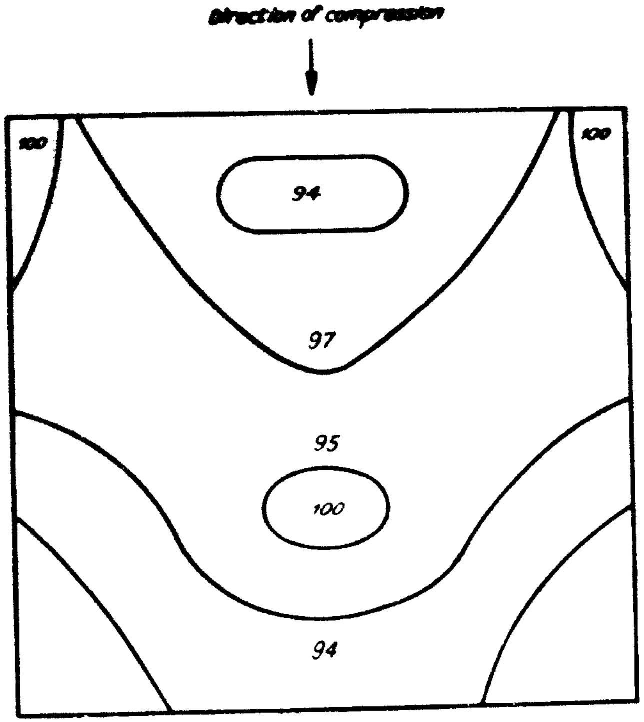


FIGURE 5. DISTRIBUTION PATTERN OF CATALYST DENSITY WITHIN THE PELLET (RELATIVE UNITS)

varies considerably, depending on the preparation of the granular material to be tableted, as well as on the type of tablet and tableting machine.

Thus, the tableting machine should not be selected simply by comparing the prices quoted in various offers. The machine characteristics should be incorporated into the development programme. For this reason the type of machine must be selected by the researcher and not by the designer.

The few aspects given in this paper were selected from industrial practice as well as from specialized literature. The purpose was to emphasize certain problems not fully considered to date. These must be the object of future studies of catalyst process development if the products are to fulfil modern requirements.

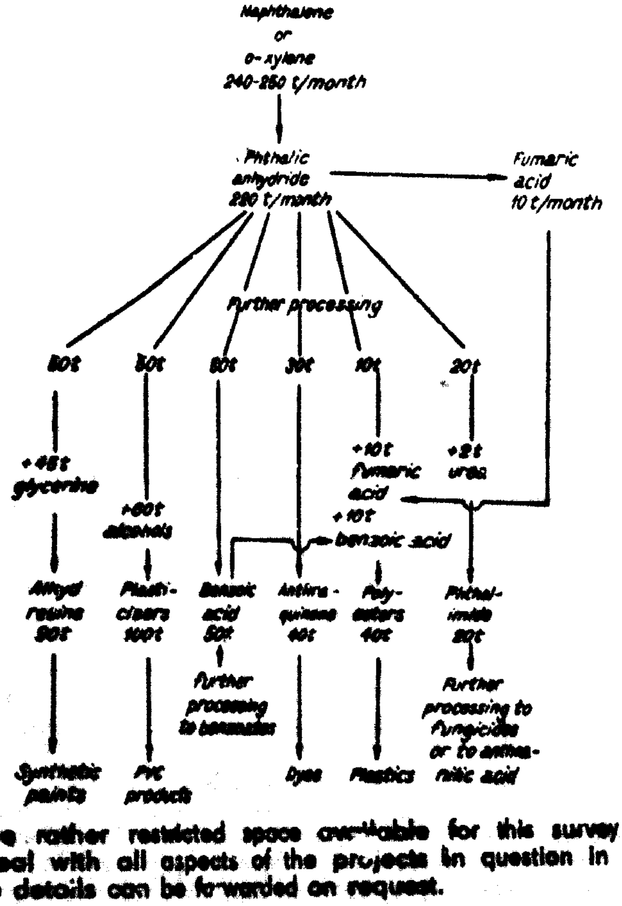
REFERENCES

1. Johnson, M, Mooi, J. — Journal of Catalysis, 10, 1968.
2. Rödel, von K., Sonntag, H. — Zeitschrift für anorganische und allgemeine Chemie, Band 343, 1966.
3. Ala Nicolescu, Maria Gruia and I. V. Nicolescu — Chemical Journal, vol. 16, December 1965.
4. Newsome, J. W., Heiser, H. W., Russell, A. S., Stumpf, H. C. — Technical report „Alumina Properties" Aluminum Co. of America, Pittsburgh, 1960.
5. Russel Maatman — Industrial and Engineering Chemistry, vol. 51, No. 8, August 1959.
6. Traina, F., Pernicon, N — Proceedings of the XXth International Congress on Industrial Catalysis, Milano, May 19—21, 1969.

ECONOMICAL SMALL SIZE PHTHALIC ANHYDRIDE PLANT AND A SMALL PLANT FOR THE MANUFACTURE OF CATALYSTS[1]

OTTO F. JOKLIK[2]

This paper describes economical small size phthalic anhydride plants and a small plant to manufacture catalysts suitable for the catalytic production of phthalic anhydride. The detailed description together with many data hitherto unpublished enables the experts from developing countries to carry out feasibility studies for the realization of similar plants which will sooner or later become a necessity for any development country.



As the rather restricted space available for this survey does not allow to deal with all aspects of the projects in question in a detailed study, more details can be forwarded on request.

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG. 123/15.

[2] Didier-Kellog Industrieanlagenbau GmbH, Essen and Rheinstahl AG, Brackwede, Federal Republic of Germany.

The production of phthalic anhydride – and subsequently of maleic anhydride – is of great importance to developing countries. In the initial stage of industrial development, phthalic anhydride serves as a valuable raw material and intermediate product, mainly in the field of PVC additives, paints, dyes and plastic materials in general. With further industrial development and the subsequent organization and growth of a petrochemical industry, a domestic production of phthalic anhydride becomes an outlet for petrochemicals such as o-xylene or petro-naphthalene.

The initial modest production capacity of a small phthalic anhydride plant can be increased stepwise according to the needs of the local industry. The transformation of this valuable product to intermediates can be organized as the market will require.

In view of the progressing consumption of maleic anhydride, the industrial experience gained in the production of phthalic anhydride, can prove to be beneficial in the erection and operating of a maleic anhydride plant, using benzene or other raw material available.

Owing to the interconnexion of phthalic and maleic anhydride production with a wide variety of smaller processing plants, even production plants, of relatively modest proportions, can prove to be beneficial and profitable. Such small production plant capacities perhaps not economic in highly industrialized countries may prove to be more advantageous as part of a large industrial complex.

In the following pages is described a combined, relatively small, multipurpose plant for the production of phthalic anhydride from naphthalene and/or o-xylene and of maleic anhydride from benzene. The main advantages of this plant is its remarkably low cost, simple concept, robust construction, extremely resistant long-life polyvalent oxidation catalyst, advanced reactor design and maximum safety in operation. Production may be optimized by the use of a process control computer in plants with fully automatic process control instrumentation (optional). The phthalic anhydride production capacity ranges are illustrated:

500–1,200 tons per year (one or two basic units of 500–600 t/y each) and

1,000–2,500 tons per year (extendable to 5,000 t/y).

A summary of potential uses of phthalic anhydride, a description of the production of oxidation catalysts and of a multipurpose pilot plant and a survey of the literature and patents completes this report.

A typical example of a series of complementary transformations based on phthalic anhydride production is shown in the following schematic diagram. The development of an initial production of 220 t/month of phthalic anhydride to some 330 t/month of valuable intermediates is illustrated. The manufacture of catalysts for the phthalic anhydride plants described here is dealt with in the second part of this survey.

PHTHALIC ANHYDRIDE PLANTS

I. INTRODUCTION

Phthalic anhydride is more and more in demand and requirements can only be met with difficulty by the present producers. Up to now, the complexity and cost of phthalic anhydride plants have discouraged many producers of crude naphthalene or o-xylene, who, however could not but realize that the conversion to phthalic anhydride constitutes a valuable improvement of a product which is often difficult to sell, chiefly in its crude state. The complexity, cost and production hazards have also discouraged many potential users of intermediates such as plasticizers, synthetic resins, and PVC-compounds, from undertaking its manufacture.

Naphthalene has been one of the important by-products of the carbonizing industries and has been marketed in various stages of purity for many years; o-xylene is a typical petrochemical product available in growing quantities in modern petrochemical plants. Until recently, however, many of the producers have not seriously considered the extension of their activities, i.e. the production of more valuable compounds starting with naphthalene or o-xylene as a prime material. While it is admitted that the chemical synthesis of other materials starting with the basic materials available from coal tar or petroleum is an extremly wide field and is dealt with in large part by specialized chemical works, there is at least one product very easily obtained from naphthalene or o-xylene which could readily be handled at the tar and by-products plant of any large carbonizing undertaking or at any petrochemical plant as well. This is phthalic anhydride which commands a ready market at the present time, especially in the plastics industry and in the synthesis of dyestuffs. Its market price is an inducement to even relatively small-scale production.

The process presented here is the result of extensive research and development work carried out with a view to simplifying installations, increasing their output, improving the catalyst, determining the optimal reaction conditions, increasing plant safety and recovering most of the reaction heat. A basic production unit has been developed which is simple automatic, of a high conversion efficiency, requiring a small amount of power only and no steam from outside. Besides, the groundspace required is very small.

The choice was made of working fully automatically, independently and continuously. A standard unit of 1,600 kg/24 hour capacity, viz. 46 to 50 tons per month (500—600 tons/year), can produce as economically as larger plants. To increase production as many units as are necessary are grouped together. This solution offers considerable advantages from the point of view of flexibility, continuous production and suitability for extension. Moreover, as the plant can be used – with minor alterations – for the production of maleic anhydride from benzene, the existence of multiple units enables one to adapt production to prevailing market requirements. Recent comparisons have shown that the cost price of phthalic anhydride produced by an installation of the type described is smaller than corresponding prime costs in all plants using other processes. The cost of the plant itself is considerably lower than that of comparable plants, due to the principle of prefabricated "package plants" with a minimum expenditure for assembly and erecting.

II. DESCRIPTION OF THE PROCESS (general)

The production of phthalic anhydride from naphthalene or o-xylene takes place in the hot gaseous phase, in the presence of a catalyst, by air oxidation. The reaction, which is exothermic, is as follows:

a) $C_{10}H_8 + 4.5\ O_2 \rightarrow C_8H_4O_3 + 2CO_2 + 2H_2O$

b) $C_8H_{10} + 3.0\ O_2 \rightarrow C_8H_4O_3 + 3H_2O$.

The naphthalene or o-xylene, or mixtures of both, are heated and evaporated in an excess of hot air which passes over the catalyst in the oxidation reactor where the reaction takes place at a controlled temperature. The gases leaving the reactor are cooled and the phthalic anhydride is precipitated directly as a crystalline solid without passing through the liquid state.

The catalyst is of particular importance in the efficient operation of the reaction. While its essential component is vanadium pentoxide on a special carrier, certain additives and modifications differentiate the various catalysts available and have an appreciable effect on the over-all efficiency. In the process here described, a new polyvalent long-life catalyst is used, which has been studied and developed particularly to enable the use of low-quality, off-specification feedstocks of various services. It is possible to switch from one feedstock to another, or even use variable mixtures of both feedstocks without changing the catalyst.

Of particular importance is the reactor engineering and design. A new type of oxidation reactor of a very simple and fail-safe concept has been developed and is being used in this process.

Control of the reaction temperature is critical and, various systems have been used. In the process in question, a double, fail-safe automatic control of the reaction is ensured by the use of a process control computer with automatic proportioning of the feedstock and the oxidation air as a function of the reaction temperature and in parallel with an automatic control of the molten salts temperature in the reactor. This automatic control is particularly beneficial in the start-up and running in operations, considerably reducing the time required.

Another feature of the process in question is the remarkably increased safety of the plant by using newly developed explosion-proof vessels and containers for all feedstocks.

Particular note should be taken of the control of the final temperature of the deposition of the phthalic anhydride, since if this is too low, the water vapour present will form phthalic acid. While it is possible to drive the water away by controlled distillation, this involves the use of additional heat. Another disadvantage lies in the fact that phthalic acid is corrosive to mild steel whereas the anhydride is not. In the process here described, a particular control system ensures the optimal temperature in the condensation section of the plant.

III. PHTHALIC ANHYDRIDE PLANT 500—600 T/Y PRODUCTION CAPACITY

1. DESCRIPTION OF THE PROCESS

Crude naphthalene melted in an internally heated kettle by pressurized water superheated to 145°C (or preheated o-xylene from a separate vessel), is pumped into a vapourizer where it is vapourized by an injection of heated air at 145°C. Then the mixture naphthalene-air (or o-xylene-air) is fed into the oxidation reactor. The reactor is of the multitubular type, salt-cooled and filled with the granular catalyst mass (fixed bed catalyst). The naphthalene of the air-naphthalene mixture (or the o-xylene of the air-o-xylene mixture) in the appropriate ratio, is catalytically oxidized to phthalic anhydride. The reaction being highly exothermic, excess heat is absorbed by the circulating molten salts in the cooling system. The vapours leaving the reactor pass into a secondary cooler heat exchanger and water preheater where their temperature is reduced to just above the dew-point. They then enter an air-cooled sublimation system where technical grade crude phthalic anhydride is sublimed in the form of long-needle-like white crystals.

The water preheater/heat exchanger supplies the required pressurized water overheated at 145°C, under a pressure which allows it to circulate in the system for air preheating and naphthalene melting. The general arrangement makes the use of steam quite unnecessary. In start-up the reactor is externally heated with gas, LPG or electrically.

The technical grade crude phthalic anhydride produced is of a high degree of purity, nearly approaching the theoretical melting point. It is then subjected to a purification distillation and solidified in the form of flakes that can easily be packed and stored.

The simple character of the plant and its high efficiency result not only from the use of a new catalyst, but also from the low-pressure, high-temperature and high space-velocity of the process.

Automatic controls regulate the flow of the air-naphthalene (or of the air-o-xylene) mixture and its constant ratio, the preheating temperature, the reaction temperature, etc.

2. PRODUCTION CAPACITY

One basic standardized oxidation unit produces 46 to 50 tons per month, which corresponds to a yearly production capacity of 500 to 600 tons of purified phthalic anhydride. The production capacity of the plant can be doubled to 1,000 and to 1,200 tons per year. In such a case it is preferable to install initially a distillation unit of the envisaged final production capacity.

3. FINAL PRODUCT

Phthalic anhydride, best commercial grade, purity 99.8% min., naphthoquinones absent, solidification point 131°C min., colouration of the molten product 15 Hazen max. (average 10 Hazen), maleic anhydride 0.1% max., benzoic acid absent, ash under 0.001%, iron under 0.0005%, water insolubles less than 0.0005%.

4. RAW MATERIALS

Crude naphthalene, preferably hot-pressed quality with a solidification point of 79°C or o-xylene 97%. However, any naphthalene with a lower solidification point and higher impurities content or a lower grade o-xylene can be used, giving a correspondingly lower yield.

5. YIELD

108 kg max. of crude naphthalene (79°C) or 110 kg of o-xylene (97%), yield 100 kg of phthalic anhydride as a purified bagged commercial product in flakes.

6. PRODUCTION COST

For the production of 1,000 kg of phthalic anhydride (99.8% min.) the requirements are:

1,080 kg of crude naphthalene 79% max.
or 1,100 kg of o-xylene 97% max.
720 kWh of electric energy max.
80 kg of fuel oil (9,400 kcal/kg)
130 m³ of cooling water for secondary cooling circuit.

7. MANPOWER

For one basic standardized production unit there are required two men per shift of eight hours, namely for one basic unit producing 1,600 kg of phthalic anhydride in 24 hours, the direct labour will be 20 hours manpower. The same crew, however, can operate up to four basic units with a substantial reduction of manpower cost in subsequent units.

8. GROUNDSPACE REQUIRED

Each basic standardized production unit of 500 t/y. production capacity requires 10 by 20 metres (8 metres high), i.e. 200 m² for the production facilities. For a plant of a more generous design, an area of 15 by 15 metres, i.e. 375 m², would be required. The plant can be erected in the open air, with a wind and rain shelter only.

9. CATALYST

The reaction is favoured by a special catalyst on a special carrier. Its normal life is at least five to eight years. During that period it is not necessary to renew or regenerate it. The polyvalent oxidation catalyst enables the switching from one feedstock to another, such as from crude naphthalene to o-xylene, without changing the catalyst and without long running-in periods.

10. CONVERSION OF THE PRODUCTION

With minor alterations in the condensation and distillation sections, the plant is capable of producing maleic anhydride from benzene. The plant can also be used as the first stage of an installation to produce benzoic acid, anthraquinone, phthalimide, anthranilic acid and a wide variety of other intermediate products of great importance to the industrial organic chemistry.

11. INSTALLATION AND ERECTION PERIOD

A basic, standardized plant can be manufactured, erected and installed in approximately 10 to 15 months. The start-up and running-in period will require another 2 months.

12. TYPE OF PLANT

Fully automatic, extremely simple and robust "package" plants, with a minimum of repairs and maintenance, safe and reliable even under rough and adverse conditions of operation. All containers for liquid hydrocarbons are explosion-proof using novel safety design. Particularly suitable as a fully independent plant for developing countries.

IV. PHTHALIC ANHYDRIDE PLANT 1,000—2,500 T/Y PRODUCTION CAPACITY

1. DESCRIPTION OF THE PROCESS

Figure 1 is a diagram of a complete plant for the production and purification of phthalic anhydride.

Air is passed by the blower (1) through the air heaters (2) which are of the tubular type employing hot water under pressure obtained from the heat exchanger (8).

Naphthalene is melted in kettle (3), where heating is also by hot pressurized water in tubular coils, and from the kettle, molten naphthalene is drawn by pump (6) and pumped to vaporiser (4). Part of the hot air coming from air heaters passes through the vaporiser where air picks up the naphthalene vapour and the mixture of air and naphthalene vapour then passes on through cyclone (5) where any carry over of liquid naphthalene is removed from the air stream and returned to the vaporiser.

The rest of the hot air then joins the stream which passes into the oxidation reactor (converter) (7) where naphthalene is oxidized by oxygen in the air to form phthalic anhydride. The oxidation reactor contains a nest of tubes filled with the special catalyst which operates at a fixed predetermined temperature. The oxidation reaction is highly exothermic and the heat is dissipated (and the temperature thus controlled) by a circulating molten salts system. The molten salts eutectic mixture is circulated around the contact tubes filled with the catalyst and passed to an external cooler/heat exchanger maintaining a closed circuit. The conditions are controlled by the automatic feed of boiler feed water into the heat exchanger/cooler where the reaction heat is utilized as steam.

The oxidation reactor is also equipped with an auxiliary electrical, LPG or gas heating system which is used when the plant is started up from cold to provide the necessary temperature at which the oxidation reaction starts.

The mixture of hot air and vapours of phthalic anhydride passes from the oxidation reactor through a tubular heat exchanger (8) in which

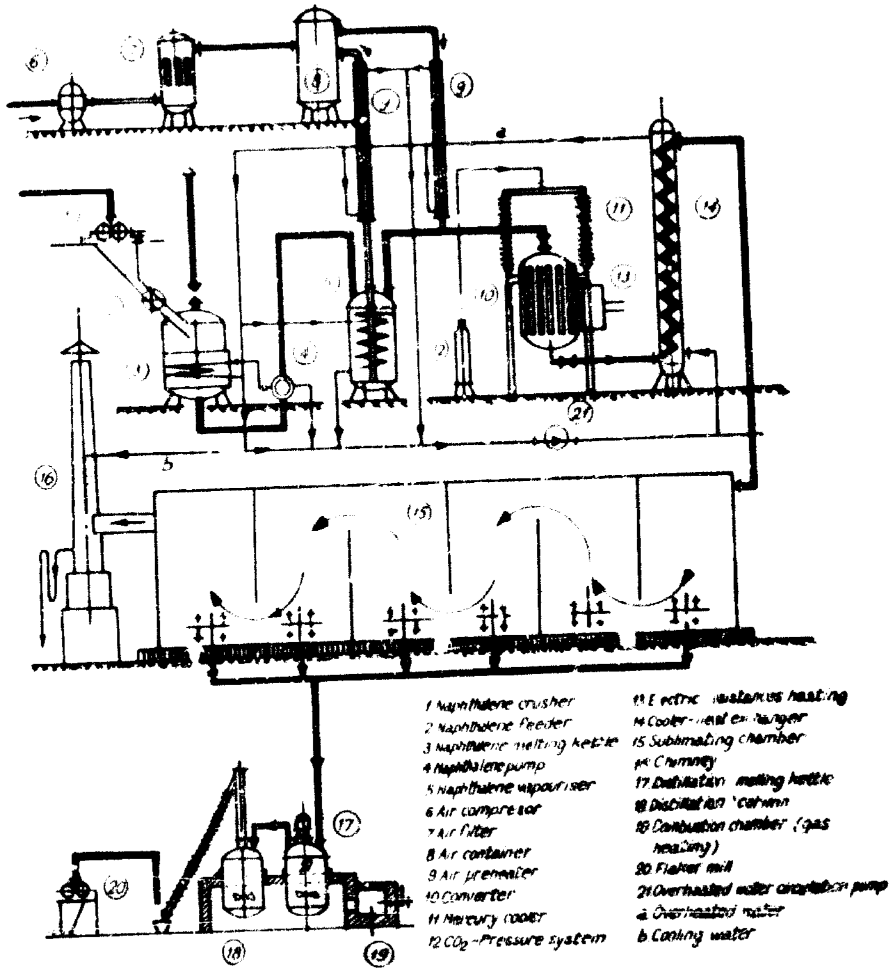


FIGURE 1. FLOW DIAGRAM OF PHTHALIC ANHYDRIDE PRODUCTION

it is partly cooled and where it gives up the greater part of its heat to the water which passes through the tubes under pressure. This hot water thus obtained is used to melt the naphthalene and to preheat the air.

From the heat exchanger the air still carrying the vapours of phthalic anhydride, passes through a series of atmospherically cooled sublimation condensers (9) in which the phthalic anhydride is sublimed in long needle-shaped crystals. The air leaving the sublimation condensers then passes to the atmosphere through chimney (10), the lower part of which is provided with special scrubbing facilities to remove residual traces of phthalic anhydride vapour carried in the air from the sublimation condensers.

The unrefined phthalic anhydride crystals are removed from the sublimation condensers on to a conveyor (11) which feeds melting vessel (12) in which the anhydride is melted and from which it is pumped to the refining section by pump (13).

According to the over-all production capacity of the plant, more than one unit for the production of unpurified phthalic anhydride can be operated in parallel and in conjunction with a common single refining plant. In such a case the naphthalene melting vessel, the phthalic anhydride conveyor and the molten anhydride tank can be common to all units.

The oxidation section of the plant is suitable for the oxidation of o-xylene to phthalic anhydride, too. In such a case, o-xylene is fed directly by means of a dosage pump from a storage tank into the vaporiser.

In the refining section the molten anhydride is pumped into still (14) which is surmounted by a column which operates in conjunction with a reflux condenser (15). Heating in the still is by diathermic oil operated from a boiler (16). The reflux carried out in this still and column is a preliminary treatment, replaces acid washing which was formerly found necessary, and substantially reduces the content of impurities without loss of phthalic anhydride.

After this preliminary treatment the molten anhydride is pumped from the still by pump (17) into the refining still (18) which is again heated from a diathermic oil boiler (19). The still is surmounted by a column and the vapours pass from the column into dephlegmator (20) and condenser (21). The condensate is returned as a reflux through reflux receiver (24) from which, part returns to the column, and part passes forward to the final phthalic anhydride receiver (27).

The vapours from the dephlegmator (20) pass to a second dephlegmator (22) connected with condenser (23) and the condensed molten purified phthalic anhydride from this dephlegmator flows to receiver (27) which in turn feeds a flaking machine (28) where flaked solid phthalic anhydride is produced, bagged and weighed.

The distillation in the refining section of the plant is carried out under a controlled vacuum exerted on the system by the vacuum pump (25) which draws away residual waste gases and vapours from the second stage dephlegmation section through separators (26) where any carry over of liquid is eliminated.

2. DESIGN PRINCIPLES

The over-all principles involved in the process of the conversion of naphthalene and/or o-xylene by oxidation over a catalyst to phthalic anhydride are now well known and the main consideration in the successful design of a plant operating on this process is the accurate control of the conditions of reaction.

The particular characteristics of the catalyst used are naturally very important and while the main effective constituent is vanadium pentoxide, its method of preparation, the addition of further chemicals and the nature of the catalyst carrier markedly effect the over-all efficiency of the reaction. Details of catalyst composition and preparation are not normally published since they are the reason for the superiority of one catalyst over another.

Assuming that the most efficient type of catalyst is used, the next most important matter is the accurate control of the temperature at which the reaction takes place. If the temperature is too low, the conversion efficiency suffers while if it is too high, the proportion of impurities increases due to the promotion of other oxidation reactions. Generally speaking, the optimum temperature lies in the range 450 to 500°C, depending on the catalyst used, but since the catalyst temperature is critical, the system of heat dissipation must be both effective and easily controlled within narrow limits.

In the system described, the coolant is an eutectic mixture of molten salts, the temperature of which is controlled by the quantity of feed-water fed into the external cooler/heat exchanger and consequently a relatively simple control of high efficiency. Another, still more precise control of the temperature in the reaction zone is achieved by an automatic variation of the raw material and air ratio, related to the reaction temperature.

For smaller plants, boiling mercury can be used as a coolant for the oxidation reactor. The temperature at which it boils is assured by the pressure at which the mercury system operates. A relatively simple pressure control is found to be highly effective. Other advantages in the use of mercury are that it is liquid at normal temperatures, is very stable and although expensive does not deteriorate in service.

A second point of control is the temperature at which the phthalic anhydride is crystallized in the sublimation condensers. Since there is always some water vapour in the air carrying the phthalic anhydride vapour it is important not to lower the temperature below the dew point, since if the water is precipitated it combines with the phthalic anhydride to form phthalic acid.

The acid can, of course, be heated to drive off the water again, but its melting point is about 70°C higher than that of the anhydride, and consequently if phthalic acid is allowed to be formed, the heat consumption of the refining section will be increased very appreciably and efficiency reduced. In order to prevent the formation of phthalic acid, the air/vapour mixture should not be cooled below 30 to 40°C, depending on the moisture content of the air Because of this a small quantity of phthalic anhydride vapour passes the air with into the chimney, and it is necessary to arrange to scrub this out at the base of the chimney.

Since the reaction in the oxidation reactor must take place in an excess of air, the quantity of vapour in the air is so small that it is impossible to condense it as a liquid. It is precipitated directly as a crystalline solid. Consequently the simplest method is to give the air/vapour mixture a relatively long contact time in atmospherically cooled sublimation condensers. This method has some disadvantages in that some manual work is required in the discharging of the crystals.

An alternative method can be used, which involves cooling in specially designed tubular vessels (switch condensers) in which the crystals are deposited on water or oil cooled tubes and subsequently steam or hot oil is passed through the same tubes melting the anhydride crystals. This is practical only in large size plants as the cost of the switch condensers is relatively high as is the cost of operation since not only is it required to melt the anhydride crystals but also the very large mass of steel in the tubes must be heated alternating cooling and heating being used.

After the foregoing considerations the next most important matter is the engineering of the reactor and the reactor design. The problem is not only to develop and find a suitable catalyst. Rather the problem is finding the reactor and conditions to perform the task efficaciously. Today more catalysts are available to perform a required task, yet more aspects of the catalytic events are recognized which must be engineered to optimize the catalytic reactor.

Since the heterogeneous catalytic reactor operates in what is usually a non-uniform field of temperatures and concentrations within which may exist both short- and long-range diffusional gradients, then the problem of reactor design and analysis is indeed complex. These extra-catalytic phenomena have allways existed in nature; however, they were not explicitly recognized decades ago when the prime concern was to find a catalyst, not to engineer its environment. Indeed, the fact that modern catalytic plants operate more efficiently than their fore-runners largely due to advances in reactor engineering as well as to intensive mechanistic studies.

Reaction engineering is that activity which attempts to find, correlate, and manipulate all those factors which affect the velocity and course of a chemical reaction network. Such factors are chemical (catalyst composition, apparent reaction order, activation energies, and Arrhenius coefficients) and physical (catalyst size, structure of pores, transport coefficients throughout the reactor, around and within the porous catalyst pellets). Reactor engineering embraces reactor shape, size and, of course, mechanical aspects of design. Intensive studies in this particular field have resulted in the design of a new advanced oxidation reactor to optimize the process in question.

The type of plant described has been designed for moderate capacities, for example one standard unit size is for the production of 500 to 600 tons of pure phthalic anhydride per year. A second standardized unit is designed for the production of 1,000 to 1,200 tons per year and yet another unit would be for a production capacity of 2,000 to 2,500 tons of pure anhydride per year. If greater production is required, it is suggested to achieve this by installing further standard oxidation units in parallel.

The control of the reaction in the oxidation reactor is less easy when the reactor is of larger diameter. For very large capacities other plant designs have employed fluidized bed reactors. Though heat control is easier in fluidized beds the limitations of the velocity of the gas used maintain fluidization means that such a plant should preferably work at a constant output. With the type of plant described here, the installation of two or three standard units working in parallel allows the over-all plant to handle much less than the maximum load, when required, and still to operate at maximum yield efficiency.

Since the plant described here is fundamentally a design for oxidation over a fixed bed catalyst it is also possible to convert it to uses other than the production of phthalic anhydride from naphthalene and/or o-xylene. An example is maleic anhydride from benzene. Naturally, in any such application, modifications of the details of construction of the standard units would be required in the case of an eventual modification of a phthalic anhydride plant to a plant for the production of maleic anhydride from benzene, the main modifications apply to the condensation and final purification systems. Nevertheless, it is interesting to note this possibility since it would mean that if for any reason in the future it became impracticable to manufacture phthalic anhydride, it would technically be possible to modify the existing plant, keeping all basic items, and produce some other compound from a different feedstock. A combined multipurpose plant can also be designed to produce alternately either phthalic anhydride from naphthalene and/or o-xylene, or maleic anhydride from benzene, and eventually from other feedstocks.

3. DESCRIPTION OF THE PLANT

a) RAW MATERIALS STORAGE

1 storage tank for o-xylene
1 storage tank for naphthalene
1 melting vessel for naphthalene
1 belt conveyor
1 pump for o-xylene
1 heated pump for naphthalene

b) OXIDATION SECTION

2 air intake filters
2 turbo-blowers
2 silencers
1 air preheater
1 carburettor
1 vapourizer
2 dosage pumps
2 heated flowmeters
1 reactor
1 heater for reactor for start-up
1 salts cooler/circulator
1 melter/storage of salts
1 heat exchanger/cooler
1 overheated water pump
1 secondary cooler/heat exchanger
1 water preheater for start-up
1 control panel

c) CONDENSATION SECTION

3 switch condensers
2 sublimation chambers for residues
1 chimney with scrubber
1 diathermic oil container
1 diathermic oil heater
1 diathermic oil cooler
2 diathermic oil filters
1 control panel
1 intermediate storage tank for crude P.A.

d) PURIFICATION SECTION

1 belt conveyor
1 phthalic anhydride pump
1 crude P.A. vessel
2 purification vessels with column, condenser etc.
1 distillation vessel with column, condenser etc.
1 phthalic anhydride pump
1 residues collecting chamber
2 Dowtherm generators
1 flaking machine
1 vacuum separator
1 vacuum decanter
1 vacuum pump
1 control panel
1 control vessel for purified liquid P.A.
1 phthalic anhydride pump

e) SUNDRIES

1 steam generator
1 water working-up section
1 fire protection system
1 plant laboratory
1 pilot plant
1 catalyst manufacturing section
1 set of spares for 3 years of operation heat insulation superstructures, steel framework etc.

FIGURE 2. PHTHALIC ANHYDRIDE UNIT 2,500 T/Y IN A 12,000 T/Y PLANT

4. PRODUCTION CAPACITY

The plant described is suitable for a production of 1,000 to 2,500 t/y of purified phthalic anhydride requiring practically the same ground space. The basic oxidation unit of 2,500 t/y can easily be doubled to a production of 5,000 t/y. In such a case it is advisable to install at the outset a distillation section of the enviseged final capacity of the plant.

5. FINAL PRODUCT

Phthalic anhydride	$C_8H_4O_3$	
Molecular weight	148.11	
Density (4 °C)	1.527	g/cm³
Purity	99.8	% by weight min.
Melting point	130.91	°C
Solidification point	131.11	°C (131 °C min.)
Boiling point	284.52	°C
Colour, molten	10	Hazen max.
Maleic anhydride	0.1	% max.
Naphthoquinone	nil	

6. RAW MATERIALS

a) Naphthalene	$C_{10}H_8$
Molecular weight	128.164
Density	1.168 g/cm³
Purity	96–98% by weight

	Melting point	78 °C min.
	Iron	0.005% by weight
	Ash	0.05 % by weight
	pH value	7.0
	Moisture	0.7 % by weight
	Sulphur	0.2 % by weight
	Nitrogen	0.02–0.06 % by weight
	Phenol and homologs	
	(bromometric method)	0.14 % by weight
	(colorimetric method)	0.2 % by weight
	Insoluble in benzene	0.024% by weight
	Non-volatile substances (160 °C)	0.1 % by weight
	Volatile substances (144 °C)	nil
b)	o-xylene	C_8H_{10}
	Molecular weight	106.16
	Density	0.883 g/cm^3
	Purity	97 % min. by weight
	I.B.P.	143 °C (initial boiling point)
	F.B.P.	145.2 °C (final boiling point)
	Sulphur (H_2S+SO_2)	nil
	Olefins	nil

7. YIELD

1,080 kg max. of crude naphthalene (79 °C) or 1,100 kg of o-xylene (97%) yield 1,000 kg of phthalic anhydride as a purified bagged commercial product in flakes.

8. PRODUCTION COST

Same as for the 500–600 t/y plant.

9. MANPOWER

For one basic unit of standardized production within the range of 1,000 to 2,500 tons/year there are required two men per each shift of 8 hours. The same crew, however can operate an enlarged plant up to a production capacity of 5,000 tons/y with an additional worker during the day shift only.

10. GROUND SPACE REQUIRED

The plant requires a ground space of approximately 40×50 metres, i.e. 2,000 m^2. Assumed average height of the buildings, approximately 10 m and of the distillation unit approximately 18 m. Total industrial area required for the realization of the plant is approximately 5,000 m^2 (preferably 10,000 m^2, in view of envisaged eventual expansion.) Depending on the climate, the plant can be erected in the open air, with an appropriate thermal insulation and a wind and rain shelter only.

11. CATALYST

See description for 500–600 t/y plant.

12. CONVERSION OF THE PRODUCTION

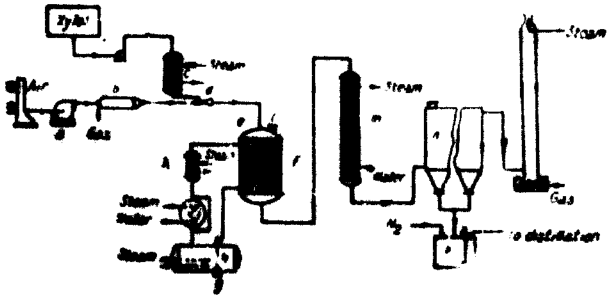
The conversions described for the 500–600 t/y plant apply in this case as well.

13. INSTALLATION AND ERECTION PERIOD

A basic standardized plant can be manufactured, erected and installed in approximately 16–18 months. The start-up and running-in period will require some further two months.

14. TYPE OF PLANT

See description for 500–600 t/y plant.



a. Air blower
b. Air preheater
c. Vapouriser
d. Injector/mixer
e. Reactor
f. Flow guides
g. Molten salts pump
h. Molten salts vessel
j. Molten salts cooler (steam generator)
k. Salts heater
l. Explosion flange/disc
m. Heat exchanger/cooler
n. Switch condenser
o. Chimney
p. Storage vessel for crude phthalic anhydride

FIGURE 3. VAPOUR PHASE CATALYTIC AIR-OXIDATION OF o-XYLENE TO PHTHALIC ANHYDRIDE

V. CONCLUSIONS

Even small size phthalic anhydride plants can operate economically. They are particularly suitable for development countries as they can be realized step by step as local markets develop, from small units of some 500 to 600 t/y, to 5,000 t/y. This would correspond to some 10,000 to 12,000 t/y of plasticizers which would be sufficient for the manufacture of some 30,000 to 25,000 tons/year of plasticized PVC-products. Of particular advantage is the flexibility of the plants in question regarding the possibility of using of various feedstocks of even poor quality, the robust configuration of the plant with an especially safe design and the possibility of its eventual extension.

CATALYST MANUFACTURE PLANT

I. INTRODUCTION

An economic small size plant for the manufacture of impregnated and/or coated catalysts is described in this survey, using as example, the manufacture of catalysts for the catalytic vapour-phase air oxidation of crude naphthalene and/or o-xylene to phthalic and of benzene to maleic anhydride in a fixed bed catalytic process.

Vanadium pentoxide catalysts, used in the manufacture of sulphuric acid, etc., are employed in this vapour phase heterogeneous catalytic reaction.

The catalyst consists in principle of an inert carrier and an active catalyst mass which in either impregnated when porous carriers or coated by a special procedure to hard solid carriers.

The quality and activity of the catalyst derive from the quality and geometry of the carrier, from the composition of the active ingredients and from the method of preparation. The product must have high durability and resistance against mechanical, thermal and chemical attacks to ensure continued operation of the industrial plant even under adverse and extremely rugged conditions. Another feature of the catalyst must be its high selectivity to obtain the highest possible yield at maximum load and to achieve an optimal quality of the final product.

II. DESCRIPTION OF THE PLANT

The catalyst production plant is subdivided into the following sections:
Raw materials storage
Preparation of silica gel
Preparation of the active catalyst mass
Coating (or impregnation) of the active catalyst mass onto the carrier
Drying of the finished catalyst
Classification, packing and storage of the finished catalyst
Pilot plant for catalyst testing and for further research and development work.

1. RAW MATERIALS STORAGE

These stores are for the various carrier qualities of different sizes and shapes and the various chemicals required for the composition of the active catalyst mass. The chemicals are stored under prescribed conditions.

The raw materials in question may be for example the following (for the manufacture of a catalyst for phthalic anhydride production):

a) Carrier: Aluminium silicate in granules of various sizes

b) Chemicals: Ammonium monovanadate C.P.
Titanium dioxide
Tin oxide
Oxalic acid
Hydrochloric acid
Potassium silicate
Distilled water

2. PREPARATION OF SILICA GEL

In this section of the plant, silica gel is produced from hydrochloric acid, distilled water and potassium silicate. The silica gel is required for the preparation of the coating liquid. It is prepared in stainless steel containers on a table equipped with four electric heating plates. Further either a water suction pump or a small vacuum pump is required for filtration. A stainless steel centrifuge can also be used. The filtered product is placed on steel plates and dried in a drying cabinet under accurately controlled heating. After drying, the silica gel is ground to a fine powder and stored in tightly sealed containers.

FIGURE 1. PREPARATION OF SILICA GEL.

3. PREPARATION OF THE COATING LIQUID

The coating liquid is prepared by boiling hydrochloric acid and distilled water together with various chemicals in determined proportions and heating under carefully controlled conditions. The chemicals are weighed out on a laboratory table provided with a precision weighing unit. Owing to the extremely corrosive nature of the liquid, the preparation is made either in enamelled vessels or Teflon bowls. The heating of the coating liquid and its concentration are carried out in a polypropylene drying cabinet provided with electric heating plates on a stainless steel support and a PVC exhaust fan for the removal of fumes. The concentrated coating liquid is stored in polypropylene containers.

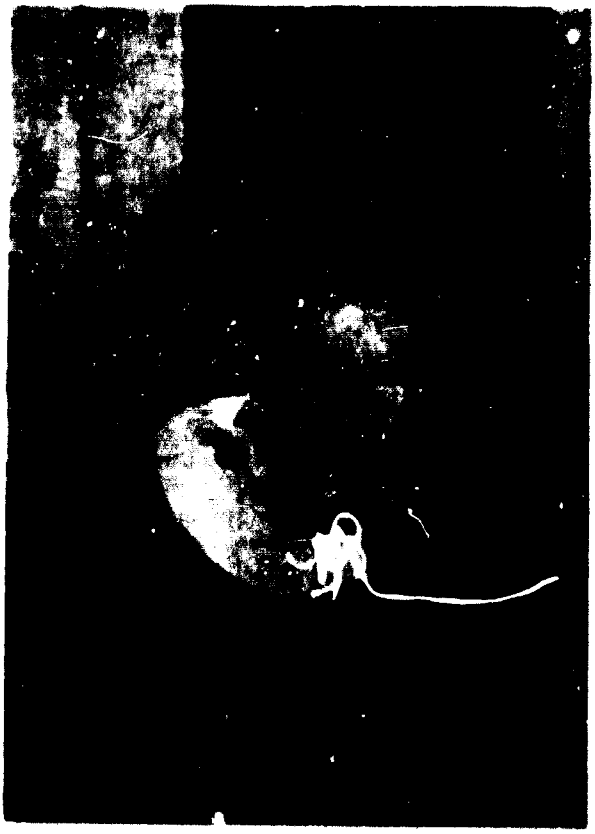


FIGURE 2. COATING OF THE SUPPORT. ROTATING DRUM WITH GAS HEATING

4. COATING OF THE CARRIER

The concentrated liquid is poured into the preheated carrier granules in a rotating drum. The drum is made of stainless steel, has a variable speed gear, a variable inclination adjustment and a precise temperature control. An exhaust fan eliminates fumes emanating from the drum during the coating process.

5. IMPREGNATION OF A POROUS CARRIER

A porous carrier can be impregnated similarly, though the viscosity of the coating liquid is different.

6. DRYING OF THE FINISHED CATALYST

The catalyst, after coating is dried under careful control in a drying cabinet made of stainless steel. Stainless steel trays are used to place on racks in the drying cabinet.

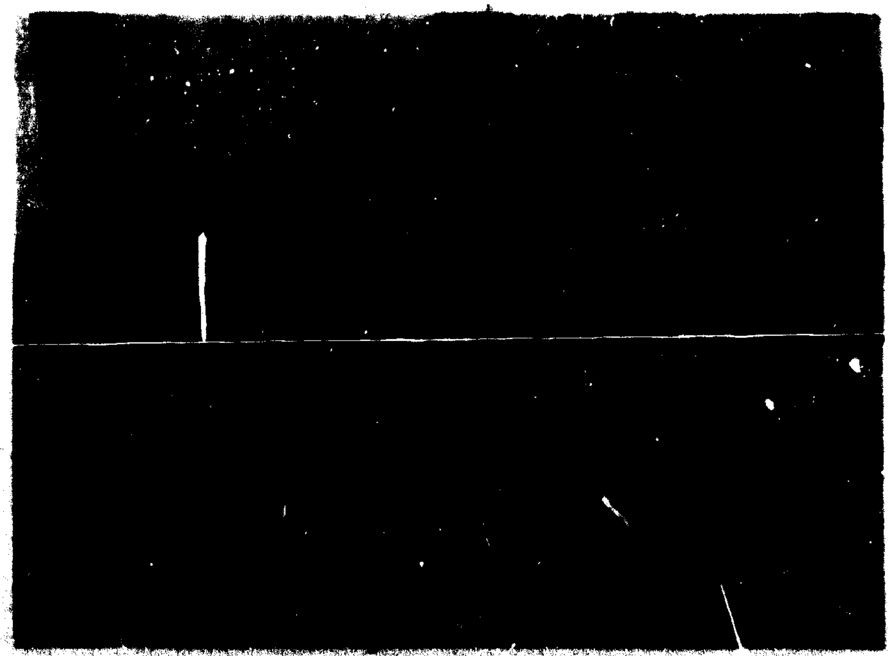
7. CLASSIFICATION, PACKING AND STORAGE

The finished catalyst is finally inspected and classified by sieving it on an appropriate mesh. It is once more inspected for impurities, conglomerates etc. and then packed into tightly sealed containers made of polyethylene. Usually, these containers are of 10 litres net content which are suitable for 20 kg net of the finished catalyst.

The filled containers, appropriately marked, are stored prior to shipment. Usually 10 polyethylene containers each containing 20 kg of catalyst are placed in a solid wooden box for shipment.

FIGURE 3. CATALYST FOR THE MANUFACTURE OF PHTHALIC ANHYDRIDE, PACKED IN POLYETHYLENE CONTAINERS

FIGURE 4. SHIPMENT OF 5.8 TONS OF A PHTHALIC ANHYDRIDE CATALYST



8. PILOT PLANT FOR CATALYST TESTING

Each charge of the finished catalyst is tested for quality in a pilot plant which is practically a miniature edition of an industrial catalytic plant. In this pilot plant catalyst activity can be examined as a function for the evaluation of newly developed catalysts and for studies and experiments in the research and development of new catalytic processes.

A particular feature of this pilot plant is its complete control and measurement equipment which parallels that of a large scale industrial oxidation unit. A process control computer, such as a pneumatic (fluidic) UNALOG computer, can be included for process optimization studies.

III. LIST OF EQUIPMENT
PLANT LIST

1. RAW MATERIALS STORAGE

1 wooden or steel rack and shelves for dry storage of plastic containers for principal chemicals
1 wooden platform for storage of carriers
1 scale, 50 kg

2. PREPARATION OF SILICA GEL

1 laboratory table with an acid proof plate
4 electric heaters (plates of 2,000 W each)
4 containers, stainless steel, 5 litres each
4 glass cylinders, graduated, 100 cc
2 water suction pumps
1 vacuum pump, complete with motor, trap, separator, connexion etc.
4 vacuum bottles
4 porcelain filters
4 Buchner funnels
1 filtering centrifuge, stainless steel, complete with motor
20 drying trays, stainless steel
1 pH meter
5 glass bottles, 5 litres, with bottom each
1 scale, 5 kg
1 drying cabinet, stainless steel, complete with heating
1 temperature control system
various accessories

3. PREPARATION OF THE COATING LIQUID

1 laboratory table with an acid [illegible]
1 precision weighing unit
20 plastic bottles for chemicals
100 small plastic [illegible]
6 [illegible]

2 Teflon bowls
2 drying cabinets made of polypropylene, with internal electric heating on a stainless steel support (3 electric heating plates of 2,000 W for each cabinet), with ventilating fan of PVC and an exhaust system for fumes
6 polypropylene containers for the concentrated liquid
1 temperature control system
various accessories

4. COATING OF THE CARRIER

2 rotating drums, of special design, made of stainless steel, complete with motor, variable speed gear, variable angle of inclination, with electric or gas or LPG heating, outside protection, fumes aspirator fan, ventilation fan, etc.
2 spare rotating drums (drums only)
8 special tools for coating, stainless steel
2 containers, stainless steel, 50 litres, with heating and agitator
1 temperature control system
1 small experimental rotating drum, 3–5 litres

5. DRYING OF THE FINISHED CATALYST

1 drying cabinet made of stainless steel, internally heated, complete with 36 trays, also made of stainless steel
1 exhaust system for fumes
1 temperature control system
various accessories

6. CLASSIFICATION AND PACKING

1 inspection table
1 Nylon or stainless steel mesh sieve
1 scale, 50 kg
plastic containers of polyethylene, 10 litres
sealing device
various accessories

7. FINISHED PRODUCTS STORES

1 wooden or steel rack and shelves for storage of the polyethylene containers containing 20 kg net weight of finished catalyst.

8. PILOT PLANT

Combined multipurpose pilot plant for catalyst testing and for the production of phthalic and maleic anhydride from various feedstocks.

a) Air supply

1 air compressor, [illegible] [illegible] and starter
1 air [illegible]
1 pressure reducing valve

1 oil filter/separator
1 purge valve
2 regulating valves
1 flow-meter for air
1 gas counter/meter for air
1 air container
2 manometers
4 valves
2 purge valves
1 special valve
1 security valve
1 air preheater
2 thermometers

b) Diathermic oil circuit

1 oil pump, complete with motor and starter
1 oil filter
1 oil container
1 manometer
1 thermometer
1 security valve
6 valves

c) Combined melting/heating vessel

1 complete melting/heating vessel of special design
1 filling device
1 purge valve
2 cleaning flanges
1 discharge valve
1 security valve
1 thermometer
1 manometer
1 inside tube
1 outer shell for diathermic oil
1 manometer
1 thermometer
1 security valve
3 heating coils
6 valves
3 electric heating resistances

d) Carburettor

1 carburettor of special design
1 injector of special design
1 heated flow-meter for naphthalene

e) Reactor

1 oxidation reactor of special design
1 molten salts circulator, complete with motor
1 set of electric heating resistances (or LPG or gas heating)
2 special valves
1 container for salts

f) Condensation system

1 four-tubes condensation system
1 sublimation chamber
1 Teflon condenser

1 gas counter/meter
1 exhaust column
4 special valves
1 additional switch-condenser
1 water wash system

g) Control equipment

1 control board, panel
2 automatic temperature regulators
1 temperature indicator and recorder, 12 colours
various telecommands, switches, control lights, alarm clock etc.

h) Dosage pump for liquid feedstocks

1 dosage pump, complete with motor and starter
1 filter
1 flow-meter
2 special valves
1 electronic pump speed regulator
1 container for liquid feedstock

i) Steel structures, piping and tubing

1 steel frame support for melting vessel and reactor
1 complete system of heated connexion piping for product line
1 complete system of piping for air circuit, partially heated
1 complete system of piping for diathermic oil circuit
2 heated flow-meters for product lines

j) Insulation

complete insulation of the plant

k) Electric connexions

all electric connexions for the plant's motors, resistances etc.
all electric wiring for 12 thermocouples, telecommands etc.
control board

l) Auxiliaries

Catalyst charge for the reactor
Eutectic salts for the molten salts cooling system
Diathermic oil for the oil circuit

m) Miscellaneous

1 apparatus to make distilled water
1 laboratory equipment
1 fire protection equipment
protective clothing, goggles, face masks, gloves etc, for operating personnel
1 small work-shop
1 small electric shop
1 first aid kit

IV. YEARLY PRODUCTION CAPACITY

The plant is capable of producing up to 200 kg of finished catalyst in 24 hours, or 60,000 kg in one year (300 days per year). With a minor additional investment the plant's production capacity can be doubled.

V. SPACE REQUIREMENTS

For the production of the catalyst an area of approximately 150 to 200 square meters is required. The layout of this production plant is shown in figure 5.

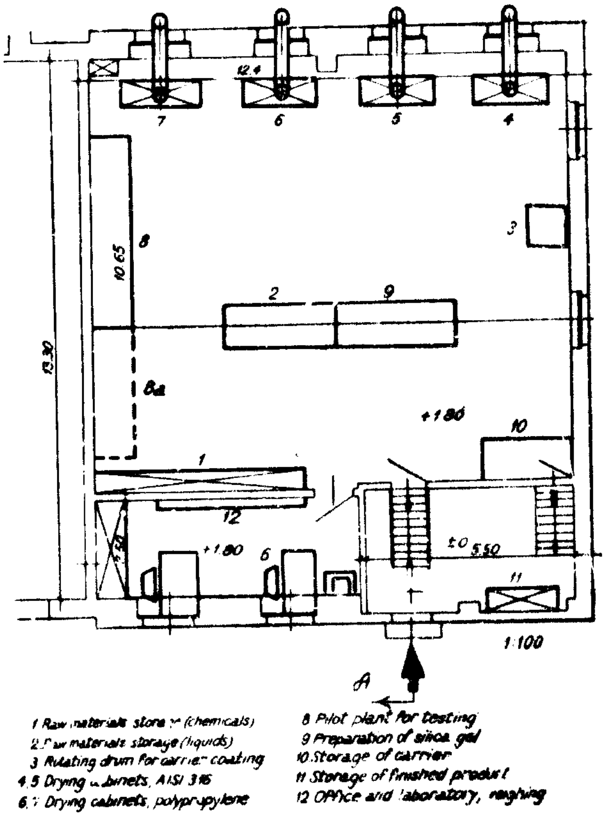


FIGURE 5. **LAYOUT OF A PRODUCTION PLANT FOR CATALYSTS**

VI. COST OF OPERATION

The plant needs an installed electric energy of 20 kW. This is sufficient to produce 200 kg of finished catalyst in 24 hours.

The manpower required are 2 specialized workers per each shift of 8 hours. A total of 8 specialized workers will be required, considering leaves, illness, etc.

For the running of the plant at pilot scale for catalyst testing, another crew of 4 workers is required (3×8 h shift+1 reserve).

Where it appears to be economical to use LPG or gas instead of electricity, the installed electrical energy can be reduced to 10 kW.

VII. CAPITAL INVESTMENT

The cost of the plant will vary from $ 45,000 to $ 50,000 according to the instrumentation chosen and the installation of a process computer.

Installation costs are $ 20,000 to $ 25,000. Therefore, the total capital investment for an operating plant of a daily production capacity of 200 kg of finished catalyst will be in the range of $ 65,000 to $ 75,000.

CATALYST SPECIFICATIONS (The Joklik-Catalyst)

Provided that the specified feedstock working conditions are used, the efficiency of the polyvalent catalyst will remain constant for at least five years.

Temperature of the gases at the entrance to the reactor: 135° to 155°C.

Reaction temperature, depending on the raw materials used:

naphthalene 78.5°C min.	460–530°C
o-xylene 97% min.	460–490°C
naphthalene/o-xylene mixture 20/80	460–495°C
naphthalene/o-xylene mixture 30/70	460–500°C
naphthalene/o-xylene mixture 40/60	460–505°C
naphthalene/o-xylene mixture 50/50	460–510°C
naphthalene/o-xylene mixture 60/40	460--515°C
naphthalene/o-xylene mixture 70/30	460–520°C
naphthalene/o-xylene mixture 80/20	460--525°C

Yield of technical grade phthalic anhydride (129.5°C min.) depending on the raw materials used:

naphthalene s.p. 78.5°C min.	96 %
o-xylene 97% min.	94 %
naphthalene/o-xylene mixture 80/20	95.75%
naphthalene/o-xylene mixture 70/30	95.50%
naphthalene/o-xylene mixture 60/40	95.25%
naphthalene/o-xylene mixture 50/50	95 %
naphthalene/o-xylene mixture 40/60	94.75%
naphthalene/o-xylene mixture 30/70	94.50%
naphthalene/o-xylene mixture 20/80	94.25%

Air/raw material ratio by weight, according to the raw materials used:

naphthalene s.p. 78.5°C	air 19--22/1	kg
o-xylene 97% min.	air 17–19/1	kg
naphthalene/o-xylene mixture 80/20	air 18.75–21.50/1	kg
naphthalene/o-xylene mixture 70/30	air 18.50–21/1	kg
naphthalene/o-xylene mixture 60/40	air 18.25–20.50/1	kg
naphthalene/o-xylene mixture 50/50	air 18--20/1	kg
naphthalene/o-xylene mixture 40/60	air 17.75–19.50/1	kg
naphthalene/o-xylene mixture 30/70	air 17.50–19/1	kg
naphthalene/o-xylene mixture 20/80	air 17.25–18.50/1	kg

Contact time 0.15—0.18 m/sec

Catalyst height in the contact tubes:

Zone A	450–550 mm
Zone B	400–500 mm

Potentiality (load) of the catalyst:

$$\frac{\text{gram raw material}}{\text{litres of catalyst}} = 300\text{–}350 \text{ g/lit. catalyst/h}$$

Specific weight of the catalyst: 1.85—1.95

SPECIFICATION OF A CONVENTIONAL COMMERCIAL PHTHALIC ANHYDRIDE CATALYST (UNITED STATES OF AMERICA)

CONVENTIONAL PELLETIZED OXIDATION CATALYST

PHYSICAL FORM

1/8"×1/8" pellets

CHEMICAL COMPOSITION

Vanadia	10%
Silica	65%
Potassium sulphate	23%

ACTIVITY

Catalyst pellets ground to 10 and to 20 mesh and activited for two hours at 800°F. placed in a test unit were run under the following conditions for the conversion of naphthalene to phthalic anhydride:

Jacket temperature	720°F
Primary air	120 cc./minimum
Secondary air	550 cc./minimum
Space velocity	1,400 V/V/hr
Air/naphthalene ratio	36 : 1/weight ratio
Volume of catalyst	33 cc. (poured volume)
Catalyst space in reactor	2×10 cm
Naphthalene used	Baker's C.P.

RESULTS

Yield phthalic anhydride	91 %
Carbon balance	95.2%
Hot spot temperature	851–966°F

POTENTIAL APPLICATIONS

OXIDATION OF:

- Naphthalene
- Benzene
- Micro-crystalline waxes
- Aliphatic side chains
- Furfural and related compounds
- Ortho-xylene
- Quinoline
- Toluene

PACKAGING

250 pounds per fibre drum – smaller lots on request.

SPECIFICATION OF A CONVENTIONAL COMMERCIAL PHTHALIC ANHYDRIDE CATALYST FOR FLUID TECHNIQUE

CONVENTIONAL POWDERED OXIDATION CATALYST

(For fluid technique)

PHYSICAL FORM

On	80 mesh	8.0% maximum
On	100 mesh	15.0% maximum
On	200 mesh	55.0% maximum
Through	200 mesh	45.0% minimum

CHEMICAL COMPOSITION

Vanadia	10%
Silica	55%
Potassium sulphate	33%

ACTIVITY

Catalyst pellets ground to 10 and to 20 mesh and activated for 2 hours at 800°F placed in a test unit were run under the following conditions for the conversion of naphthalene to phthalic anhydride:

Jacket temperature	720°F
Primary air	120 cc./minimum
Secondary air	550 cc./minimum
Space velocity	1,400 V/V/hr
Air/naphthalene ratio	36 : 1/weight ratio
Volume of catalyst	33 cc. (poured volume)
Catalyst space in reactor	2×10 cm
Naphthalene used	Baker's C.P.

RESULTS

Yield phthalic anhydride	95.1% based on naph. feed
Carbon balance	95.2%
Hot spot temperature	851–866°F

POTENTIAL APPLICATIONS

OXIDATION OF:

Naphthalene
Benzene
Micro-crystalline waxes
Aliphatic side chains
Furfural and related compounds
Ortho-xylene
Quinoline
Toluene

PACKAGING

300 pounds per fibre drum – smaller lots on request.

VIII. CONCLUSIONS

Catalyst production in a developing country already using catalytic processes is quite feasible and can be realized at a relatively small capital investment. This would enable the country to become independent of foreign catalyst supplies. Owing to strikes, political motives or for other reasons, foreign supply of catalyst might be interrupted or stopped, leading to serious economic losses, particularly when the product obtained by the catalytic process is partly exported.

Furthermore, a developing country can economize expenditures in hard currencies, by replacing the import of catalysts required by establishing the local manufacture of such catalysts.

The inclusion of a pilot plant in the catalyst production plant helps in the development of proprietary processes adapted to local requirements of production and raw materials. Thus new technologies can be developed and the technical standard of the developing country, gradually improved.

An example of such a development of new technology based on various raw materials is illustrated in figure 6, where the possibilities offered by a multipurpose pilot plant to make phthalic anhydride and maleic anhydride from various feedstocks are suggested.

Combined multipurpose gas-phase catalytic oxidation pilot plant using fixed bed polyvalent catalyst.

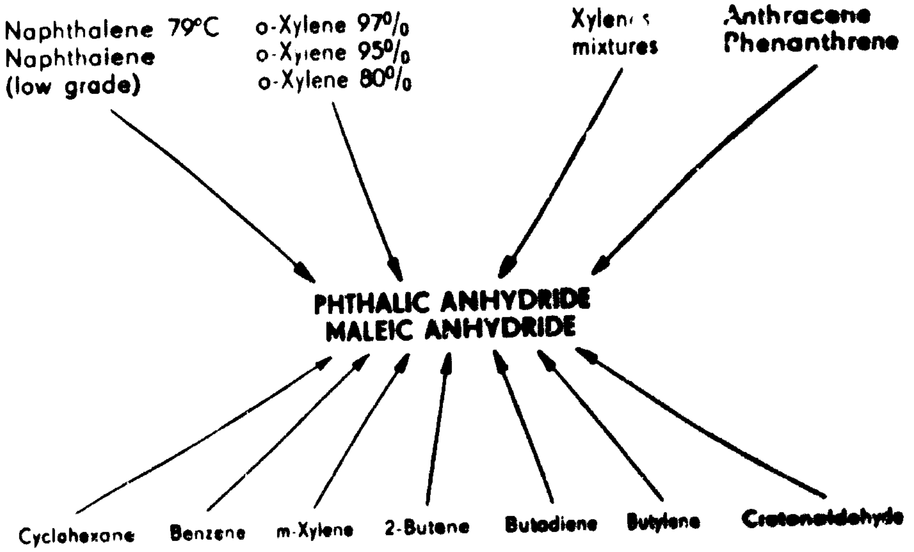


FIGURE 6

APPENDIX

The term catalyst, as it is used in this survey refers to the classic definition of a substance which changes the rate of a chemical reaction. On a commercial basis, catalysts only rarely consist of a single component. Promoters, activators and co-catalytic agents may be introduced into the catalyst system during preparation to enhance the performance of the major catalytic constituents. This basic catalyst formulation may then be distributed or dispersed on, or in some cases conformed with, a catalyst carrier. The catalyst carrier serves as a support for the active catalyst and can vary widely in its own intrinsic activity for the specific reaction being catalyzed.

Despite the relative inertness and normal lack of catalytic activity on the part of some carriers, particularly those with low surface areas, significant differences in product yield, selectivity, and product distribution have been achieved by changing the basic type of carrier employed in a given system. A catalyst carrier should provide the following properties to a catalyst system:

1. A suitable framework for deposition of the catalyst, often resulting in a greater total surface.
2. Optimum catalyst costs (as in the case of expensive catalyst materials such as noble metals).
3. An increase in resistance to sintering on the part of the catalyst.
4. An improved thermal conductivity to and from the catalyst surface and in the catalyst bed.
5. An increased resistance to poisoning.
6. A reduction in pressure drop in the reactor.
7. An improvement in mechanical strength of the system, resulting in lower abrasion losses and reduced possibility of plugging of catalyst tubes.

The industry offers a wide variety of materials, shapes, sizes, porosities, and structures to the catalyst chemist. Low surface area materials are available in fused alumina, silicon carbide, zirconia, zircon, silica, and fused mullite. Intermediate surface area materials are supplied in alumina.

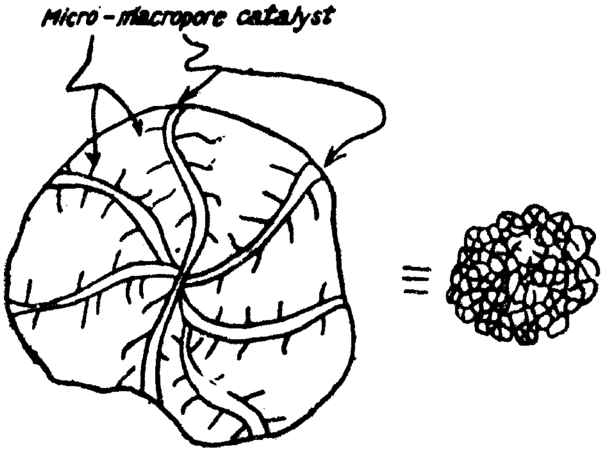


FIGURE 1. MICRO-MACROPOROUS CATALYST STRUCTURE

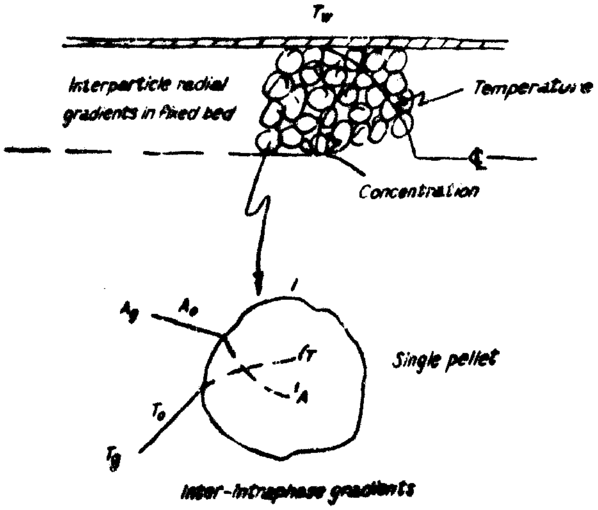


FIGURE 2. SCHEMATIC OF INTERPARTICLE GRADIENTS IN A FIXED BED AND INTER-INTRAPHASE GRADIENTS FOR A CATALYST PELLET

LOW SURFACE AREA CARRIERS

MATERIALS

Fused alpha alumina
Silicon carbide
Silica
Zircon
Mullite
Zirconia

PORE DIAMETER RANGE

2–70 microns

AVAILABLE SHAPES

Spheres, pellets, grooved pellets, rings, grooved rings

TABLE I

LOW SURFACE AREA CATALYST CARRIERS
Typical chemical analysis*

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZrO_2 + HfO_2	SiC
Aluminum oxide									
90.40	8.46	0.26	0.28	0.04	0.07	0.33	0.09	0.05	–
86.96	11.65	0.30	0.42	0.05	0.11	0.32	0.17	0.02	–
76.60	16.80	1.20	2.5	0.80	0.60	0.40	1.00	–	–
92.67	6.03	0.22	0.22	0.11	0.16	0.43	0.11	–	–
86.96	11.65	0.30	0.42	0.05	0.11	0.32	0.17	0.02	–
99.3	0.4	0.10	–	0.10	–	0.10	–	–	–
95.9	3.5	Tr.	Tr.	Tr.	Tr.	0.20	0.40	–	–

* All elements reported as metal oxides. Actual presence of the metals in the form of complex silicates and / or aluminates.

TABLE II

LOW SURFACE AREA CATALYST CARRIERS
Typical chemical analysis*

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZrO_2 + HfO_2	SiC
Silicon carbide									
4.73	28.48	0.34	Traces	0.24	0.06	0.23		–	65.8
Silica									
3.1	96.0	0.26	0.26	0.04	0.11	0.16	0.(	–	–
0.8	96.9	0.10	–	–	0.10	0.50	B_2O_3 1.6%		–
Zirconium silicate									
2.97	32.33	0.17	0.20	0.16	0.25	0.01	0.06	63.84	–
Mullite									
70.02	28.90	0.29	0.36	0.13	0.15	0.10	0.05	–	–
Zirconia									
0.38	1.57	0.16	0.25	3.50		–	–	94.14	–

* All elements reported as metal oxides. Actual presence of the metals in the form of complex silicates and / or aluminates.

TABLE III

LOW SURFACE AREA CATALYST CARRIERS

Physical properties

Apparent porosity, %	Water absorption, %	Bulk density, g/cc	Apparent specific gravity	Packing density, lbs/ft^3	Attrition loss, % 1 hr	Pore dia. range (microns), % volume	Surf. area, m^2/g
Aluminum oxide							
38 – 47	17 – 24	1.9 – 2.1	3.5 – 3.7	58 – 78	15 max.	90% 2 – 40	< 1
43 – 52	21 – 30	1.7 – 1.9	3.5 – 3.7	55 – 73	15 max.	90% 3 – 60	< 1
39 – 45	18 – 24	2.0 – 2.3	3.5 – 3.7	75 – 80	10 max.	90% 3 – 30	< 1
42 – 48	20 – 26	1.7 – 1.9	3.5 – 3.7	64 – 71	15 max.	90% 3 – 60	< 1
39 – 44	16 – 22	1.7 – 1.9	3.5 – 3.7	72 – 78	10 max.	90% 3 – 30	< 1
36 – 42	15 – 20	2.0 – 2.2	3.4 – 3.6	63 – 83	10 max.	80% 2 – 30	< 1
40 – 46	19 – 24	1.8 – 2.0	3.2 – 3.4	71 – 75	15 max.	90% 2 – 40	< 1
35 – 40	15 – 19	2.1 – 2.3	3.4 – 3.7	72 – 80	12 max.	85% 2 – 40	< 1
40 – 45	19 – 23	1.9 – 2.1	3.4 – 3.6	69 – 74	15 max.	90% 2 – 60	< 1
36 – 44	15 – 21	2.0 – 2.4	3.5 – 3.8	77 – 84	10 max.	85% 2 – 40	< 1
32 – 40	12 – 18	1.9 – 2.1	3.3 – 3.5	71 – 83	15 max.	80% 2 – 30	< 1
31 – 36	12 – 16	2.0 – 2.2	3.3 – 3.5	78 – 84	5 max.	80% 2 – 30	< 1
6 – 14	1 – 5	3.0 – 3.2	3.5 – 3.7	110 – 120	1 max.	95% 1 – 3	< 1
48 – 54	25 – 31	2.0 – 2.4	3.5 – 3.8	58 – 65	15 max.	95% 4 – 70	< 1
48 – 54	25 – 31	1.7 – 2.0	3.5 – 3.8	58 – 65	15 max.	95% 4 – 70	< 1
40 – 44	16 – 20	2.2 – 2.4	3.9 – 4.0	85 – 89	12 max.	95% 1 – 20	< 1
30 – 34	10 – 14	2.6 – 2.8	3.9 – 4.0	97 – 102	5 max.	95% 1 – 10	< 1

MACROPORE CATALYST CARRIERS
LOW SURFACE AREA

MATERIALS

Fused alpha alumina
Silicon carbide
Zircon
Mullite

TABLE IV

LOW SURFACE AREA CATALYST CARRIERS
Physical properties

Apparent porosity, %	Water absorption, %	Bulk density, g/cc	Apparent specific gravity	Packing density, lbs/ft³	Attrition loss, % 1 hr.	Pore dia. range (microns), % volume	Surf. area, m²/g
Silicon carbide							
39 – 43	22 – 25	1.6 – 1.8	2.8 – 3.0	60 – 64	10 max.	95% 10 – 40	< 1
42 – 48	26 – 30	1.5 – 1.8	2.8 – 3.0	54 – 62	10 max.	95% 10 – 40	< 1
Silica							
35 – 39	22 – 26	1.3 – 1.5	2.3 – 2.4	59 – 63	5 max.	90% 1 – 5	< 1
32 – 38	19 – 25	1.5 – 1.7	2.3 – 2.4	55 – 59	6 max.	90% 1 – 5	< 1
48 – 52	44 – 48	1.0 – 1.2	2.1 – 2.3	42 – 46	–	–	< 1
Zirconium silicate							
3 – 8	1 – 3	3.8 – 4.0	4.1 – 4.3	141 – 147	2 max.	85% 2 – 10	< 1
24 – 32	7 – 12	3.0 – 3.4	4.4 – 4.6	112 – 121	5 max.	–	< 1
Mullite							
34 – 40	16 – 22	1.9 – 2.1	3.1 – 3.3	67 – 73	5 max.	–	< 1
34 – 40	16 – 22	1.9 – 2.1	3.1 – 3.3	64 – 70	5 max.	–	< 1
Zirconia							
42 – 47	12 – 16	3.0 – 3.3	5.5 – 5.8	103 – 110	22 max.	–	< 1

TABLE V

LOW SURFACE AREA „MACROPORT" CATALYST CARRIERS
Typical chemical analysis*

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZrO_2 + HfO_2	SiC
Aluminum oxide									
84.7	13.4	0.20	0.30	0.02	0.04	0.60	0.70	–	–
83.0	14.0	0.40	0.30	0.50	0.50	0.60	0.70	–	–
85.5	12.4	0.20	0.10	0.60	0.40	0.30	0.50	–	–
Silicon carbide									
2.6	6.5	0.20	0.10	0.10	0.10	0.10	0.20	–	90.0
Zirconium silicate									
4.8	39.9	0.3	0.5	0.1	–	0.2	0.8	53.4	–
Mullite									
69.91	28.38	0.21	0.17	0.59	0.39	0.14	0.21	-	–

* All elements reported as metal oxides. Actual presence of the metals in the form of complex silicates and / or aluminates.

PORE DIAMETER RANGE

20–1,500 microns

AVAILABLE SHAPES

Spheres, pellets, rings, aggregate

TABLE VI

LOW SURFACE AREA CATALYST CARRIERS
Physical properties

Apparent porosity, %	Water absorption, %	Bulk density, g/cc	Apparent specific gravity	Packing density, lbs/ft³	Attrition loss, % 1 hr	Pore dia. range (microns), % volume	Surf. area, m²/g
Aluminum oxide							
53—59	33—39	1.5—1.7	3.3—3.6	53—59	6 max.	95% 100—1,500	< 1
55—61	37—43	1.4—1.6	3.3—3.6	50—56	8 max.	95% 100—1,500	< 1
55—61	37—43	1.4—1.6	3.3—3.6	44—48	10 max.	100% 100—1,500	< 1
43—47	20—24	1.8—2.0	3.5—3.8	63—67	15 max.	100% 20—180	< 1
36—42	15—21	2.0—2.4	3.4—3.8	66—74	10 max.	100% 20—180	< 1
Silicon carbide							
43—48	24—30	1.6—1.8	3.0—3.2	53—57	15 max.	100% 3—100	< 1
Zirconium silicate							
44—48	19—23	2.0—2.3	3.9—4.1	63—67	5 max.	—	< 1
Mullite							
41—45	23—27	1.9—2.1	3.1—3.3	55—59	6 max.	—	< 1
41—45	23—27	1.6—1.9	3.0—3.2	55—59	6 max.	—	< 1

INTERMEDIATE SURFACE AREA CARRIERS

MATERIALS

Sintered alumina (bonded)

AVAILABLE SHAPES

Spheres, pellets, rings

→

75. II. 20

3 OF 4

06639

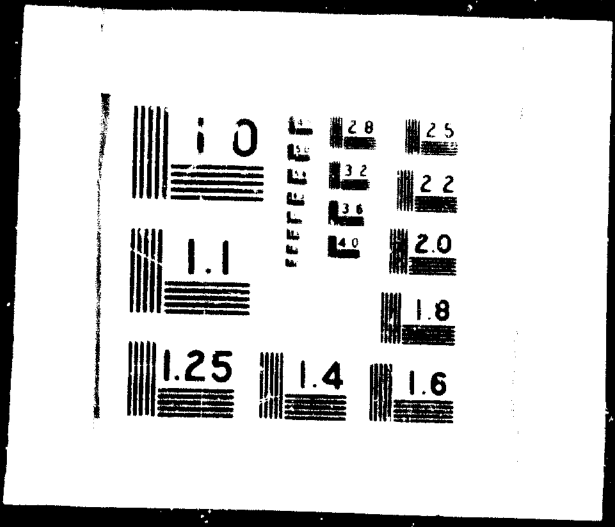


TABLE VII

INTERMEDIATE SURFACE AREA CATALYST CARRIERS
Physical properties

Apparent porosity, %	Water absorption, %	Bulk density, g/cc	Apparent specific gravity	Packing density, lbs/ft³	Attrition loss, % 1 hr	Pore dia. range (microns), % volume	Surf. area, m²/g
Aluminum oxide							
62 – 66	53 – 57	1.1 – 1.3	3.1 – 3.3	42 – 46	—	—	10 – 20
62 – 66	52 – 56	1.1 – 1.3	3.2 – 3.4	40 – 44	—	—	10 – 20
62 – 66	54 – 58	1.1 – 1.3	3.1 – 3.3	40 – 44	—	—	35 – 45
62 – 66	55 – 59	1.1 – 1.3	3.1 – 3.3	37 – 44	—	—	35 45

TABLE VIII

INTERMEDIATE SURFACE AREA CATALYST CARRIERS
Typical chemical analysis*

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	ZrO_2 + HfO_2	SiC
Aluminum oxide									
83.0	15.3	0.44	0.50	0.09	0.07	0.34	0.16	—	—

* All elements reported as metal oxides. Actual presence of the metals in the form of complex silicates and / or aluminates.

CRYSTALLINE MATERIALS

Crystalline materials are produced in high temperature electric furnaces and further processed to meet demands of industry for purity, density, shape and size. These high temperature crystalline materials are available in granular and powdered form.

REGULAR FUSED ALUMINA: Al_2O_3

HOW PRODUCED

Regular fused alumina is a dark brown grain, produced by fusing a mixture of calcined bauxite, coke, and iron filings in the Higgins electric arc furnace at a temperature above 3,630°F (2,000°C). During the process, purification and crystallization of the grain takes place.

PROPERTIES

TYPICAL CHEMICAL ANALYSIS

Al_2O_3 – 94.47% (by diff.)
SiO_2 – 1.70
Fe_2O_3 – 0.20
TiO_2 – 3.10
ZrO_2 – 0.15
CaC – 0.08
MnO – 0.10
MgO – 0.20

CHARACTERISTICS

Crystal form	Alpha alumina
Max. usable temperature	About 3,450°F (1,900°C)
Chemical nature	Amphoteric
Reaction with acids	Subject to mild attack by aqua regia and or hydrofluoric acid
Reaction with alkalies	Very slight with strong hot solutions only
Oxidation-reduction effects	None
True specific gravity	3.95
Packing density	110–128 lbs. cu. ft. depending on grain size and shape
Hardness (Knoop)	2,000
(Mohs)	9.0
Electrical resistivity	10^{16} at 80°F (30°C) 10^{5} at 1,650°F (900°C)

GRAIN SHAPES

Two shapes are available, strong and intermediate. These grain shapes are determined by the degree of crushing and milling.

Strong shape – a strong, blocky-shaped grain.

Intermediate shape – a wedge-shaped grain intermediate between a stronger blocky shape and a weaker slivery shape.

GRAIN SIZES

Crude	Lumps 1-½" and finer.
Grit sizes	In either strong or intermediate shape.

Coarse to fine

4
6
8
10
12
14
16
20
24
30
36
46
54
60
70
80
90
100
120
150
180
220

WHITE FUSED ALUMINA: Al_2O_3

There are many applications that demand high purity white grain. White in colour, it is somewhat more refractory than regular fused alumina.

HOW PRODUCED

This white grain is electrically fused from Bayer process alumina. Although considerably purer, its physical properties are comparable to regular grain.

PROPERTIES

TYPICAL CHEMICAL ANALYSIS

Al_2O_3 – 99.28% (by diff.)
SiO_2 – 0.05
Fe_2O_3 – 0.15
TiO_2 – 0.02
Na_2O – 0.50

CHARACTERISTICS

Crystal form	Alpha alumina
Maximum usable temperature	3,630°F (2,000°C)
Chemical nature	Amphoteric
Reaction with acids	Less attack than regular grain
Reaction with alkalies	Very slight with strong hot solutions
Oxidation reduction effects	None
True specific gravity	3.97
Packing density	Approx. 107–119 lbs./cu. ft. depending on grain size
Hardness (Knoop)	2,000
(Mohs)	9.0
Electrical resistivity	10^{16} at 80°F (30°C) 10^5 at 1,650°F (900°C)

GRAIN SHAPE

A wedge-shaped grain intermediate between a strong or blocky shape and a weak shape.

GRAIN SIZES

Crude	Lumps 1-½" and finer.
Grit sizes	

Coarse		to		fine
6	16		70	120
8	20	46	80	150
10	24	54		
12	30	60	90	180
14	36		100	220

FUSED MULLITE: $3Al_2O_3$ $2SiO_3$

PROPERTIES

Refractory products using mullite grain have good high temperature strength and thermal shock resistance. The following table presents a typical chemical analysis and other technical data.

HOW PRODUCED

Mullite grain is an aluminium silicate ($3\,Al_2O_3 \cdot 2\,SiO_2$) fused in an electric furnace to insure complete reaction of the raw materials. An excess of alumina is used in the fusion, causing the resultant composition to be on the high alumina side of theoretical mullite (i. e. – 72% Al_2O_3). Petrographic examination reveals about 2 per cent free alumina and 1 per cent glass. These factors enable mullite grain to remain in the crystalline form (i. e. – no liquids are formed) up to the eutectic melting point 3,340°F (1,840°C) between mullite and alumina.

TYPICAL CHEMICAL ANALYSIS

Al_2O_3 – 75.10% (by diff.)
SiO_2 – 24.35
Fe_2O_3 – 0.12
TiO_2 – 0.03
Na_2O – 0.35
C – 0.05

CHARACTERISTICS

Crystal form	Orthorhombic (excess alumina – present as corundum)
Melting point	Congruently at 3,340° F (1,840°C)
Chemical nature	Slightly acid
Reaction with acids	Insoluble in most acids
Alkalies and general	Attacked by molten alkalies and many basic slags
Maximum usable temperature	3,340°F (1,840°C)
True specific gravity	3.23
Packing density	85 to 103 lbs./ft.^{3} depending on grain size
Hardness (Knoop)	820
(Mohs)	7

PRESSURE DROP

A study has been completed on pressure drop data for air flowing through packed beds of catalyst carriers. In this study all products tested were in dense packed beds 4" in diameter and 2′ length. All materials were loose filled and the outer columns were pounded with a hammer until no more settling was observed. Additional make-up was added to top off the bed and the pounding repeated. Thus, all materials were tested at maximum packing density and minimum bed voidage for the imposed particle to tube geometry.

Following is a tabulation on pressure drop data for spheres, pellets, rings, grooved rings and aggregate.

TESTS

Porosity	
H_2O absorption	
Specific gravity	**ASTM C20–46 (except boiling time changed to 30 minutes)**
Bulk density	
Packing density	
Attrition loss	
Separate section for fluid	
Pore diameter	
Surface area	
Pressure drop	

TABLE IX

CATALYST CARRIERS PRESSURE DROP

P L (inches of HOH per foot of packed depth)

Spheres	Gas mass velocity (Air) lb-Hr-ft^2									
	100	200	300	400	500	600	700	800	900	1 000
1/8	0.31	0.84	1.6	2.4	3.5	4.7	6.1	7.4	9.2	11.0
3/16	0.17	0.46	0.88	1.4	2.0	2.8	3.6	4.4	5.5	6.7
1/4	0.097	0.27	0.54	0.84	1.3	1.7	2.2	2.7	3.4	4.1
5/16	0.075	0.22	0.43	0.68	0.99	1.4	1.9	2.3	2.9	3.5
3/8	0.059	0.19	0.38	0.61	0.90	1.3	1.7	2.1	2.6	3.1
1/2	0.042	0.13	0.25	0.40	0.59	0.62	1.1	1.4	1.8	2.1
1	0.011	0.036	0.075	0.13	0.19	0.27	0.35	0.44	0.55	0.68
Pellets										
1/8 × 1/8	0.39	1.0	1.9	2.9	4.2	5.6	7.4	9.1	11.0	14.0
3/16 × 3/16	0.21	0.59	1.13	1.79	2.6	3.4	4.5	5.5	6.9	8.3
1/4 × 1/4	0.15	0.46	0.82	1.3	1.9	2.6	3.4	4.2	5.2	6.5
3/8 × 3/8	0.088	0.26	0.51	0.81	1.2	1.7	2.2	2.7	3.4	4.1
Grooved pellets										
5/32 × 5/32	0.19	0.53	0.99	1.6	2.3	3.1	4.0	5.0	6.2	7.6
7/32 × 7/32	0.12	0.33	0.63	1.0	1.5	2.0	2.6	3.2	4.0	4.8
Rings										
1/8 × 5/16 × 5/16	0.089	0.26	0.49	0.78	1.2	1.6	2.1	2.7	3.4	4.2
3/16 × 3/8 × 7/16	0.052	0.16	0.31	0.51	0.78	1.1	1.5	1.9	2.4	3.0
1/4 × 1/2 × 1/2	0.040	0.12	0.24	0.39	0.59	0.84	1.1	1.4	1.8	2.2
Grooved rings										
1/8 × 5/16 × 5/16	0.069	0.16	0.32	0.52	0.78	1.1	1.4	1.8	2.3	2.8
Aggregate										
3 – 5 Mesh	0.10	0.28	0.51	0.83	1.2	1.7	2.3	2.7	3.4	4.1

Note: All materials were tested at maximum packing density and minimum bed voidage for the imposed particle to tube geometry.

Gas temperature 77°F	Bed diameter 4.03"
Gas pressure 14.7psia	Bed height 2'

Procedure for determination of apparent porosity, water absorption, apparent specific gravity and solid bulk density

METHOD

ASTM C20 – 46 except boiling time 1/2 hour

EQUIPMENT

1. Rectangular stainless steel wire mesh basket (2½"×2½"×1" deep with wire handle) for holding sample.
2. Balance weighing to nearest 0.1 gram.
3. Deep porcelain dish.
4. Damp cloth.
5. Small aluminium or plastic container.

TEST PROCEDURE

1. Weigh dry wire mesh basket in air to nearest 0.1 gram.
2. Place about 80–100 grams of dry carriers in basket and reweigh in air.

   Note: This weight suggested for 1/2" size and smaller, weight per cubic foot 40 to 80 pounds. For sizes larger: than 1/2" or dense materials, sample weight 250 grams.

3. Subtract # 1 from # 2. This is dry weight of carriers in air. Call this weight "D".
4. Fill porcelain dish with water and heat to boiling
5. Immerse wire basket containing carriers in the boiling water. Boil gently for 30 minutes.

   Note: Keep carriers covered with water at all times during boiling. Do not let basket rest on bottom of porcelain dish.

6. Remove porcelain dish from heat, place under cold water faucet and run in cold water until mass has cooled to room temperature.
7. Remove wire mesh basket containing carriers from cold water and weigh entire mass suspended in water at room temperature.
8. Weigh dry aluminium or plastic container in air.
9. Soak a piece of cloth towel in water and wring out thoroughly by hand
10. Transfer sample from basket to damp cloth towel and blot lightly to remove all drops of surface water.
11. Transfer sample to weighed aluminium or plastic container and weigh entire mass in air.
12. Subtract weight # 8 from weight # 11 to get weight of saturated carriers. Call this weight "W".
13. Weigh wire mesh basket submerged in water.
14. Subtract weight # 13 from weight # 7 to get suspended weight of carriers. Call this weight "S".

CALCULATIONS

Exterior volume V

This volume V, in cubic cm. of the carriers is obtained by subtracting the suspended weight from saturated weight.

$$V = W - S$$

Apparent porosity "P"

The apparent porosity expresses as a percentage the relationship of the volume of the open pores of the carriers to its exterior volume and is calculated as follows:

$$P = \frac{W - D}{V} \times 100$$

Water absorption "A"

The water absorption expresses as a percentage the relationship of the weight of water absorbed to the weight of dry carriers. Calculated as follows:

$$A = \frac{W - D}{D} \times 100$$

Apparent specific gravity "T"

The apparent specific gravity is that portion which is impervious to boiling water. Calculated as follows:

$$T = \frac{D}{D-S}$$

Bulk density "B"

The bulk density in grams per cubic cm. is the quotient of its dry weight divided by its exterior volume including pores. It is calculated as follows:

$$B = \frac{D}{V}$$

PROCEDURE FOR DETERMINATION OF PACKING DENSITY (VOLUMETRIC BULK DENSITY)

A. EQUIPMENT

1. Metal cone
   - (a) 90° angle at vertex
   - (b) 12-3/4″ diameter at top
   - (c) 1-1/2″ diameter hole at bottom
   - (d) 1″ height from bottom of cone to top of weighing cylinder facilitated by three legs on outer surface of cone.
2. Metal base plate (10×10×1″ thick)
3. Standard 1/8 cubic foot grain density com
   - (a) Dimensions
     - 3-7/8″ I. D. at bottom
     - 3-7/8″ I. D. at top
     - 17-15/32″ inside height
   - (b) A multiplication factor should be applied to the results – as the grain density com is slightly under 1/8 cubic foot.

Note: This factor must be obtained for each container.

B. TEST PROCEDURE

1. Weigh out 3–5 pounds of carriers. This weight dependent on density of material to be tested.

   Note: Amount to weigh out should fill container half full.

2. Place grain density cam on 10×10×1″ thick steel plate. Steel plate must be placed on solid rigid surface. A concrete floor is advisable.
3. Place metal cone on grain density cam.
4. With one hand under 1–1/2″ cone opening pour the sample to be tested into cone.
5. Release hand under cone opening allowing constant flow of carriers through 1–1/2″ cone opening into cylinder.
6. (a) Raise container 1/2″ until it touches a bar clamped to a laboratory clamp stand.
   - (b) Allow to fall freely onto the steel plate.
   - (c) Repeat to a total of 10 drops.

7. Repeat steps 1 through 5.
8. Level overflowing cylinder with metal straight edge.
9. Repeat step # 6.
10. Add additional carriers to fill grain density cam to overflow.
11. Level overflowing cylinder with metal straight edge.
12. Weigh contents of grain density cam and convert to weight per cubic foot using proper factor for cylinder.

PROCEDURE FOR DETERMINATION OF ABRASION RESISTANCE

This test is designed to measure how well catalyst carriers will resist abrasion. The abrasion loss is determined in terms of material finer than 10 mesh (0.07″±0.1″ screen openings ten per inch) which is removed from the carriers by tumbling under controlled conditions.

A. EQUIPMENT

1. Fibre drum with lid (Continental Can Company No T-158-2 X) having the following dimensions.

Outside diameter	8–5/16″
Inside diameter	8″
Inside length	7″

The inside surface of the bottom of the drum, and the lid shall be covered by discs of smooth wear resistant rubber 1/64″ thick, cemented to the respective surfaces by rubber cement (Goodyear Pliobond).

After attaching the rubber disc to the inside of the bottom of the drum, the entire inside wall of the container shall be covered by one piece of ribbed rubber cemented to the walls by rubber cement. This rubber shall be attached so that the ribs are parallel to the length of the drum.

2. Laboratory ball mill rollers capable of rotating corrugated rubber lined drum charged with sample at 60±1 rpm.
3. A 10 mesh wire screen (0.07″±01″ screen openings 10 per inch).
4. Scales capable of weighing up to at least 10 pounds to two decimal places.

B. TEST PROCEDURE

1. Weigh out sample of screened material and place this weighed sample in container.

   Note: Sample weight depends on size, shape and density. Sample weight generally 5 pounds however, for „Macroport" series sample weight is 3–1/2 pounds.

2. Place lid on container and seal lid joint with 2″ wide rubber band.
3. Place container and contents on rollers and rotate for 15 minutes at 60 rpm.
4. After 15 minutes remove the container and empty all contents onto the 10 mesh wire screen.
5. Shake screen by hand to remove all fines.
6. Weigh material remaining on screen.
7. Calculate percent loss for a total of 15 minutes.
8. Replace pellets in corrugated rubber lined drum.
9. Repeat steps 2, 3, 4, 5 and 6.
10. Calculate percent cumulative loss for a total of 30 minutes.
11. Repeat step 8.
12. Repeat step 2.

13. Replace container on rollers and rotate for a 30 minutes at 60 rpm.
14. Empty all the contents onto the 10 mesh wire screen.
15. Repeat steps 5 and 6.
16. Calculate percent cumulative loss for a total of 60 minutes.

PRESSURE DROP

EXPERIMENTAL TEST METHOD

All materials were loose filled in a 4.02 I.D. tube 2' in length. The outer walls were pounded with a hammer until no more settling was observed. Additional make-up was added to top off the bed and the pounding repeated. Thus, all materials were tested at maximum packing density and minimum bed voidage for the imposed particle to tube geometry.

Pressure taps were installed in the column just above and below the bed. The pressure differential was observed by sighting through a cathetometer, a water filled manometer. The empty tower provided a negligible pressure drop of less than 0.01 inches HOH at a G equalling 1 000 pound air per hour per foot squared. Use of the cathetometer allowed detection of a pressure drop of less than 0.04 inches HOH with excellent accuracy and reproductibility.

Pressure regulated plant compressed air was fed to two needle valves in parallel. These needle valves acted as critical flow orifices above a 25 psig supply pressure at the maximum back pressure created by the air line, column, bed and gas meter. The open area of each needle valve was set at positions which would provide coverage of the flow regime desired. Both needle valves were calibrated individually and together to provide a straight line plot of superficial mass velocity as inlet pressure to the needle valve. Air was directed down flow through the bed. Air flow was measured using a standard 60 light gas meter.

All data were obtained by measuring the pressure differential over the bed data minimum of 15 values of superficial mass velocity. A disproportionately greater number of points were obtained at low superficial mass velocities for large particle sizes to average out any errors in reading the manometer at small pressure differentials.

LITERATURE AND PATENTS

Arnold, US Pat. 2 439 880, 1948
Aussiger Verein, DRP 778 192
Barrett Co., US Pat. 1 667 197, 1920
Bailey M. P., US Pat. 2 510 852 (Allied Chemical & Dye Corp.), 1950
BASF, DRP 55 588
Beach L. K. Conolly G.C., US Pat. 2 471 853 (Standard Oil Development Co.), 1949
Beilstein, 4. Ausg., IX, 791; X_1, 1 349; X_2, 580; XVI, 469; VII_1, 251; $XVII_2$, 463
BIOS Final Report 1124, Item 22

BIOS Final Report 1482, Item 22
BIOS Final Report 1598, Item 22
BIOS 1007
Bone, J. Soc. Chem. Ind. 53, 963, 1934
Bone, Trans. Chem. Soc. 61, 871; 71, 26, 46; 78, 1042; 81, 535, 693, 1637; 87, 910, 1232, 89, 652, 660, 939, 1614; 93, 1198
Bone, J. Chem. Soc. 85, 1074
Bone et al., Trans. Roy. Soc. (London). 215 A, 288–308, 1915
Bone, Nature, 122, 203–204, 1928
Bureau A. C., The production of phthalic anhydride from naphthalene, Gas Journal. Oct. 12, 78–84, 1960
Burwell, Ind. Eng. Chem. 26, 204–207, 1934
Burrows & Fuller, US Pat. 2 455 405, 1948
Canon & Andrews, US Pat. 1 614 185 (The Selden Company) 1927, reissue US Pat. 16 824, 1927
Cavanough, US Pat. 2 291 211, 1942; US Pat. 2 343 534, 1944
Chem. Zentralblatt, 11, 1484, 1937
Chem. Inds., 68–69, July, 1946
Chem. Met. Eng., 53, 116, 1946
Chem. Eng. 53, 125, 1946; 54, 123–131, 1947
Chem & Eng. News, Dec. 8, 1952
Clark, Brit. Pat. 41 229; BIOS Final Report 591
Commercial Solvent Co., DRP 509 937, 1925
Craver, US Pat. 1 489 741 (The Barrett Co.), 1924
Crooks D. A., J. Chem. Soc. (London), 899, 1946
Crooks & Feetham, Journal of the Chemical Society, Part II, The Chemical Society, London 1946
Doumani Coe & Attane, US Pat. 2 459 690, 1949; US Pat. 1 274 020, 1921; US Pat. 1 374 021; US Pat. 1 604 739, 1926
Downs C. R., Catalytic Oxidation of Organic Compounds in the Vapour Phase, J. Soc. Chem. Ind. 46, 18 T/193 T, 1926; Ind. Chem. Eng. 32, 1294/98, 1940
Downs C. R., US Pat. 2 441 873, 1948
Downs & Rushton, Chem. Eng. Process, 1, 12, 1947
Driwear Inc., US Pat. 2 253 192, 1942
Drossbach, US Pat. 2 285 914, 1942
Drugman & Done, J. Chem. Soc. 89, 660–671, 1906
DuPont de Nemours, US Pat. 2 742 505, 1924; US Pat. 2 097 435, 1935
Van Dyke, Chem. Eng. Progress, 44, 20, 38, 42, 1948
Faith, Keyes, Clark, Industrial Chemicals, John Wiley Sons, NY, 1952
FIAT Final Report 649
Fierz-David, Grundlegende Operationen der Farbenchemie, 2, Ausg., S. 153, 1922
Fisher, Goldblatt, Kniel & Snyder, Ind. Eng. Chem. 43, 671, 1951
Fleming, US Pat. 2 452 741, 1948
Ellis Foster Co., US Pat. 2 289 737, 1940
Franklin N. L. et al., Trans. Instn. Chem. Eng. 34, 282, 1956
Frolich, Harrington & Waitt, J. Am. Chem. Soc., 50, 3216, 1938
Frolich & Forrest, US Pat. 1 902 550, 1933; US Pat. 1 936 427, 1918
Gardner N. A., US Pat. 2 155 539, 1929
Gibbs & Conover, US Pat. 1 284 888, 1918; US Pat. 1 285 117, 1918
Goodyear Tire & Rubber Co., Österr. Pat. 12 781, 1933
Hale & Haldeman, Chem. Age 23, 272–276, 1930
Hale & Haldeman, Brit. Pat. 287 064, 1927; Franz. Pat. 650 771, 1928

Hamblet & McAlevy, US Pat 2 439 513 1948

Hathaway N. E., Myrick A. D., German Phthalic Anhydride Catalyst, Chem. Ind. 64, 581–583, 1949

Henkel & Cie. DRP 724 037, 1942

Honyon & Heyl. US Pat. 2 298 387, 1942

Horman, US Pat. 2 382 148, 1945

Hougen-Watson, Chemical Process Principles, John Wiley Sons, NY

Hock & Lang, Ber. 768, 1130–1131, 1943; 778 257–264, 1944

Hock & Lang, Ind. Eng. Chem. 43, 2880, 1951

IG Farben, DRP 512 230; DRP 442 901

Ioklik O. F., Verfahren und Vorrichtung zur Herstellung von Phthalsäureanhydrid, Österr. Pat. 258 892, 1967

Joklik O. F., Herstellung von Phthalsäureanhydrid, Monographie, Karlsruhe 1957

Joklik O. F. Herstellung von Phthalsäureanhydrid, Prakt. Chem. Wien, 11. Jg., 284–290, 442–457, 522–532, 1960

Ioklik O. F., Strahlenchemische Oxydation von Naphtholin zu Phthalsäureanhydrid, in NOIE L'ATOMO, Biblioteca di Studi e Notize sugli idrocarburi, 1961

Ioklik O. F., Pneumatische Logik-Systeme in der Regelung einer Phthalsäureanhydridanlage, 38. Internat. Kongress Ind. Chem., Istanbul, 1969

Koohiman, US Pat. 2 461 988, 1949

Koschitz Parai, Russ. Pat. 33 148, 1933

Krauch. Proc. 2nd. Intern. Bituminous Conf., I, 43. 1928

Kuchenbuch J., Reichhold Chem. Mitteilung

Lange, Handbook of Chemistry & Physiks, 8th E.

Lacombe, US Pat. 2 376 257, 1945

Lee. Chem. Met. Eng., 52, No. 7, 100–101, 1945

Leibnitz F. et al., J. prakt. Chem., 4, 4, 298, 1957

Lescure de H., Les acides phtaliques, leur préparation, leur dérivés, Chim. et Ind. 77, 1292–1306, 1957

Levine I. E. US Pat. 2 474 001; US Pat. 2 474 002, 1949; US Pat. 2 521 466, 1950, California Research Corp

Levine I. E., Phthalic Anhydride Manufacture from Orthoxylene, Chem. Eng. Progress 43, 168–171, 1943

Levine I. E., Oxidation of Ortho-Xylene to Phthalic Anhydride, Chem. Petr. Hydrocarbons, 3, 1–7, 1955

Lobo, Chem. Eng. Progress, 1, 21, 1947

Longwell J. P., US Pat. 2 491 500 (Standard Oil Development Co.), 1949

Loder, US Pat. 2 223 493, 1940; Amend. US Pat. 2 316 543, 1943

Mardles, Trans. Faraday Soc., 27, 681, 1931

Marek L. F. & Hahn D. A., The Catalytic Oxidation of Organic Compounds in the Vapour Phase, Amer. Chem. Soc. Monograph Series, 401–433, NY, 1932

Marek L. F. & Hahn D. A., Catalytic Oxidation of Organic Compounds, 305–311, Reinhold Publishing Co., NY, 1932

Marek L. F., in Groggins P. H., Unit Processes in Organic Synthesis, 4th ed., McGraw Hill, NY, 459–474, 1952

Maxted, J. Soc. Chem. Ind., 47, 101–105 T, 1928

Modern Plastics, Oct., 86–87, 1951

Monnet, Chem. Ztg., 22, 929, 1898; 23, 872, 1899

Monnet, Franz, Pat. 276 258

Monsanto Chemical Co., US Pat. 2 234 959; US Pat. 1 948 281, 1934

Moyer & Klingelhoefer, US Pat. 2 223 383, 1940

Meier, US Pat. 2 300 955, 1942

Natta, US Pat. 2 308 229, 1943

Newitt & Haffner, Proc. Roy. Soc. (London), A 134, 591–604, 1932

North American Rayon Corp., US Pat. 2 0[illegible] 74[illegible]

Parks & Story, Oil Gas J., 39, 54, 56, 58, 61, 1940

Parks G. S. et al., J. Chem. Phys., 18, 152, 1950

Parks G. S. et al., J. Am. Chem. Soc., 58, 398, 1936

Parks & Yula, US Pat. 2 289 036, 1946

Pease & Taylor, J. Am. Chem. Soc., 43, 2279, 1921; 44, 1637, 1922

Petrolite Co. Ltd. US Pat. 2 192 993, 1940

Pietzsch K. F., US Pat. 2 455 314 (American Cyanamid Co.), 1948

Porter F., US Pat. 2 294 130, 1942; US Pat. 2 382 944, 1945; US Pat 2 415 531, 1947 (The Colvay Process Co.)

Pope, Dykstra & Edgar, Am. Chem. Soc., 51, 1875–1876, 2103–2113, 1929

Raschig, Chem. Ztg., 24, 346, 1900

Riegler R., US Pat. 2 067 019 (National Aniline & Chem. Co.), 1937

Riley H. L., Chem. and Ind., 1464, 1956

Riley H. L., Brit. Chem. Eng., 2, 8, 1957

Roessler, DRP 323 059, 1927

Roehm & Haas, US Pat. 1 815 886, 1932

Rollman W. F., US Pat. 2 489 347, 1949; US Pat. 2 526 689 689, 1950; US Pat. 2 604 479 (Standard Oil Development Co.), 1952

Rushton & Stevenson, Trans. Chem. Eng. Progress, 43, 61–67, 1947

Ruthruff R. F., Petroleum Refiner, 32, No. 10, 113, 1953

Schulein C., US Pat. 2 194 988, 1940

Schultz F., DRP 707 018, 1937

Scott & Walker, US Pat. 2 223 500, 1940

Selden Co., US Pat. 1 727 102, 1930

Sherwood P. W., Chem. Eng., 56 (12), 97–100, 1949

Sherwood P. W., Phthalic Acids, Petrochemicals of the Future, Petroleum Refiner 32, 113–117, 155–158, 1953

Sherwood P. W., Modern Methods of Phthalic Anhydride Production, The Ind. Chemist 35, 447–450, 492–494, 1959, 21–24, 1960

Sherwood P. W., Petroleum Processing 82, Nov. 1956

Simard G. L. et al., Ind. Eng. Chem. 47, 1424, 1955

Skeen J. R., Chem. Eng. News, 4 Oct. 1948, 2958–2959

Standard Oil Development Co., US Pat. 1 727 305, 1930

Stanley, Chem. Inds., 93, 1938

Steel, 123 (12), 103–104, 136–146, 1948

Stone H. G., US Pat. 1 656 575, 1928

Toland W. G., US Pat. 2 574 511; US Pat. 2 574 512 (Calif. Res. Corp.), 1951

Toland W. G., & Nimer E. L., Oil Gas J., 54, 232, 1955

Toland W. G. & Nimer E. L., Proc. 4th World Petroleum Congress Section IV/8, 39–54, Rome 1955

Ullmann, Encyclop., XII, 717–727

Weiss J. M., Chem. Eng. News, 32, 1820, 1954

Weiss & Downs, Ind. Eng. Chem., 12, 228, 1920

Weiss & Downs, J. Am. Chem. Soc., 45, 1003, 2341, 1923

Weiss & Downs, J. Soc. Chem. Ind., 45 T, 193, 1926

Welty A. B. Jr. et al., US Pat. 2 439 346 (Standard Oil Development Co.), 1949

Werner et al., J. Am. Chem. Soc., 75, 5244, 1953

Winstrom L. D., Ind. Eng. Chem., 41, 2584, 1949

Winteler, Chem. Zentralblatt 32, 692, 1900

Wohl A., DRP 379 822, 1916

Wohl A., US Pat. 1 971 888 (IG Farben), 1934

Zabel H. W., Phthalic Anhydride Twentyfold in Twenty Years, Chem. Industries, 64, 573–575, 1949

BASIC LITERATURE AND PATENTS

O. F. JOKLIK Industrial manufacture of phthalic anhydride. Lecture. Technical University Aachen, Federal Republic of Germany, July 19, 1957.

O. F. JOKLIK Catalytic oxidation of crude naphthalene in vapour phase to phthalic anhydride. Transcontinental monograph No. 1, July 1957, 88 pages.

O. F. JOKLIK Radiochemical oxidation of naphthalene to phthalic anhydride. Transcontinental monograph No. 2 August 1957.

O. F. JOKLIK Radiochemical oxidation of naphthalene to phthalic anhydride. Introduction into the radiation technology. Technical Review, Bern 1959, 44 pages.

O. F. JOKLIK Catalytic oxidation of crude naphthalene to phthalic anhydride. Practical Chemistry, Vienna 1960, Vol. II, p. 284–290, 442–457 and 522–532.

O. F. JOKLIK Radiation induced oxidation of naphthalene to phthalic anhydride. CIREN Research reports, Vol. 1, 1961, p. 24–43, Rome 1961.

O. F. JOKLIK The production of phthalic anhydride by radio-oxidation of naphthalene. In: "We and the atom", Biblioteca di Studi e Notizie sugli idrocarburi, Padova 1961, 287 p.

O. F. JOKLIK Process and apparatus to make phthalic anhydride. Austrian patent Nr. 258.892.

O. F. JOKLIK A new process to make phthalic anhydride. Research reports, Biotechnology, Vol. 2 1/1967, p. 1–4.

O. F. JOKLIK Radiochemical oxidation of naphthalene to phthalic anhydride.

Lectures:

a) 10th annual meeting of the German Society for Petroleum Sciences and Coal Chemistry, Berlin, October 10–11, 1957.
b) Max-Planck-Institute for Chemistry, Mainz University, Dec. 16, 1957, Feb. 12, July 2, 1958.
c) Permanent seminar for nuclear technology. Aachen Technical University, Feb. 25, 1958.
d) State Engineering School, Essen, Feb. 25, 1958.
e) State Naval Engineering College, Flensburg, Dec. 19, 1958.
f) Polytechnic University, Lausanne, Nuclear Engineering Courses, March 5, 1959.
g) Oscar-von-Miller Polytechnical College, Munich Engineering School, May 20, 1959.
h) Technical College, Winterthur, Reactor Engineering Courses, June 18, 1959.
i) Association of German Engineers VDI, Ravensburg, Sept. 20, 1959.
j) Design College, Ulm, seminar "Introduction in nuclear technology, Oct. 26, Nov. 9, Dec. 24, 1959.
k) Austrian Association for Electrotechnics, Vienna, Oct. 20, 1959.
l) Internat. Conference on Industrial Chemistry, Linz/Donau, Austria, Sept. 1960.
m) CIREN, Rome, Italy, July 20, 1969, Jan. 1, 1961. Haarler University, May 21, 1961.

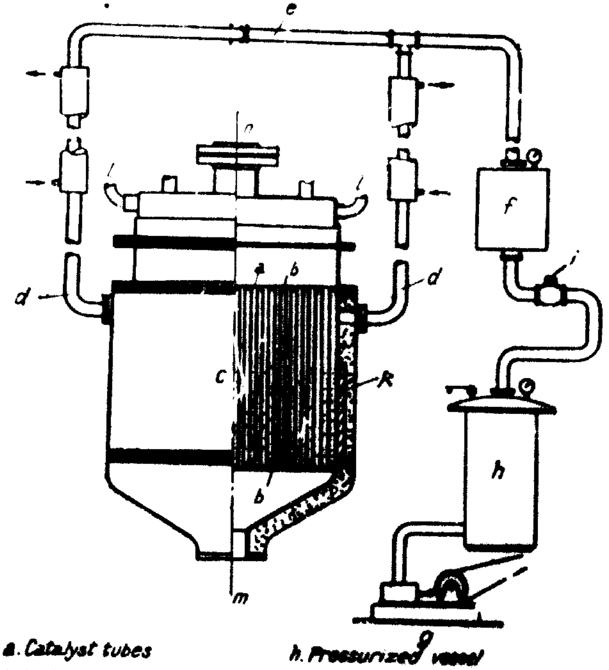
O. F. JOKLIK	Pneumatic logic systems in control engineering, shown on the example of an automatic control system of a modern phthalic anhydride plant. Paper, Baden Symposion on Fluidic Logic Systems, May, 1967.
O. F. JOKLIK	Pneumatic logic system in the control of an advanced phthalic anhydride plant. 38th Internat. Congress on Industrial Chemistry, Istanbul, Sept. 1969.
O. F. JOKLIK	The production of phthalic anhydride from other raw materials than naphthalene. Lecture. 10th annual meeting of the German Society for Petroleum Sciences and Coal Chemistry, Berlin, Oct. 1957.

A SURVEY OF DEVELOPMENTS IN CATALYTIC GAS PHASE OXIDATION REACTORS[1]

OTTO F. JOKLIK*

The subject of catalysis is not concerned only with finding the catalyst but also the reactor and conditions to perform the catalytic task efficaciously. As the heterogeneous catalytic reactor network consists of the catalyst (with carrier, promoters, inhibitors and the active substances), operating in what is usually a non-uniform field of temperature and concentrations within which may exist, short- and long-range diffusional gradients, the problem of reactor design and engineering is indeed complex.

The following survey deals with developments in reactor technology and reactor engineering in the field of heterogeneous gas-phase catalysis, illustrated by a fixed-bed catalytic reactor for the production of phthalic or maleic anhydride.



a. Catalyst tubes
b. Distancing rods
c. Mercury coolant
d. Reflux cooler
e. Ring collector
f. Pressure equalizing vessel
g. Compressor
h. Pressurized vessel
i. Regulating valve
k. Electric heating
l. Entrance of air naphthalene mixture
m. Exit of the reaction gas
n. Explosion disc

FIGURE 1. MERCURY-COOLED REACTOR (DOWNS-TYPE)

I. INTRODUCTION

ORIGINAL DEVELOPMENTS IN REACTOR TECHNOLOGY

Modern advanced reactor technology derives from two basic engineering concepts, – mercury and salt bath cooled reactors.

1. MERCURY COOLED REACTORS

The mercury cooled reactor – known as the Downs-Type reactor in the United States literature – was patented by Charles R. Downs in 1926 (US Patent

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/21.

* Rheinstahl AG, Brackwede, Federal Republic of Germany.

1 604 739, The Barrett Company). This reactor consisted of 1,300 square contact tubes, (18×1,150 mm), containing 300 litres of catalyst and required a cooling bath of approximately 3,000 kg of mercury. The production capacity of this reactor was 30 to 35 tons of phthalic anhydride per month, the reaction temperature being in the range of 400 to 500°C, with a space velocity of 4,000–5,000 and a contact time of 0.6 sec. Reactors of this type were built and used in the United States of America and Europe even in the late 1950s, e.q. in the phthalic anhydride plants of ACNA/Montecatini in Italy and SOAB in Sweden.

Further developments brought a change from square to round contact tubes. Such reactors are particularly suitable for production units up to 50–100 tons of phthalic anhydride per month. When the coolant is boiling mercury and the control of the temperature at which it boils is set by the pressure a relatively simple pressure control is found to be highly effective. One other advantage in the use of mercury is that it is liquid at normal temperatures and does not solidify on shutting down the plant. It is also very stable and although expensive does not deteriorate in service.

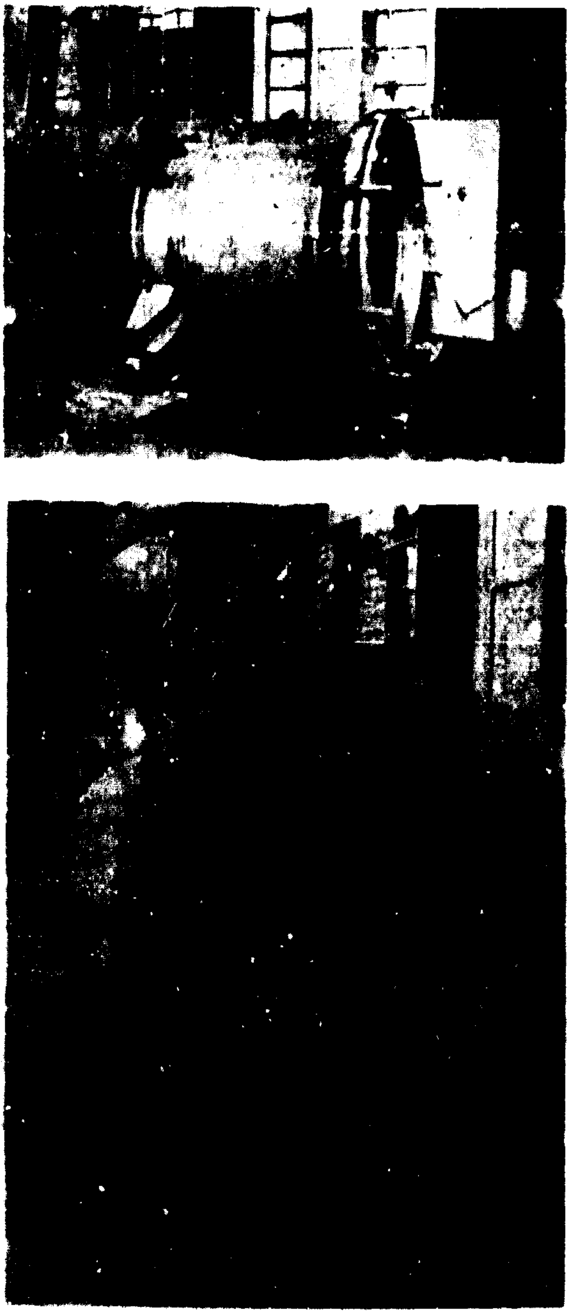


FIGURE 2. RYMER-CUCOOLED OXIDATION REACTOR FOR PHTHALIC ANHYDRIDE, 600 t/y.

Figure 1 is a diagram of a mercury-cooled reactor (Downs-Type).

Figure 2 illustrates a mercury-cooled reactor for the production of phthalic anhydride, designed by the author.

2. SALT BATH COOLED REACTORS

The salt bath cooled reactor is based on the substitution of mercury as coolant by a high temperature salt (KNO_3NaNO_3) melt under forced circulation by an agitator or a pump. This principle was first realized in Germany by the IG-Farben at the beginning of the Second World War (viz. BIOS Final Report No. 649). The concentration of naphthalene in the feed was 63 g/Nm^3 (1 : 20), the reaction temperature being within the range of 420 to 550°C, the space velocity 5,000 to 7,000, and the contact time 0.4 sec. The production capacity was 300–600 t/month.

An example of a salt bath cooled reactor (IG-Farben) of a somewhat modified design is shown in figure 3. The catalyst volume is approximately 3,000 litres. The reaction temperature is between 360 and 400°C with a 20 to 30°C spread.

The space velocity (volume ratio of air catalyst 3,000 : 3) is 1,000, the contact time 1.5 sec. The production capacity of this reactor is approximately 90 t/month.

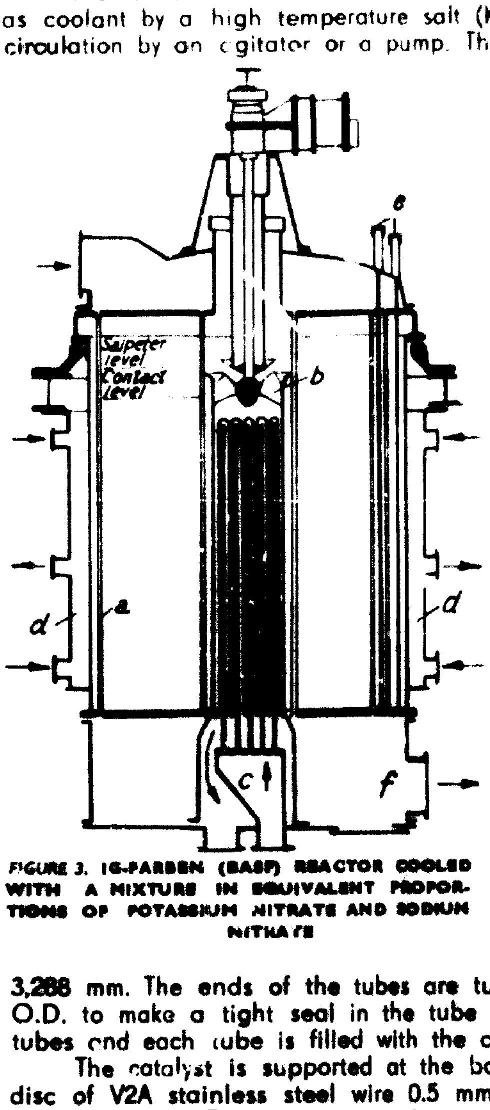


FIGURE 3. IG-FARBEN (BASF) REACTOR COOLED WITH A MIXTURE IN EQUIVALENT PROPORTIONS OF POTASSIUM NITRATE AND SODIUM NITRATE

SIZE OF CATALYST TUBES

The tubes are of steel and of the following size: I.D.=25 mm; O.D.=30 mm; Length=3,288 mm. The ends of the tubes are turned down to a slightly smaller O.D. to make a tight seal in the tube plates. A reactor contains 2,946 tubes and each tube is filled with the catalyst to a depth of 2,500 mm.

The catalyst is supported at the bottom of each tube by a screen disc of V2A stainless steel wire 0.5 mm diameter. The screen mesh is about 1.0 mm. The screens are fastened inside each tube by a spring clamp or lock rings located just above the lower tube plate.

[illegible] REACTOR VESSEL

Material: steel. I.D.=2,580 mm; Wall thickness= 16 mm. The cooler, which is axially oriented in the reactor, is 650 mm O.D. The I.D. of the cooler is 540 mm. The 37 tubes in the cooler are of 2,500 mm length. Each of the tubes has a second one installed concentrically inside. The outer tube has an O.D. of 57 mm and a wall thickness of 2.75 mm and the inner tube has an O.D. of 40 mm and a wall thickness of 2.50 mm.

The salt mixture in the reactor is kept circulating from the catalyst zone to the inner zone, containing the tubular air condenser, by an agitator, with specially designed blades, rotating at 200 r.p.m. The inner cylinder, 54 cm in diameter, encloses the air cooling tube, acts as a thermal barrier between the cooler central zone and the warmer catalyst zone. The salt bath is equipped with 14 pyrometer pockets, each containing 6 couples measuring temperatures at various depths in the bath.

PRODUCTION CAPACITY

Each reactor has a rated output of 75 tons of phthalic anhydride per month although this figure could be increased to 100 tons per month.

II. FURTHER DEVELOPMENTS IN REACTOR TECHNOLOGY

1. THE DWE-REACTOR

In a later design of salt bath cooled oxidation reactors a forced salt melt circulated by a central agitator combined with a steam generator and introduced into the reactor core by an opening in the upper tube plate. (Design and engineering by Deggendorfer Werft und Eisenbau DWE, Deggendorf, Federal Republic of Germany.) These reactors are largely used in phthalic anhydride plants operating on BASF or Von Heyden processes.

Figures 4 and 5 show the design of the DWE-reactor as specified in the relevant patent specification. The central molten salts agitator and steam generator are shown in figure 6. Figure 7 shows a series of four oxidation reactors of a production capacity of 300 tons/month of phthalic anhydride each (total 14,600 t/y), manufactured by DWE in 1967.

Oxidation reactor (conventional design for BASF and Von Heyden processes) with central salts cooling and heat exchange system. Manu-

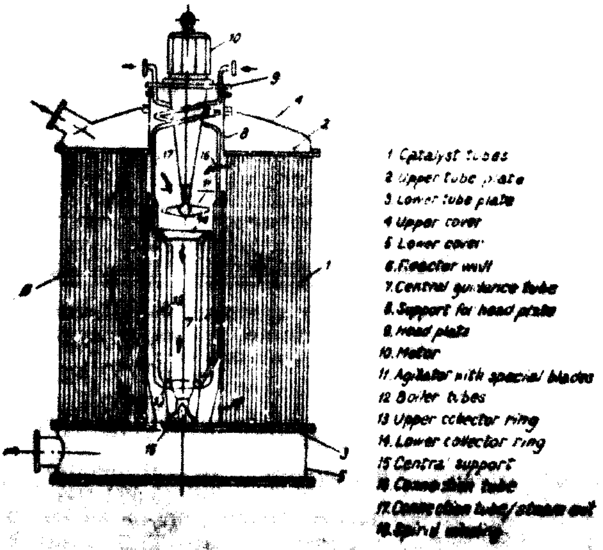


FIGURE 4. THE DWE-REACTOR

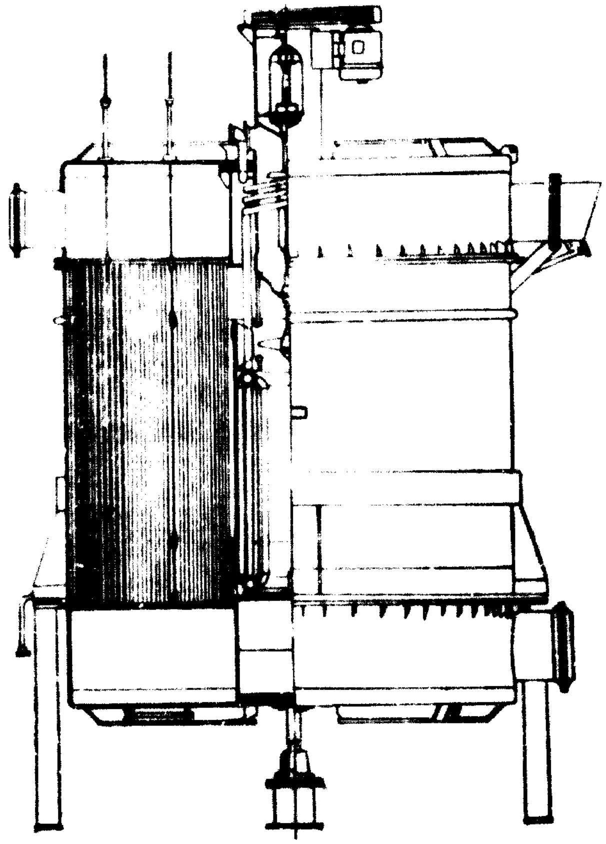


FIGURE 5. THE DWE-REACTOR (300 t/MONTH)

facturer of the reactor: Deggendorfer Werft und Eisenbau DWE, Deggendorf, Federal Republic of Germany (Patent 1 181 177).

Oxidation reactor (conventional design for BASF and Von Heyden processes) with central salts cooling and heat exchange system. Manufacturer of the reactor: Deggendorfer Werft und Eisenbau DWE, Deggendorf, Federal Republic of Germany.

8,928 contact tubes, I.D. = 25 mm
O.D. = 30 mm
length = 3,072 mm
Diameter of the reactor = 4,540 mm
Height of the reactor = 6,800 mm
Volume of the catalyst tubes = 13,500 litres
Weight of the catalyst = 9,450 kg
Weight of the reactor = 62,750 kg
Weight of the salt bath = 38,800 kg
Operating weight of the reactor = 111,000 kg
Production capacity of the reactor = 300 t/month (3,600 t/y)

Design temperature = 480°C
Reaction temperature = 380°C

FIGURE 6 THE DWE-REACTOR, CENTRAL SALTS COOLER – HEAT EXCHANGER – STEAM GENERATOR

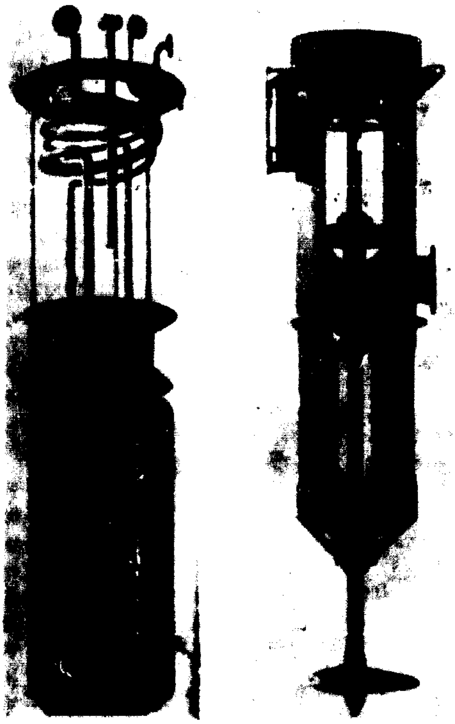


FIGURE 7. FOUR OXIDATION REACTORS FOR PHTHALIC ANHYDRIDE, 300 t/MONTH EACH = 1200 t/MONTH (14,400 t/y). MANUFACTURER: DEGGENDORFER WERFT UND EISENBAU, DWE, DEGGENDORF

2. THE POLIMEX-CEKOP REACTOR

The DWE-reactor design was adopted by other manufacturers later on. Figure 8 shows a very similar design offered by Polimex-Cekop of Warszawa, Poland, and used in phthalic anhydride plants in Poland (Zaklady Azotowe Kedzierzyn) and in the Union of Soviet Socialist Republics (Awdiejewka Donieck, etc.). The production capacity of the plant in Poland is 4,000 t/y and of those supplied to the Union of Soviet Socialist Republics (in 1967) 24,000 and 16,000 t/y.

Two new phthalic anhydride plants, using the same type of reactor have been contracted recently by Polimex-Cekop for supplies to the USSR in 1973. The manufacturers of these reactors are Zaklady Urzadzeń Chemicznych i Aparatury Przemyslowej in Kielce and Zaklady Urzadzeń Przemyslowych in Nysa, Poland. The new phthalic anhydride reactors supplied by Polimex-Cekop will use a new catalyst developed by the author, permitting higher conversion rates.

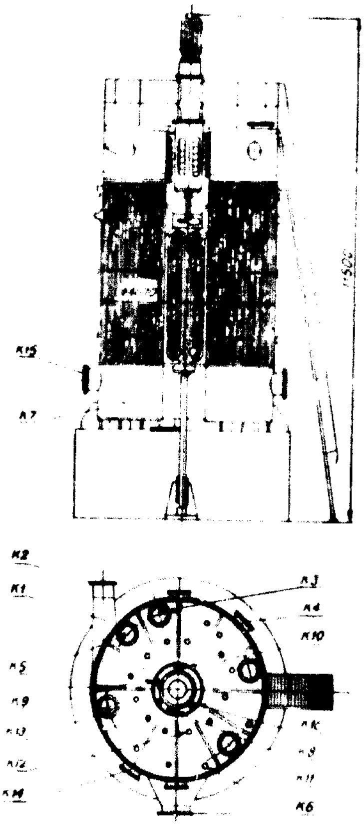


FIGURE 8. THE POLIMEX-CEKOP REACTOR

Volume in the contact tubes	18,500 litres
Volume outside the contact tubes	25,500 litres
Volume of the catalyst mass	13,400 litres
Working pressure in the contact tubes	0.7 at
Working pressure outside the tubes	0 at
Working pressure in the steam generator	24.0 at
Temperature at the contact tubes entry	140.0 °C
Temperature in the contact tubes exit	380.0 °C
Temperature in the contact tubes	420.0 °C
Temperature outside the contact tubes	370.0 °C
Agitator for molten salts, motor	40.0 kW
r.p.m.	725.0
Total head	7.0 mWG
Capacity	1,100.0 m^3/h
Steam generator, heat exchange area	21.0 m^2
Contact tubes	8,540
Weight of the catalyst	8,300 kg
Diameter of the reactor	4,070 mm
Height of the reactor (without support)	9,500 mm
Total height of the reactor	11,500 mm
Weight of the reactor	88,200 kg
Weight of the salt bath	38,800 kg
Total weight of the reactor (working)	135,300 kg
Material of construction	C–Steel
Contact tubes, 30×2.5×4,000 mm	C–Steel
Production capacity of the reactor	4,000 t/y

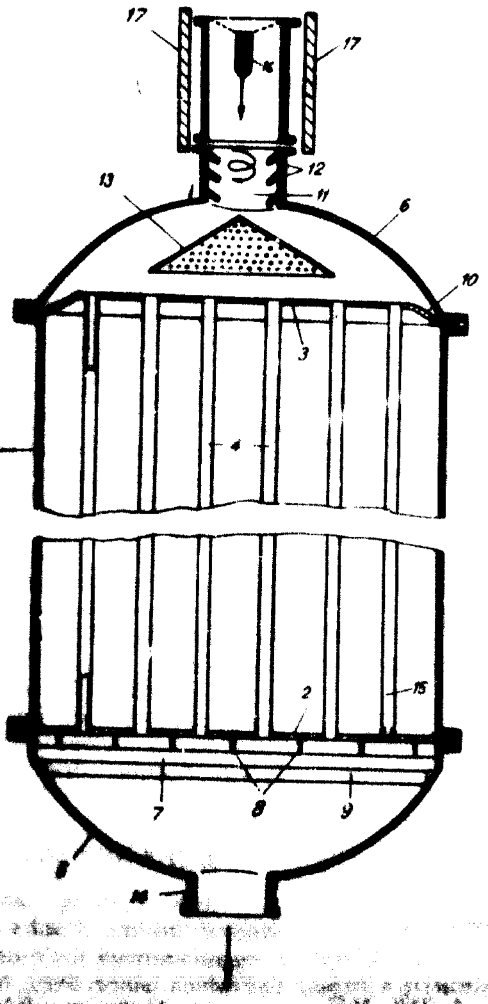
3. THE ROLLE REACTOR

Another type of oxidation reactor with a central molten salts agitator has been suggested by the author in 1965. A reactor of such a design, was engineered and manufactured by Ariosto Rolle, Padova, Italy for a plant in Turkey. The production capacity of this reactor is approximately 7,000 t/y. This reactor uses the Joklik catalyst.

III. OXIDATION REACTOR DESIGN INCORPORATING RADIATION TECHNOLOGY

1. THE JOKLIK-REACTOR

An advanced oxidation reactor design has been engineered for a process utilizing high energy gamma radiation from a cobalt 60 gamma source for the catalytic conversion of crude naphthalene and/or o-xylene to phthalic anhydride or for the conversion of benzene to maleic anhydride. (O.F. Joklik: Austrian patent 258 892, 1967). This reactor is described in figure 9.



THE JOKLIK-REACTOR

1 – Reactor wall
2 – Lower tube plate
3 – Upper tube plate
4 – Contact tubes
5 – Lower reactor cover
6 – Upper reactor cover
7 – Support of the lower tube plate
8 – Support of the lower tube plate
9 – Support of the lower tube plate
10 – Expansion element
11 – Gas inlet
12 – Turbulence device at the gas entrance
13 – Distributor for the gas stream
14 – Gas exit
15 – Contact tube closing device
16 – Gamma radiation source
17 – Gamma radiation shielding

IV. NEW DEVELOPMENTS IN REACTOR TECHNOLOGY

REACTORS WITH LATERAL SALT BATH COOLER

1. THE ROLLE/JOKLIK-REACTOR

Reactors with a central salt bath agitator and an incorporated steam generator have the disadvantage that considerable contact tube space is occupied by the agitator and steam generator. Owing to the rather complicated design of such reactors, their cost is quite elevated. A further disadvantage, especially when using catalysts on carriers of weak mechanical resistance, is that the vibration causes an undesired increase of catalyst erosion with subsequent partial or total obstruction of the contact tubes.

These considerations induced the author to suggest (in 1960) a new design for a catalytic oxidation reactor, in which the molten salts agitator and steam generator were removed from the central zone and placed outside, i.e. lateral to the reactor itself. The first reactor of this new design was engineered in Italy and manufactured in 1965 by Ariosto Rolle, Padova, for Carbochimital SpA, Padova, where it has been in continuous operation since 1966. The production capacity of this reactor is 3,000 t/y.

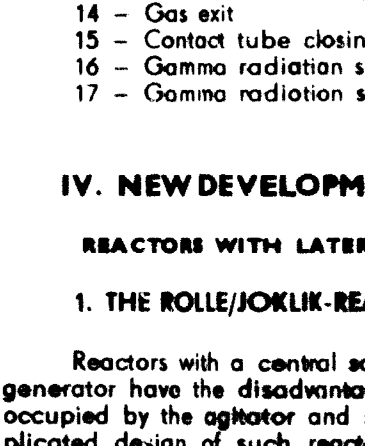


FIGURE 10. COMPARISON OF A CONVENTIONAL AND A NEW BASF-REACTOR

2. THE NEW BASF-REACTOR

BASF, among others, adopted the idea of the lateral salts circulators. In 1969 they announced their new oxidation reactor which since then has been installed in many plants using BASF processes.

The BASF-reactor is manufactured by the Deggendorfer Werft und Eisenbau DWE, Deggendorf, Federal Republic of Germany (Viz. Ellwood P Chem. Eng., June 1969, p. 80 etc).

Figure 10 compares a conventional (central agitator) and a new BASF-reactor with a lateral agitator and steam generator. The reactor itself is a departure from tradition in the sense that the heat-exchange system is located outside the vessel. This allows the reactor core to include additional catalyst tubes, and thus increases reactor through-put.

BASF-reactor with external cooler 16.4-ft high×13.8 ft. dia, contains nearly 10,000 contact tubes. Its capacity is 15,840 t/y. In the BASF design the molten salts, previously cooled in the external heat exchanger, enter the reactor through several wall ports simultaneously fed from a circumferential wall ring. This provides better cooling near the walls, as well as more uniform heat transfer throughout the reactor.

V. ADVANCED REACTOR TECHNOLOGY

1. THE RHEINSTAHL/JOKLIK-REACTOR

The Rheinstahl/Joklik-reactor, represents the latest development in this particular field. A simplified, but yet very robust construction increases the reactor life and minimizes its weight and cost. The salt bath circulator and the steam generator have been entirely removed from the reactor core, thus leaving additional space for contact tubes, increasing the capacity of the reactor. The salt bath circulator and the steam generator form an independent unit together with the salts storage container and the salt bath circulating pump. The reactor itself thus becomes very accessible and the assembly of the whole oxidation unit is very simple. The salt bath circulates radially to the contact tubes in an ideal stream and at high velocity, thus ensuring optimal heat removal. Figures 11, 11 a show this new type of reactor, suitable for a wide variety of high-temperature gas-phase heterogeneous catalytic reactions over fixed-bed catalysts, such as the conversion of naphthalene and/or o-xylene to phthalic anhydride and the conversion of benzene to maleic anhydride.

In processes requiring a longer contact time and consequently longer contact tubes, the reactor can be supplied in two separated sections with separate salt bath cooling circuits, so that an over-all lenght of contact tubes of up to 6,000 mm can be assured. The two separate reactor parts are assembled on the site the plant. Figure 11 b shows such a type of reactor.

The Rheinstahl/Joklik-reactor is designed and engineered in two versions. One is applicable to reactors of up to 9,000 contact tubes, the other, to reactors up to 11,000 contact tubes and more. A reactor with 11,000 contact tubes would be suitable for a production capacity of approximately 16,000 tons of phthalic anhydride per year. The large size reactors are designed in such a way that road transport even for the biggest sized reactors becomes feasible. (Viz. Benton A., "Selection of Projects and Production Processes for Basic and Intermediate Petrochemicals in Developing Countries", UNIDO Petrochemical Industry Series Monograph No. 2, p. 84, 1969). A new fast clamp-spring lock has been developed for the support of the catalyst in the contact tubes, thus ensuring a safe and yet uncomplicated containment of the catalyst in the contact tubes.

A new automatic device has been designed, which ensures a uniform distribution of catalyst in the contact tubes in a fraction of the time hitherto required for the task of loading.

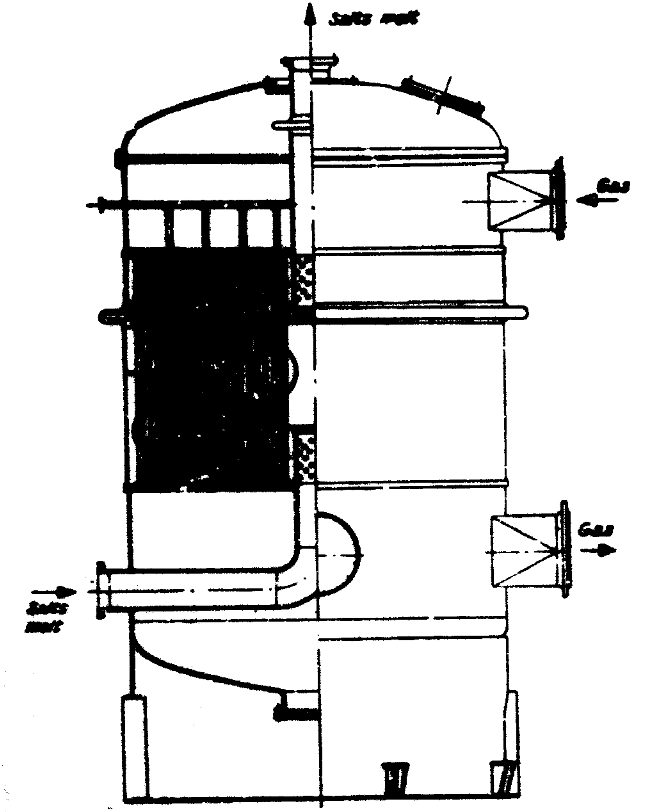


FIGURE 11. THE RHEINSTAHL/JOKLIK-REACTOR FOR PRODUCTION UP TO 12,000 t/y

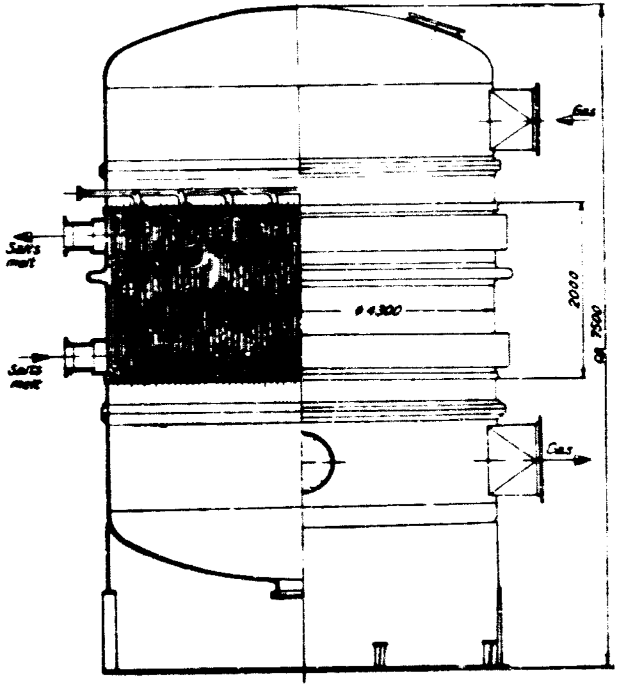


FIGURE 11 a. THE RHEINSTAHL/JOKLIK REACTOR FOR PRODUCTION UP TO 16,000 t/y

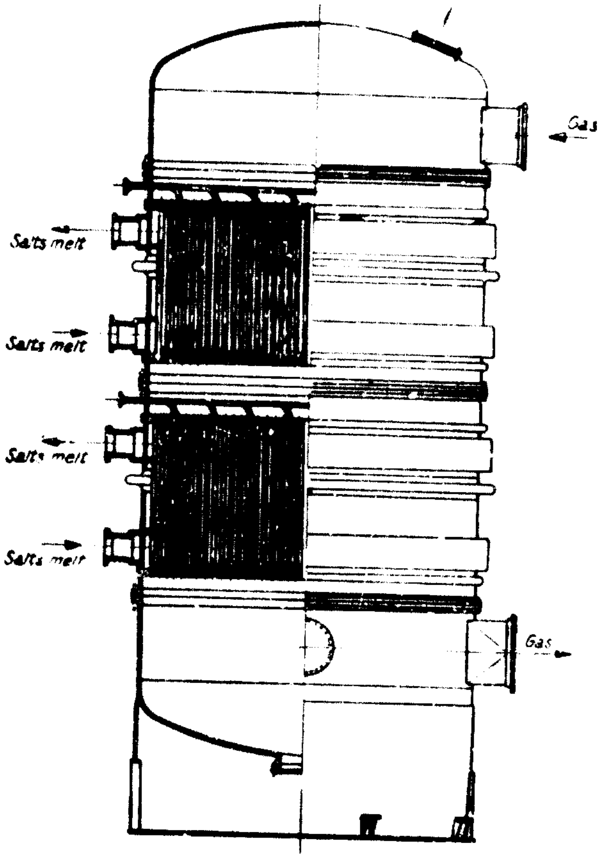


FIGURE 11 b. A TWO-STAGE RHEINSTAHL/JOKLIK-REACTOR

The reactor can be placed upon a special carriage support on wheels and rails to permit its easy movement for maintainance etc. without the necessity of employing cranes or similar equipment.

2. THE OXIDATION GROUP

The oxidation group forms a complete unit consisting of the reactor itself, the salts storage and melting container, the salt bath circulator, the steam generator, the gas cooler/heat exchanger and the steam drum. In figure 12 is shown a typical schematic diagram of the oxidation group. Figure 13 gives more details of the assembly of the oxidation group.

The same principle can be applied to phthalic anhydride and maleic anhydride plants.

3. THE CONTROL OF THE REACTOR

Reactor technology is incomplete without efficient control. Conventional processes use the variation of the salt bath temperature as a means to control the reaction temperature. It is more appropriate to control the reaction temperature by a variation of the feedstock concentration in the air stream prior to its entrance into the reactor. When the reaction temperature surpasses a preset maximum value, then the concentration of the feedstock in the air is automatically reduced and vice versa. Another

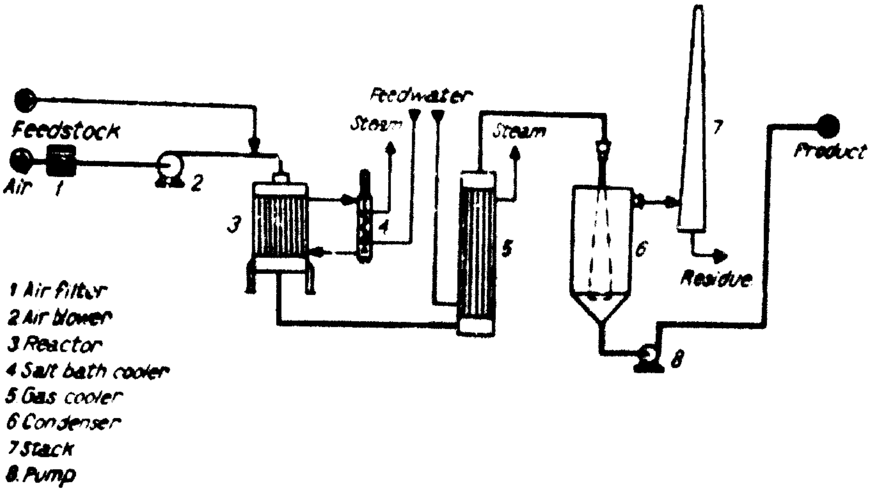


FIGURE 12. SIMPLIFIED SCHEMATIC DIAGRAM OF THE OXIDIZING SECTION AND THE OXIDATION GROUP OF A PHTHALIC ANHYDRIDE PLANT

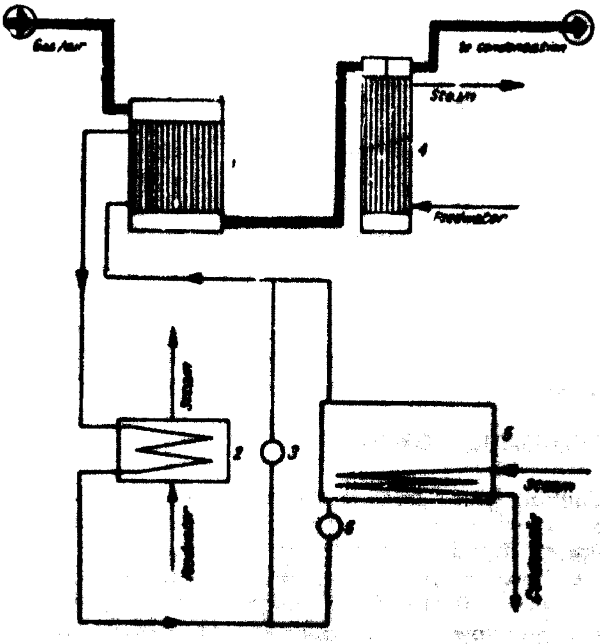


FIGURE 13. THE OXIDATION GROUP – DETAILED SCHEMATIC DIAGRAM

automatic control ensures that the ratio air: feedstock remains constant, to avoid explosive mixtures, even during start-up or running-in operations. An advanced electronic level control of the feedstock intermediary storage vessel ensures a much more precise dosage. This digital control system doses an exact quantity of the feedstock as a function of the quantity of liquid crude product coming out of the switch condensers. By this system optimal production rates are achieved. Fluctuations in the pressure in the mains are compensated for by this system, too and thus maximum reliability and operating safety is achieved. Figure 14 shows the control

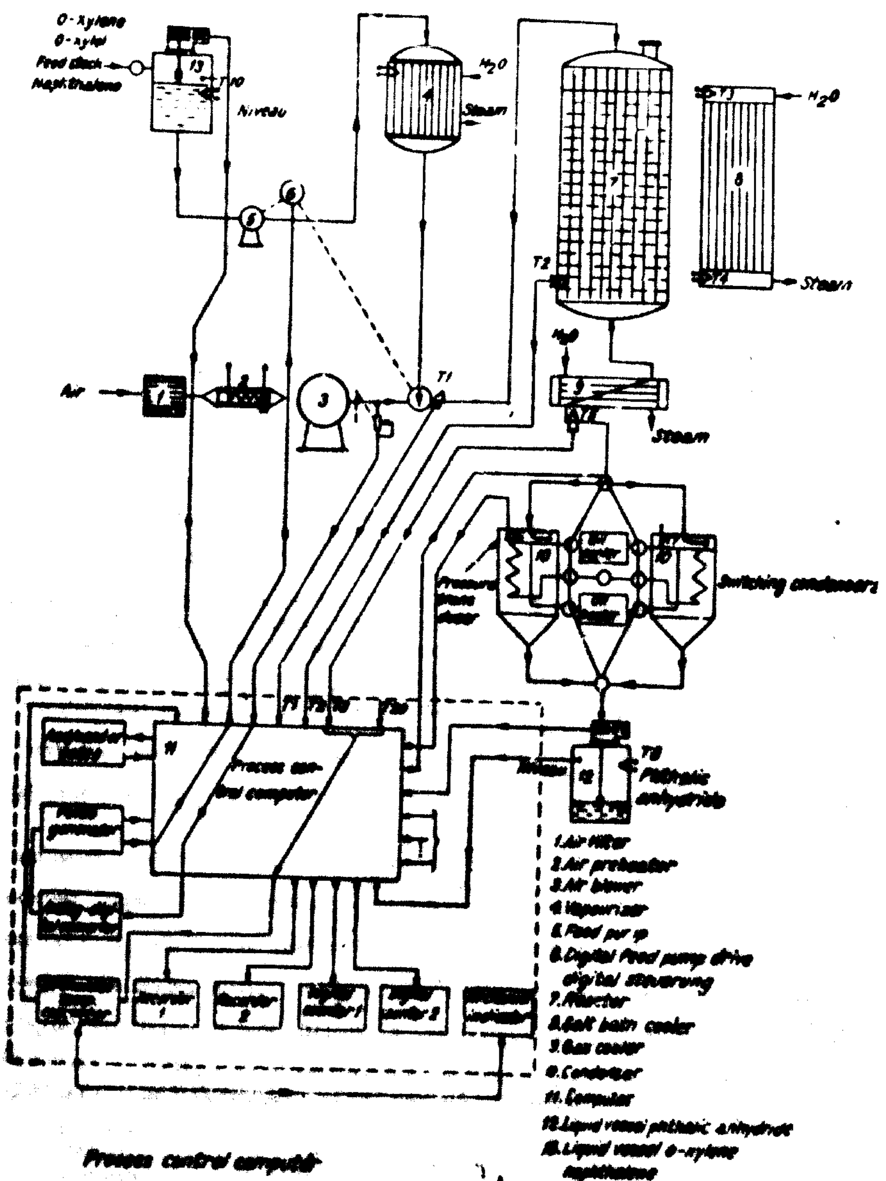


FIGURE 14. THE SCHEMATIC DIAGRAM OF THE REACTOR AND REACTION CONTROL

system of the reactor and of the reaction, designed by the author. The process control equipment is manufactured and engineered by Ingenieurbüro Eugen Rapp, Bremen and Rapp GmbH, Federal Republic of Germany.

VI. PILOT REACTOR

For pilot plant operations, a reactor has been developed having a [illegible] and an universal con[illegible] system using [illegible] tubes made of [illegible].

VII. CONCLUSIONS

The newly developed Rheinstahl/Joklik-reactor is suitable for a variety of catalytic oxidation reactions e.g. the conversion of naphthalene and/or o-xylene to phthalic anhydride or the conversion of benzene to maleic anhydride. This reactor has been designed and engineered to meet the special requirements of high-temperature and high space velocity catalytic processes.

The design of the reactor is equally suitable for plants with a small production capacity of 50 to 100 tons per month as for large scale industrial plants with production capacities ranging up to 18,000 tons per year and more per unit.

REACTOR TECHNOLOGY BASIC PATENTS

1. Downs, Ch. R., (to Barrett Company), „Apparatus for Promoting Catalytic Reactions", US 1,604,739 (Oct. 26, 1926)
2. Canon, F., et al. (to Selden Company), „Process of carrying on Catalytic Reactions", US 1,614, 185 (Jan. 11, 1927)
3. Forrest, H. O., et al. (to National Synthetic Corporation), „Process of Oxidizing Naphthalene and related Condensed Aromatic Ring Compounds," US 1,936,427 (Nov. 21, 1933)
4. Rogers, D.A., et a. (to Solvay Process), „Catalytic Oxidation of Naphthalene", US 2,071,361 (Feb. 23, 1937)
5. Porter, F. (to Solvay Process), „Phthalic Anhydride Production", US 2,117,359 (May 17, 1938)
6. Andrews, C. E. (to American Cyanamid & Chemical), „Process of Oxidizing Naphthalene to Phthalic Anhydride", US 2,120,538 (June 14, 1938)
7. Weity, A. B., Jr. (to Standard Oil Development), „Method for Oxidation of Aromatic Hydrocarbons", US 2,485,342 (Oct. 18, 1949)
8. Jewett, J. E. (to American Cyanamid), „Tubular Catalytic Converter", US 2,986, 454 (May 30, 1961)
9. Pietzsch, K. F. „Catalytic Converter", US 3,043,651 (July 10, 1962)
10. Benichou, S., et al. (to Société d'Etudes de Techniques Industrielles Nouvelles), „Production of Phthalic Anhydride", US 3,072,682 (Jan. 8, 1963)
11. Wanka, O., et al. (to Deggendorfer Werft und Eisenbau GmbH), „Heat Exchanger", German 1,181,177 (Nov. 12, 1964)
12. Chemiebau Dr. A. Zieren, „Phthalic Anhydride from Naphthalene", German 1,222,490 (Feb. 23, 1967)
13. Joklik, O., „Process and Apparatus to make Phthalic Anhydride", Austrian 258,892 (Apr. 15, 1967 (Apr. 15, 1967)
14. Wanka, O., et al. (to Deggendorfer Werft und Eisenbau GmbH), „Heat Exchanger", US 3,503,439 (Mar. 31, 1970)
15. Joklik, O., „Multistage Oxidation Reactor", Austrian 301,579 (Jan. 15, 1972)
16. Joklik, O., „Catalytic Fixed-bed Reactor", Austrian Application A 1987/72 (filed March 7, 1972)

FACTORS AFFECTING THE DECISION TO MANUFACTURE CATALYSTS[1]

BRUCE CRAMER*

To provide a framework for the discussion which follows, it will be useful to have a classification of various catalysts of potential interest (table I). Neither large volume petroleum catalysts such as the fluid catalytic cracking type or platinum-alumina used for reforming, nor catalysts used in large scale petrochemical operations, such as nickel catalyst for hydrogenation, or the several catalysts employed in ammonia plants are within the realm of our experience. The area of specialty petrochemical catalysts, such as those we manufacture for processes making intermediate chemicals such as ethylene oxide and maleic anhydride will be discussed specifically. These intermediates are used as „building blocks", the majority of which eventually become polymer products or additives.

TABLE I

SIGNIFICANT CATALYST MARKETS

PETROLEUM REFINING

- Alkylation
- Cracking-fluid
- Cracking-moving beds
- Desulphurization
- Hydrocracking
- Hydrotreating
- Isomerization
- Polymerization
- Reforming (Pt)

PETROCHEMICAL

- Major markets (1,000 tons or more annual catalyst production)
  - Alkylation
    - $AlCl_3$
  - Ammonia
    - Reforming
    - Shift conversion
    - Methanation
    - Synthesis
  - [illegible]

[illegible]

Other markets

- Ethylene oxide
- Formaldehyde
  - Ag or mixed oxides
- Maleic anhydride
- Methanol
- Nitric acid
- Pharmaceuticals
- Phthalic anhydride
- Polymerization
  - Titanium trichloride

It may be an over-simplification but it is vital to recognize that catalyst performance is always an important factor and in many cases the critical one in determining the economics and successful practice of a chemical process. There is a tremendous variety of commercially available catalysts which may find usage in relatively broad chemical process areas such as nickel catalysts in hydrogenation reactions, while others have been designed for and may only be used successfully for a very specific reaction. Just as there are a myriad of products bearing the name catalyst, there is a wide variety in the methods used to make them. Testing methods and requirements also vary widely and may sometimes be limited to relatively simple chemical and physical tests as opposed to frequently employed, very sophisticated testing in pilot plant prototype units. In some cases there is a real need for on-site preparation of a catalyst such as a situation where the catalyst is consumed or its physical form is altered beyond the point of continued utility in the reaction itself.

With the foregoing general remarks as a very brief background, let us explore in more detail the specific technical and economic factors which must be carefully considered when examining the possibility of catalyst manufacture. These factors are raw materials; material, equipment and personnel aspects of production, product testing; technical service.

RAW MATERIALS

Availability of key raw materials and an adequacy of supply, preferably from multiple sources, must be established in terms of suitable chemical and physical properties. This might be interpreted as a statement of the obvious but one particular example will point up the difficulties in what seemingly is a relatively simple situation. In our manufacture of catalyst for maleic anhydride, one of the principal constituents is a vanadium bearing compound. During the laboratory development of this catalyst, a certain commercial grade of this compound was used in the variety of catalyst formulations tested. As the process evolved to commercial status, and the need for commercial quantities of catalysts came closer to reality, efforts were undertaken to qualify less expensive and more readily available commercial grades of this vanadium compound but all of the efforts proved unsuccessful, primarily due, it was discovered, to different combinations of impurity levels. It was necessary, therefore, to manufacture the initial commercial charges of catalyst using the laboratory qualified product and that catalyst is still prepared today using this same quality vanadium compound in significant quantities. During the time that this catalyst has been manufactured, numerous sources of this compound have been evaluated and only one, the original, allows the preparation of catalyst of superior quality.

In many cases, one cannot overemphasize the possible modifications in catalyst activity or selectivity caused by seemingly trace amounts of impurities or a different set of the same impurities. Naturally occurring or semi-refined raw materials such as clays or zeolites, whose chemical analysis may vary over a fairly broad spectrum, can be the source of major problems in the performance of finished catalysts. It is vital that raw materials manufacturing procedures and quality control are not only known to the catalyst manufacturer but also monitored by him on a regular basis. The establishment of specifications for catalyst raw materials is many times in itself a lengthy, tedious development programme wherein the effect of the impurities on catalyst performance must be determined independently. Where precious metals are used as catalysts, frequent accurate assays are essential, metal recovery systems must be devised, contamination prevention procedures constantly monitored and security programmes implemented and continuously maintained. As one example, in the area of raw material testing let us look at the critical properties of a catalyst carrier. Table II is a tabulation of such physical and chemical properties that are measured to provide a definition of a catalyst carrier as a suitable substrate or co-catalyst. The list is rather a lengthy one; some of the tests required are rather elaborate and the understanding of the inter-relationship of all these factors with respect to catalyst performance is an essential element in the control of catalyst quality.

TABLE II

CATALYST CARRIER

PHYSICAL PROPERTIES

Size and shape
Attrition loss
Crushing strength
Total porosity
Pore volume
Pore size distribution
Specific gravity
Packing density
Surface area
Crystal form
Water absorption
Absorption isotherms

CHEMICAL PROPERTIES

Spectrographic analysis
Reactivity
Leachable impurities
Resistance to acid or alkali

PRODUCTION

Process steps or conditions for the manufacture of catalyst either on a batch or continuous basis cover a wide range of possibilities. Table III is intended only as a partial listing of the varied operations one might encounter in commercial catalyst manufacture. The size of equipment in the plant depends, of course, on the annual market for the catalyst. This is determined by the amount of catalyst used in the chemical process, and the frequency with which catalyst is replaced. In the manufacture of intermediate chemicals where catalysts life may be from one to ten years, it is not uncommon to find that a minimum sized catalyst manufacturing operation [illegible] [illegible] to [illegible] over a period of only one, two or three weeks in order to manufacture a complete plant charge of catalyst. Such a [illegible] of [illegible] [illegible] [illegible] questions regarding the advisability of an investment in the catalyst manufacturing facility and the maintenance of an adequate level of training among operating personnel. During the long period the plant is not operated, people can and will lose the art. There remains a measure of art and specialized know-how needed in the continuing successful production of catalysts.

In process controls are a vital factor not only of such variables as weight, volume, temperature, viscosity, or dryness but also in the frequent evaluation of finished catalyst quality to ensure that current production ist meeting preset standards during every step of the manufacturing process. In cases where a catalyst plant is charged with the manufacture of more than one type of catalyst the dangers of contamination of one catalyst by the constituents of another must be carefully considered during design stage of the catalyst plant. Fumes from surrounding chemical plant, operations must also be considered in this category. For example the presence in the atmosphere of even small amounts of halogen compounds near an ethylene oxide catalyst manufacturing plant could be intolerable since these could be expected to poison freshly manufactured catalyst to the point of inutility. Some catalysts used commercially are relatively weak from a physical standpoint and must be handled during the manufacturing operation with a great deal of care to prevent attrition, crushing or loss of active ingredients. In the catalyst manufacturing business it is probable that a manufacturer or potential manufacturer will find that the specialized type of equipment required to make one particular catalyst is not at all suitable for another type because of the process steps involved or potential contamination. In many cases it is necessary to acquire, build and operate separate and distinct facilities.

TABLE III

MANUFACTURE OF HETEROGENOUS CATALYSTS
PROCESS STEPS AND EQUIPMENT

PREPARATION

- **Solution preparation**
  - **heating/cooling**
  - **viscosity control**
- **Formula control**
- **Solids — solids mixing**
- **Solids — liquids mixing**
- **Evaporation / crystallization**
- **Drying**
- **Grinding and sizing**
- **Ball milling**
- **Ageing**
- **Pollution control**

FORMING

- **Extrusion**
- **Pelletizing**
- **Spherodizing**
- **Coating**
- **Impregnation**
- **Spray drying (fluid catalyst)**
- **Pollution control**

FINAL STEPS

- **Activation**
  - **heating/controlled atmosphere**
  - **oxidation/reduction (not in situ)**
  - **pollution control**
- **Blending/screening**
- **Protective packaging**

TESTING

To a potential catalyst manufacturer the area of catalyst testing and evaluation is as great a concern as the care necessary in the raw material control and the production process steps for that catalyst. It is possible to conduct a variety of chemical tests and in some cases necessary to conduct numerous chemical tests in those areas where manufacturing conditions are not easily controlled. The definition of the precise amount of each of the key catalyst components and the levels of known critical impurities is frequently imperative. Similarly, depending upon the particular catalyst, physical tests may be warranted such as attrition loss, surface area, or volume and size, or some of the others which were pointed out earlier as being critical for incoming quality control of catalyst carriers.

In addition to all the chemical and physical tests that may be indicated as necessary controls, what interests both the catalyst manufacturer and the chemical plant operator is the question of catalyst performance. Does the charge of catalyst conform to the performance standards which will allow the chemical plant to operate as it was designed? The key factor is that performance testing carried out by the catalyst manufacturer must be closely related to the chemical plant reaction system and a close correlation developed between the operation of the plant reactor and the laboratory or pilot plant test reactor. Perhaps a relatively simple example, which is pertinent to many chemical reactions, is the use of a tubular reactor. Such a test reactor can be designed to simulate the plant reactor by using one or only a small number of tubes of the same dimension as the tubes used in the plant reactor. The test reactor should have the same catalyst bed height so that heat transfer, flow and recycle conditions are simulated as closely as possible. The catalyst manufacturer must determine the frequency with which he proposes to test the manufactured catalyst. Waiting until a complete plant charge has been completed is not recommended. It is a very expensive crisis when one finds 10,000 or even perhaps 50,000 kilograms of catalyst have been made and none of several representative samples tested have been able to pass the performance test.

Analytical facilities associated with the catalyst test equipment must be designed as accurately and dependably as those which are used to monitor chemical plant reactor operations on a continuing basis. Even after the catalyst manufacturing plant is built and operating, and the quality of the catalyst has been confirmed by frequent testing of representative samples from reasonably sized production lots, there remains one trouble some question which is frequently left unanswered. That question is: What is the life expectancy of a given charge of catalyst if operated under normal plant design conditions? The shutting down of a plant reactor and the consequent loss of production can very seriously affect the economic success of a process if it occurs earlier or more frequently than expected. Ensuring that such shut-downs do not occur because of catalyst quality is a factor that the catalyst manufacturer must consider and be in a position to evaluate above and beyond the initial catalyst performance characteristics used as a quality control procedure. It is apparent that the expertise of the process designer, chemical plant operator and catalyst manufacturer must be carefully co-ordinated to avoid problems and optimize plant performance.

In the manufacture of various catalysts, it is not unusual to find that the investment in testing facilities and the training of people to operate these facilities is more expensive and time consuming than the catalyst manufacturing operation itself. If no other point is made in the course of these remarks I do want to stress the very important and critical step that catalyst performance testing represents.

TECHNICAL CONSIDERATIONS

A corollary to catalyst manufacturing and testing is the need for the support of high quality technical manpower. Various experts are needed beginning with the design phase of the catalyst manufacturing plant, including those responsible for its day-to-day operation, maintenance engineers, a diversity of analytical talent and detailed knowledge and understanding of the commercial process or processes in which the catalyst or catalysts may be used. Never is the availablity of this talent more necessary or vital to success than those times when problems occur. I refer not so much to those problems which might be associated with the breakdown of catalyst manufacturing plant equipment but to those situations where the catalyst has been manufactured in accordance with well delineated procedures using all the specified precautionary controls and then the performance tests show repeatedly that the catalyst is of inadequate quality to afford economic operation using the plant charge. At a point in time such as this the catalyst manufacturer must have a group of individuals, each with unique skills, who can be called upon to investigate and solve the catalyst manufacturing problem in a very short period of time.

There is a great deal of art involved in the manufacture of many catalysts and it is difficult if not impossible to define specifically all of the variables critical to the preparation of good quality catalyst. The economic considerations at stake are great. The loss of two or three yield points in the initial performance of a catalyst charge or a greater than expected rate of decline in activity can be extrapolated to millions of dollars in product losses and a completely unacceptable, uneconomical plant situation.

During the remarks made thus far, the basic assumption has been made that well-practiced technology would be available to any organization desiring to establish a new catalyst manufacturing facility. When this technology is translated into a new plant facility it is essential that the fewest possible number of changes in equipment size and type be made. One of the major problems in the commercial manufacture of a new catalyst is the necessity for scaling up to economical size the successful catalyst preparation technique that has been developed in the laboratory.

In the case of many catalysts, production operations may appear very simple or even backward in the light of known, readily available equipment that might have been chosen. Often the reason for this is the fact that such relatively primitive techniques have been shown to produce catalyst of superior quality, whereas seemingly more complex, automated techniques could produce inferior quality catalyst.

It should be recognized that two processes for making the same chemical commodity may very likely employ two entirely different catalysts each one of which is entirely consistent with the unique process conditions for which it was designed. They will not, however, be found to be interchangeable and a catalyst manufacturing plant for the preparation of one may very well be completely unsuited for the preparation of the other. This is another of the market factors that must be considered in deciding whether or not to manufacture catalyst. A similar point might be made with regard to catalysts which may have the same basic constituent but are used for entirely different processes. A good example of this is vanadium pentoxide catalyst used for sulphuric acid or the vanadium pentoxide based catalyst used for phthalic anhydride or maleic anhydride. The catalyst manufacturing processes in all three of these cases are significantly different and very little of the equipment would be interchangeable. A universal catalyst plant is a desirable objective, but unreal from a practical standpoint.

The decision to manufacture catalyst is a complex one as the foregoing remarks have indicated. It is a decision which requires the careful consideration of: the availability of appropriate technical know-how and manpower, the obtaining and evaluation of raw materials, the design and building of a facility which may be under utilized causing technical and personnel problems due to infrequent use, extensive and in some cases elaborate testing facilities and thorough understanding of the use of the catalyst in a chemical plant.

The decisions which will be contemplated relate to specific catalysts and specific plant situations. The problems involved and the approach to their solution will undoubtedly be different in each case. However, the factors which will affect the solutions of these problems must universally take into account all of those which have been discussed.

NEW TRENDS IN CATALYSIS[1]

JOOST MANASSEN[2]

I. INTRODUCTION

Although it is advisable for developing countries to buy proven know-how, there is always the danger of buying processes that are obsolete. Many obsolete processes may actually be in use the world over, but their capital investment has been written off long ago and therefore they can compete with more modern processes.

If, on the other hand, the investment has to be done from the beginning, it is important to buy the most modern process which, however, must have proven itself technologically. Also local conditions, such as the price of power, the size of the plant and the availability of certain raw materials, are of great importance in defining the choice of process to be used. Therefore, we present in this paper some examples of chemical processes which, by the improvement of catalysts, have undergone or will undergo drastic changes.

A great research effort has been invested the world over in homogeneous catalysis and, in spite of original pessimism in some quarters, processes have started to appear which compare favourably with the parallel processes, using heterogeneous catalysts.

Improvements in existing heterogeneous catalysts have also brought down drastically the reaction temperature and pressure of some processes, but this does not always necessarily mean that the new process is better under all conditions.

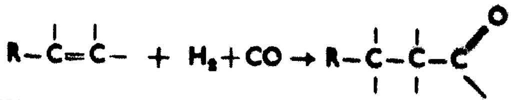
We shall give some significant examples of processes for which new catalysts have been developed, and instead of giving an exhaustive review, intend more to give some typical examples as to which factors, from the chemical point of view, should be taken into account when one considers buying new technology.

II. EXAMPLES

1. THE OXO-PROCESS (HYDROFORMYLATION)

The OXO-synthesis is concerned with the addition of CO and H_2 to a double bond. Two isomeric products are usually formed:

a)

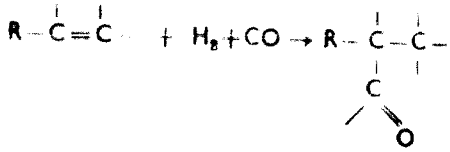


$$R-C=C- + H_2 + CO \rightarrow R-C-C-C\!\overset{O}{\lt}$$

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.129/7.

[2] Weizmann Institute of Science, Rehovot, Israel.

b) 

$$\mathrm{R-\overset{|}{C}=\overset{|}{C} + H_2 + CO \rightarrow R-\underset{\underset{\displaystyle C{=}O}{|}}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-}$$

Because, for many applications, the linear product is the more desirable one, the task of the catalyst is to give a maximal linear to branched ratio. Moreover, it is often the alcohol and not the aldehyde which is the desired product, and a catalyst which not only catalyzes the hydroformylation but also the hydrogenation of the aldehyde into alcohol, is even more preferable.

The classical catalyst for this reaction is based on cobalt, which is brought into the reaction mixture in the form of one of its salts. The active catalyst has been shown to be cobalt-hydrogencarbonyl, $HCo(CO)_4$, which is soluble in the reaction mixture. Being concerned with a homogeneous catalyst, one of the important features of the process therefore is the recovery of cobalt.

One of the pioneers in improving this process has been the Shell Company, which improved the performance of the cobalt catalyst by adding extra ligands which are almost exclusively tertiary organophosphines, R_3P. Although hundreds of ligands are claimed to be effective in the patent literature, it seems that tributylphosphine and tricyclohexylphosphine are the ones actually used. Although the reaction has to be run under more severe conditions using these catalysts, they give a higher normal to branched ratio and also hydrogenate part of the aldehydes formed.

A newer development is the use of rhodium instead of cobalt. Rhodium is one of the most expensive metals known, and a process using this metal as a catalyst is only possible when catalyst losses are brought down to the absolute minimum.

It has been shown that monovalent rhodium in the presence of triphenylphosphine is very efficient in catalyzing the hydroformylation reaction. It is possible to use concentrations in the range of $10^{-3}-10^{-4}$ M, to work at relatively low pressures and to obtain high linear to branched ratios. Especially when done with an excess of triphenylphosphine, the linear product is formed almost exclusively. Only aldehydes are formed and no alcohols, and higher boiling condensation products are less prominent with the rhodium catalyst than with the cobalt catalyst.

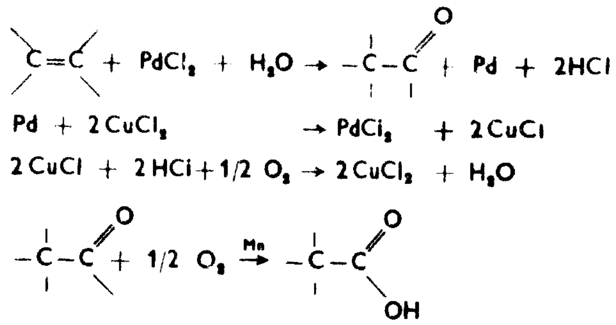
If only low boiling products are being produced, no catalyst separation is necessary and the products can be distilled directly out of the reaction mixture. The catalyst does not decompose under these conditions.

These features are so advantageous that it is rather probable that OXO-technology using rhodium catalysts instead of cobalt will appear on the market in the near future.

2. THE PRODUCTION OF ACETIC ACID

The classical way of producing acetic acid is by the oxidation of paraffins, especially n-butane. Cobalt and manganese salts are the catalysts used, and the reaction is run in the liquid phase, using a solvent. The oxidation is not very specific and many by-products have to be removed.

A serious competitor for this method is the Wacker process, which can be formulated as follows:



$Pd + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$

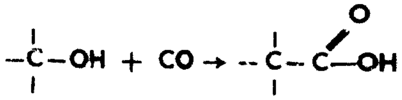
$2CuCl + 2HCl + 1/2\ O_2 \rightarrow 2CuCl_2 + H_2O$

Palladium chloride oxidizes ethylene to acetaldehyde and is reduced itself to palladium metal. Palladium metal is oxidized by copper chloride. The cuprous chloride formed is oxidized by air. This means that in the net reaction, ethylene is oxidized by air to acetaldehyde. Acetaldehyde can be oxidized into acetic acid, using a manganese acetate catalyst.

The same Wacker process is used for producing vinyl acetate, when a mixture of ethylene, acetic acid and oxygen is led over a palladium catalyst. It is even possible to produce the acetic acid in situ and to produce vinyl acetate from ethylene, air and water directly.

There exists a liquid phase process, using a homogeneous catalyst and a gas phase process, in which the palladium catalyst is precipitated on a carbon or alumina support. It seems that the heterogeneous gas phase process is more economical, because of the inevitable catalyst losses of the homogeneous process, which must be prevented when using an expensive material like palladium.

A more recent development in this field is the Monsanto process of making acetic acid out of methanol and carbon monoxide:



According to the patent literature, the catalyst is based on rhodium. This process is said to have important economic advantages over the Wacker process.

3. THE PRODUCTION OF AMMONIA AND METHANOL

The changes in ammonia production in recent years have been mostly of a technological nature. Because of improvements in the manufacture of synthesis gas, which enables operation of the plant at 35 atmospheres instead of 5 and the use of centrifugal compressors which can compress the gas in one step to 200 atm., ammonia synthesis presently run at 200 atm. instead of 300 atm. previously. The lower conversions per pass are more than compensated for by the greater ease of recycling the gases. The conventional synthetic ammonia catalyst has not undergone drastic changes.

The conventional way of synthesizing methanol from synthesis gas uses technology similar to that used in ammonia synthesis. Temperatures of several hundred degrees Celsius and pressures of several hundreds of atmospheres are used. In this case, new catalyst development has brought about a decrease in working temperature and pressure. By using zinc-copper chromites instead of the zinc-chromite catalyst, it has become possible to design plants that work at 50 atm. pressure and approximately 250°C.

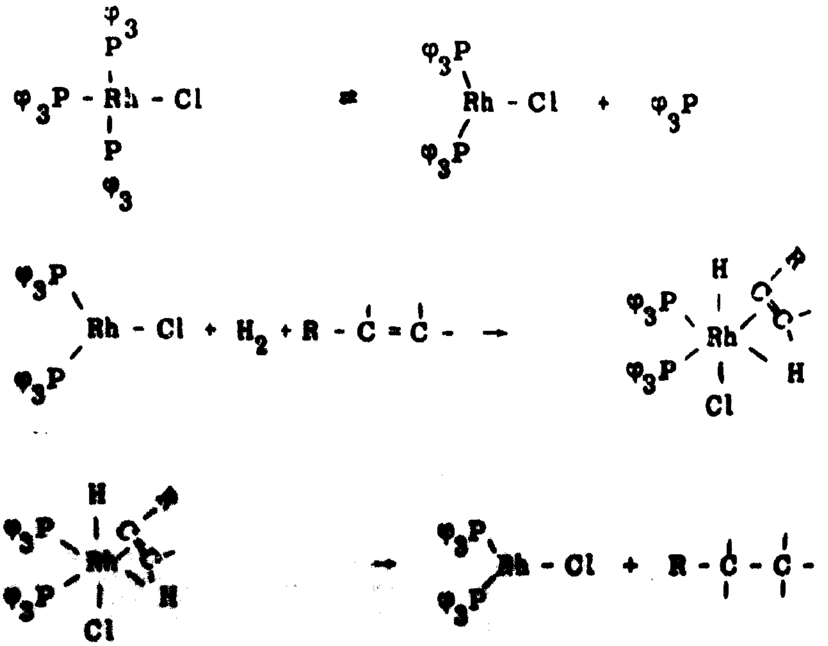
These technological and chemical considerations have some interesting implications. As in a developing country, the need for ammonia is probably felt at an earlier stage than the need for methanol, because ammonia is a fertilizer ingredient and methanol, a chemical intermediate, one might consider planning an ammonia plant such, that at a later stage it can be converted into a methanol plant, when ammonia capacity has to be extended. In such a case it would not be advisable to use the low pressure methanol technology. But also in other cases, the fact that a process can be run at lower pressures and temperatures does not always mean an economic advantage. This should always be weighed carefully against factors such as the price of electrical power and the turnover of the plant.

4. HYDROGENATION

Hydrogenction is an operation which is used in many processes and ranges from the massive hydrogenation of benzene into cyclohexane to the specific partial hydrogenation of fatty acids employed in modern margarine manufacture.

Although heterogeneous catalysts based on the conventional noble metals and nickel and cobalt still dominate the field, new developments in homogeneous hydrogenation are so rapid that we should like to discuss some of these aspects. It is quite conceivable that some homogeneous catalysts will find a place in this field in the near future.

The best studied of all homogeneous hydrogenation catalysts is tris (triphenylphosphine) rhodiumchloride, wich is assumed to work as follows:



The tris (triphenylphosphine) rhodiumchloride loses one triphenylphosphine ligand in solution and the resulting bis (triphenylphosphine) rhodiumchloride complexes with one molecule of hydrogen and the olefin. The hydrogen adds to the double bond of the olefin in the complex shell and the paraffin thus produced leaves to make place for a new set of hydrogen and olefin.

This catalyst works efficiently at ambient conditions of pressure and temperature in organic solutions at very low concentrations. The fact that the catalyst is a homogeneous might be a drawback in many cases, because the expensive catalyst has to be recovered quantitatively.

Several patents describe methods to bind the homogeneous catalyst to an insoluble carrier, by which means this disadvantage can be circumvented.

For instance, the carboxylates of noble metals like rhodium, ruthenium, iridium or rhenium in their bivalent states are good hydrogenation catalysts in the presence of triphenylphosphine in methanol solution. If the carboxylate anion is replaced by a cation exchanger:

$$Rh_2(CH_3COO^-)_4 + \text{cation exch.} \rightarrow Rh^{2+}\ (\text{cation exch.}) + CH_3COOH$$

A heterogeneous catalyst is obtained which, in the presence of triphenylphosphine in methanol solution is capable of hydrogenating olefins. In such a case catalysts are obtained that combine the virtues of a homogeneous and a heterogeneous catalyst in such a way that, after the reaction, the catalyst can be removed by filtration.

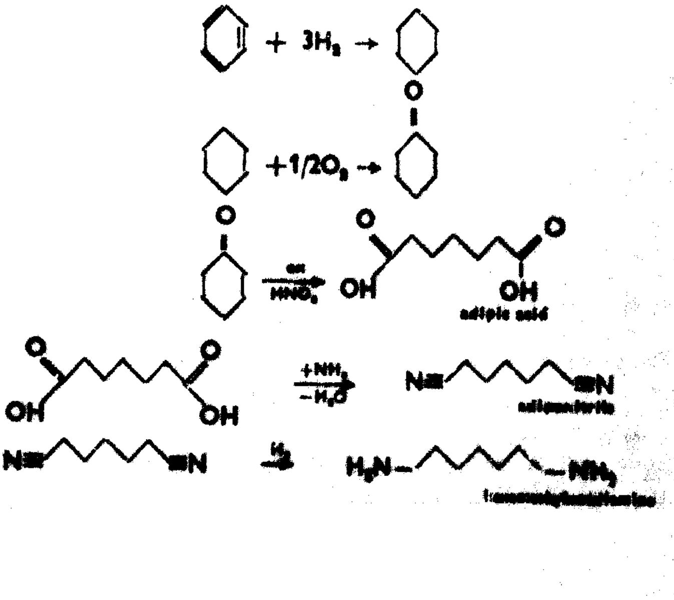
Other very active hydrogenation catalysts can be obtained by the combination of a transition metal salt and a derivative of lithium aluminium hydride. In particular, salts of titanium and cobalt are extremely effective. For instance, a mixture of cobalt bromide and $LiAlH(OtBu)_3$ in a ratio of one to four at a concentration of 3 m mol/L is capable of hydrogenating cyclopentene in tetrahydrofuran at a rate of 0.44 mole H_2/litre/min., which is extremely fast.

There are numerous examples of other very active homogeneous hydrogenation catalysts and certainly several of them will find their way into technological hydrogenation processes in the near future.

5. NYLON 6–6 INTERMEDIATES

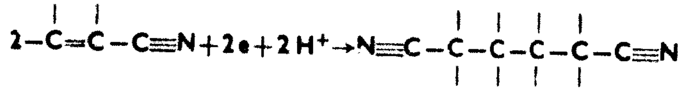
The conventional way of producing nylon 6–6 intermediates is based on cyclohexanone, which is obtained by the oxidation of cyclohexane which, in turn, is based on benzene.

In short:



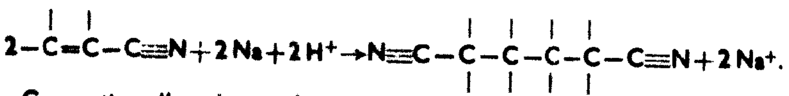
The production of adipic acid following this route is quite satisfactory, and the improvement which is sought is to perform the oxidation of cyclohexanone by air and not by nitric acid, which would be expected to lower its price.

Hexamethylenediamine, on the other hand, is too expensive by this route and several other routes are being tried, some of which will appear as available technology in the near future. One of these is the dimerization of acrylonitrile, itself a raw material for artificial fibres. Many catalysts have been developed to effect this dimerization, but none seems to be too successful. An electrochemical route has been developed by Monsanto and is in actual production:



$$2-\overset{|}{C}=\overset{|}{C}-C\equiv N+2e+2H^+\rightarrow N\equiv C-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-C\equiv N$$

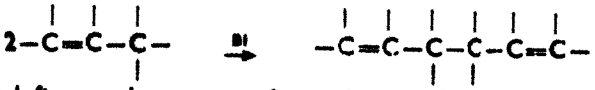
Another interesting possibility has reached the pilot stage. It utilizes sodium amalgam, which is formed during conventional salt electrolysis for chlorine production:



$$2-\overset{|}{C}=\overset{|}{C}-C\equiv N+2Na+2H^+\rightarrow N\equiv C-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-C\equiv N+2Na^+.$$

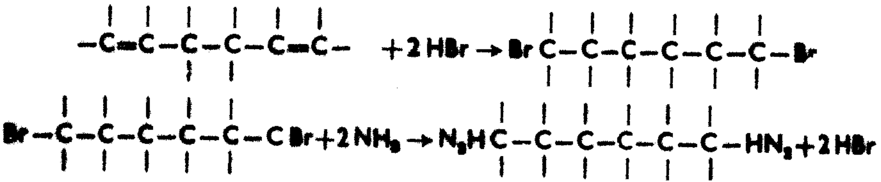
Conventionally, the sodium amalgam is subsequently decomposed with water to give a caustic soda solution. In the proposed process the amalgam would be used for adiponitrile production, still ending up with a caustic soda solution.

One drawback of all the methods in which adiponitrile is an intermediate is the rather cumbersome reduction of nitrile to primary amine, which suffers from short catalyst life and the formation of secondary and tertiary amines. There are patents that describe other methods of synthesis in which the amine is not formed via a nitrile. For example propylene can be dimerized rather efficiently using a bismuth catalyst:



$$2-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\xrightarrow{Bi}-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-$$

This diolefin can be converted into hexamethylenediamine by the addition of HBr and reaction with ammonia:



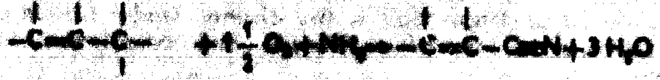
$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\overset{|}{C}=\overset{|}{C}-+2HBr\rightarrow Br\,\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-Br$$

$$Br-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-C\,Br+2NH_3\rightarrow N_2H\,\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-HN_2+2HBr$$

Although the technology for converting a terminal double bond into a primary amine with the help of HBr is known and has been used for years to produce nylon eleven, no processes are on the market at the moment to produce hexamethylenediamine this way, but they might well be developed in the future.

6. AMMOXIDATION

The production of acrylonitrile by the oxidation of propylene in the presence of ammonia in a fluidized bed reactor has been a major advent in the last decade:



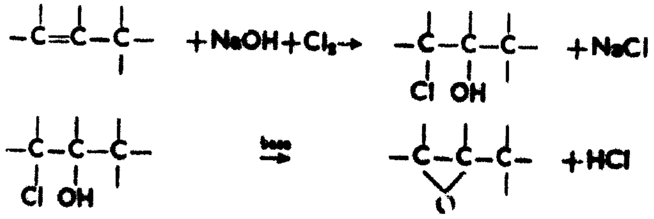
$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}-+1\tfrac{1}{2}O_2+NH_3\rightarrow-\overset{|}{C}=\overset{|}{C}-C\equiv N+3H_2O$$

The catalyst most used is bismuth molybdate, which produces about 10 per cent of acetonitrile as a by-product. The Sohio Company in the United States of America has developed a uranyl antimonate catalyst, which yields more acrylonitrile and less acetonitrile. The Montecatini-Edison Company in Italy has developed a tellurium molybdate catalyst which seems to be as satisfactory as the other catalysts in use.

A drawback of the ammoxidation process is that its minimum size of economic production is rather large, as is the case with most fluidized bed processes. Therefore, a process to make hexomethylenediamine from acrylonitrile is very important because the same acrylonitrile plant delivers raw materials for acrylic fibres as well as nylon.

7. EPOXIDATION

The epoxidation of ethylene with air to give ethylene oxide is an established process, using silver catalysts. The direct oxidation of propylene, however, according to this method, is very difficult and most propyleneoxide is still made according to the established chlorohydrin route:



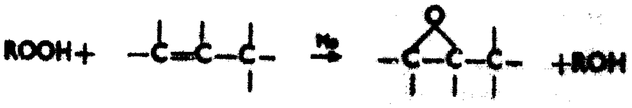
$$-\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}- \;+ NaOH + Cl_2 \rightarrow -\underset{Cl}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \;+ NaCl$$

$$-\underset{Cl}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}- \xrightarrow{\text{base}} -\overset{|}{C}-\overset{|}{C}-\underset{|}{\overset{|}{C}}- \;+ HCl$$

Several new processes have been developed recently or are being developed. One is to effect the same chlorohydrin reaction in an electrochemical cell. This route might be important for countries which do not have enough chlorine available. By electrolysis of NaCl, chlorine is formed at the anode; it is brought into contact with propylene and forms chlorohydrin. This diffuses to the cathode, where, because of the high pH, it is decomposed into propylene oxide and NaCl is formed again. The net process is thus an electrochemical oxidation of propylene into propylene oxide. This process is under development and might, under special circumstances, be competitive with the clorine route.

An entirely different process has been developed by Scientific Design Inc. It is based on an interesting catalytic reaction between organic hydroperoxides and an olefin:

$$RH + O_2 \rightarrow ROOH$$



$$ROOH + -\overset{|}{C}=\overset{|}{C}-\underset{|}{\overset{|}{C}}- \xrightarrow{Mo} -\underset{|}{C}-\underset{|}{C}-\underset{|}{C}- \;+ ROH$$

A hydrocarbon is oxidized to a hydroperoxide with air and the hydroperoxide reacts with propylene to give propylene oxide and an alcohol. Compounds of molybdenum seem to be the best catalysts for this latter reaction.

One of the disadvantages of this process is that the production of propylene oxide is coupled with that of an alcohol, for which a market has to be found. If, for instance, ethylbenzene is the hydrocarbon, styrene can be produced by dehydration of the alcohol. Under certain conditions it might be attractive to produce styrene and propylene oxide in the same plant.

Several companies are actively studying the oxidation of propylene to the oxide directly with air, as is done with ethylene, and technology based on this direct oxidation might well be available in the near future.

III. CONCLUSIONS

Some of the newer trends in catalysis for the production of chemicals have been described. Any choice concerning the type of process to be bought is dependent on local conditions. An electrochemical route, for instance, might be advantageous in countries where electrical power is cheap and only a small factory size is necessary for the time being. OXO-technology and the production of ammonia and methanol are in a state of flux, and more advanced technology may be expected in the near future. Nylon production can be coupled with salt electrolysis and acrylonitrile production, and styrene, with that of propylene oxide. Although processes which give coupled products are not always attractive to the big producer in a developed country, they may be attractive to a developing country. Therefore, local conditions dictate the choice of processes to be bought. The trends described here may be of help to those who have to make this choice.

ACTIVITY AND LIFE OF CATALYSTS FOR THE PRODUCTION OF AMMONIA[1]

S. P. S. ANDREW[*]

The ammonia plant manager is more concerned about the life and reliability of the catalysts which form the heart of modern plants than he is about their initial activity, provided this is adequate. Yet there is no aspect of the technology of catalysis less quantified than life and the factors which determine it, and no phenomenon more open to being dismissed with the pseudo-explanation that the catalyst was "poisoned" than an undesirably early loss of activity of a plant catalyst. In this paper many of the catalysts which are required in modern ammonia plants will be considered with particular reference to their activity and life, with the aim of showing how the catalyst manufacturer, through a knowledge of the structural changes which take place in catalysts over long periods of time in use, can so formulate his products and recommend to the plant operator the optimum conditions for their use that they are better able to retain their activity over years of ammonia production.

I. CATALYSTS FOR AMMONIA PRODUCTION

The process unit sequence employed in ammonia synthesis (figure 1) consists essentially of three synthesis reactions, each preceded by the appropriate gas purification operations which are designed to reduce greatly the concentration of components which would otherwise cause rapid deactivation of the synthesis catalysts. Thus the production of CO and H_2 from naphtha in the primary and secondary reformers is preceded by feedstock desulphurization. During desulphurization sulphur is liberated as H_2S by hydrogenolysis of the sulphur-containing species in the feedstock using hydrodesulphurization catalyst, followed by removal of this H_2S by reaction with solid ZnO to form ZnS. The efficacy of this removal crucially affects the performance of the primary reforming catalyst, so that the duty of the desul-

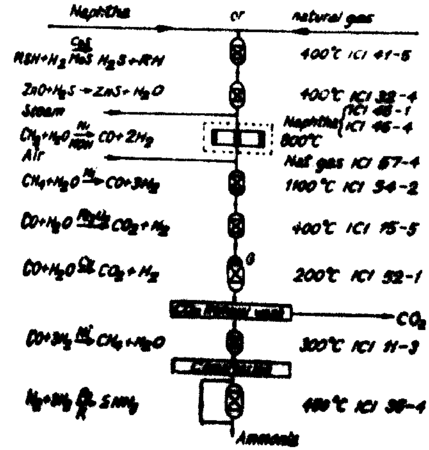


FIGURE 1. THE MODERN AMMONIA SYNTHESIS ROUTE

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/16.

[*] Imperial Chemical Industries Ltd., Billingham, Teesside, United Kingdom of Great Britain and Northern Ireland.

phurization section is determined by the sensitivity to sulphur of the reforming catalyst.

It has been recently discovered that the life of the low temperature shift catalyst, used for converting CO to CO_2, is markedly influenced by the presence of halogens in the gas stream. A halogen guard absorbent is therefore, on modern plants, often inserted before the low temperature shift catalyst.

It has long been known that oxygen-containing compounds, if in excess, cause rapid loss of activity of the ammonia synthesis catalyst. The methanation stage immediately preceding ammonia synthesis is the means by which CO_2, and even more important, CO are removed.

Because of these relations between synthesis catalysts and purification operations this paper will consider each of the synthesis catalysts in turn and the manner in which its activity and life are affected by poisons. The requirements of the appropriate purification operations, and the catalysts used in them, are then sketched with particular emphasis on recent developments in both stages. Naturally in a paper as short as this only highlights can be included.

II. STEAM NAPHTHA REFORMING

The discovery that a sufficient addition of potash in an available form enabled a supported nickel catalyst to be capable of steam reforming naphtha at low steam ratios was made in 1959 and revolutionized the gasmaking stage in ammonia production for localities where natural gas was not available. The mode of action of this catalyst (ICI 46-1) is shown in a simplified manner in figure 2. The ability of this catalyst to operate without carboning up is obtained not so much by inhibiting the carbonforming reaction (thought the non-acidic support used does not promote carbon formation) but rather by introducing a second active component into the catalyst formulation, mobile alkali, which serves to catalyze the steam oxidation of any carbon that does form. Although both alkalies and alkaline earths have been shown to be capable of catalyzing the steam oxidation of carbon when they are intimately mixed prior to reaction, the alkaline earths are refractory and are not capable of self-mixing, by diffusion, with carbon forming on a nickel surface. Potash, at the temperature of steam reforming, is, however, able to do so. This is the likely cause of its unique efficacy.

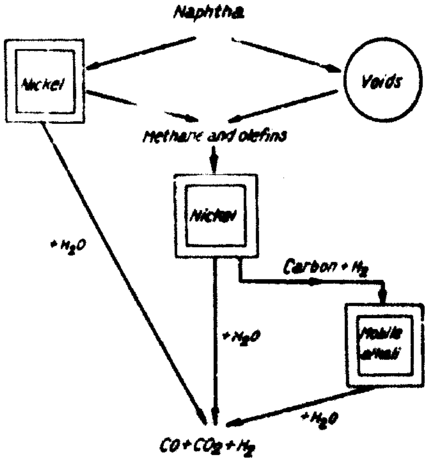


FIGURE 2. DUAL FUNCTION ACTION IN STEAM NAPHTHA REFORMING CATALYST (ICI 46-1) REQUIRED TO SUPPRESS DEACTIVATION BY CARBON FORMATION

The necessary mobility of potash in two dimensions unfortunately results in some mobility in three dimensions. The potash slowly vaporizes and passes out of the reformer, on occasions depositing in the waste heat boiler or the inlet of the high temperature shift catalyst and in time reducing the performance of these units so that ultimately they must be cleaned. The potash also tends, by obscuration, to reduce somewhat the activity of the nickel surface for methane reforming. During the past ten years, means have therefore been sought of overcoming these disadvantages without losing the proven good abilities of 46-1 in steam naphtha reforming. A dual catalyst system employing catalyst 46-1 in the top (inlet) part of the reformer tube and a non-potash-evolving catalyst in the lower part of the tube has been shown to be the preferred method. A combination of three quarters tube of 46-1 and one quarter tube of 46-2 has been used for several years for this purpose. Recently, as a result of further research, a combination of one half tube of 46-1 and one half tube of 46-4 has been developed. Figure 3 shows that as a result of these innovations it is now possible to reduce potash evolution to about one quarter of that for 46-1 alone, whilst at the same time reducing the approach to the methane-steam equilibrium at the exit of the reformer tube by about a factor of four.

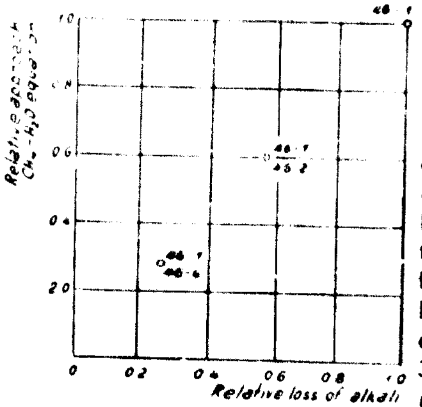


FIGURE 3. RELATIVE LOSS OF ALKALI. THE USE OF 46-1 and 46-4

The latter change permits, for instance, such improvements as reducing the tube temperature for a given methane content of the product gases.

III. STEAM METHANE REFORMING

The carbon forming tendencies of hydrocarbons undergoing pyrolysis diminish with decrease in their molecular weight and boiling point to such an extent that it is possible to steam reform methane at low steam ratios without the necessity of using a catalyst containing mobile alkali, provided the catalyst has an adequate low temperature activity. The reason for this requisite may be seen by reference to figures 4 and 5. Carbon formation renders the catalyst ineffective when its rate of formation by pyrolysis on the surface of existing pyrolysis carbon exceeds the rate at which this carbon is being removed by steam gasification.

The hydrocarbon pyrolysis reactions have a markedly higher activation energy than the uncatalyzed steam gasification reaction, in consequence high temperatures favour carbon build-up. This feature is illustrated on figure 4, which very roughly indicates the relative rates of carbon formation and carbon removal for a range of hydrocarbons as a function of temperature for both uncatalyzed and potash catalyzed carbon removal reactions at low steam ratios. The addition of potash, it will be seen, increases the carbon removal rate at temperatures above 525°C at least one thousand fold. Below 475°C the effect of potash rapidly decreases and is small at 400°C because of its low mobility at these lower temperatures.

For methane reforming the formation rate line intersects the uncatalyzed removal rate line at about 660°C showing that provided the methane concentration is reduced in the steam reforming below the carbon-methane equilibrium partial pressure before the reforming gas mixture reaches 660°C then carbon build-up should not occur on a non-potash containing

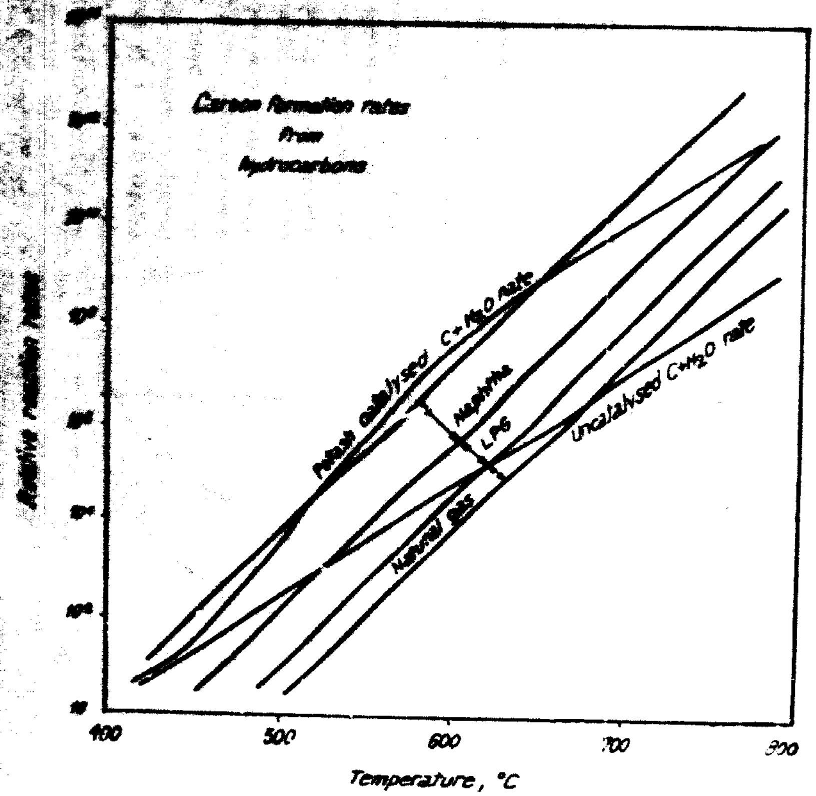


FIGURE 4. CARBON FORMATION AND REMOVAL IN THE STEAM REFORMING OF HYDROCARBONS AT LOW STEAM RATIOS

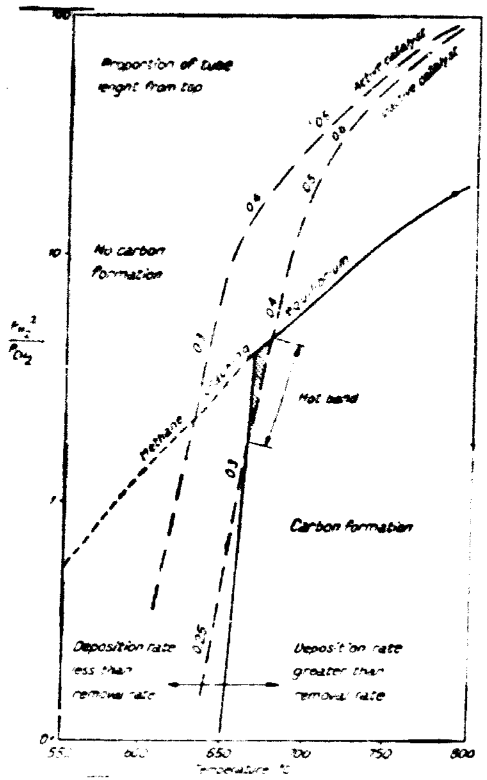


FIGURE 5. FORMATION OF A HOT BAND IN A METHANE REFORMER

catalyst. With higher boiling point hydrocarbons this critical temperature is, as can be seen from figure 4, lower, and the requisite reforming activity is so difficult to obtain at the lower temperatures particularly in view of sulphur poisoning that a potash containing catalyst must be employed if long catalyst life is required.

The necessity for using a steam reforming catalyst having a good low temperature activity when reforming natural gas or methane in the absence of potash catalyst is readily seen from figure 5 which is plotted to demonstrate why "hot bands" occur in reformer tubes when the catalyst is insufficiently active. Figure 5 is based on the methane pyrolysis equilibrium, $CH_4 \rightleftharpoons C + 2H_2$ plotted as a function of temperature, and the equal rate line where carbon deposition rate equals removal rate. If gas compositions anywhere in the reformer fall in the right-hand bottom corner of figure 5 as defined by these two lines, then carbon will be formed and will accumulate. With an inactive reforming catalyst the composition-temperature sequence down the reformer shown by the right-hand broken line is followed. Carbon formation occurs between 660°C and 675°C and a "hot band" is visible on the reformer tube where the carbon acts as an internal insulant. With an active catalyst the composition-temperature sequence follows the left-hand broken line being well clear of the carbon formation region and hence no "hot band" is formed.

IV. DESULPHURIZATION

Sulphur, either in the form of H_2S, COS or organic sulphur compounds is normally present in all hydrocarbon feedstocks for steam reformers and must be removed down to low levels as it poisons the nickel catalyst. The extent of nickel poisoning for two different sulphur levels is shown in figure 6 as a function of temperature. Used in conjunction with figure 4 which requires substantial removal of hydrocarbons by steam reforming before the steam/hydrocarbon mixture attains a temperature of about 650°C (whether reforming natural gas over a non-potash catalyst or naphtha over a potash containing catalyst) then it is evident that the nickel must have substantial activity in the temperature range 550 to 650°C. Figure 6 there-

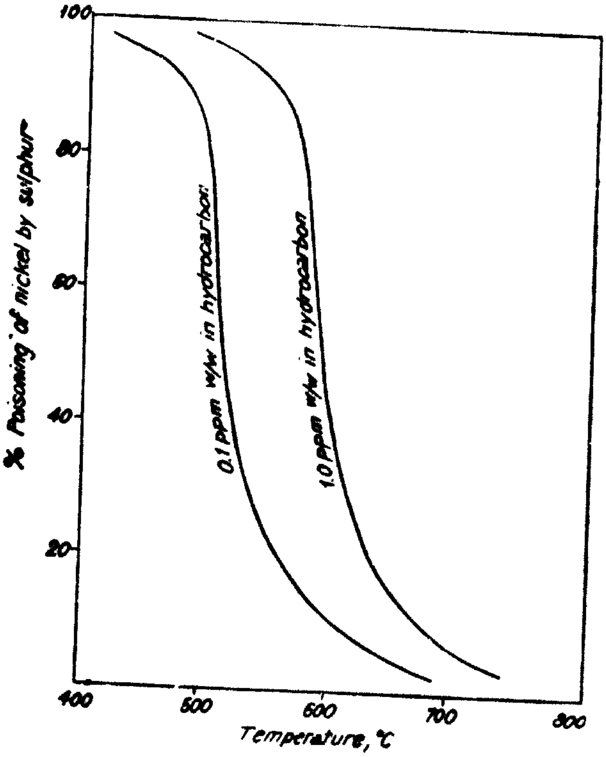


FIGURE 6. SULPHUR POISONING OF NICKEL IN HYDROCARBON STEAM REFORMING

fore indicates that sulphur must not be present in the feedstock to an extent greater than about 0.5 ppm.

In order to attain the almost complete removal of sulphur required by the reforming stage a sulphur removal unit is necessary for prior processing of the hydrocarbon. The form of this unit depends on the type and amount of sulphur compounds in the feedstock and these are primarily dependent on the feedstock boiling points. Thus naphthas contain substantial quantities of thiophenic compounds which must be treated with an active hydrodesulphurization catalyst (typically a cobalt molybdate catalyst) in order to liberate H_2S to be subsequently absorbed in zinc oxide, whereas natural gas may contain sulphur compounds such as H_2S, COS, RSH or RSR and very occasionally small quantities of a stenching agent such as tetrahydrothiophene. Active carbon is used on many plants to remove sulphur from natural gas, but its capacity for H_2S and COS is limited. The system, however, often proves unreliable due to uncertainties in regeneration or because of the presence of higher hydrocarbons in the natural gas. This can lead to premature sulphur break-through. A more efficient and reliable system uses a cobalt molybdate catalyst with recycle hydrogen to convert all the sulphur to H_2S which is absorbed by zinc oxide. If only H_2S and COS are present, zinc oxide alone is adequate for sulphur removal.

As with most catalysts operating on hydrocarbon systems, cobalt molybdate catalysts can become deactivated in time due to carbon deposition. The formulation of the catalyst support and the operating temperature are most important factors in determining the rate at which carbon deposition occurs. Alumina silicates are acidic and promote cracking and carbon deposition. Even alumina is somewhat acidic, and the more basic a support is, the less the rate of carbon formation at a given temperature of operation. Typical data from accelerated laboratory tests in which an acidic alumina-supported cobalt molybdate was compared with a non-acidic-support cobalt molybdate (ICI 41-5) with respect to carbon deposition are shown in figure 7. With suitable formulation both these cata-

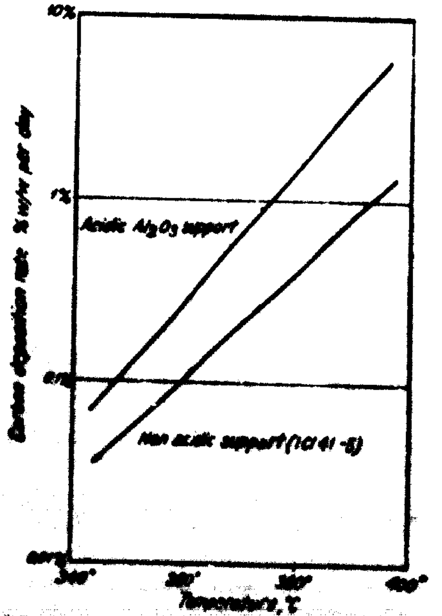


FIGURE 7. INFLUENCE OF COMPOSITION ON RATE OF CARBON DEPOSITION ON COBALT MOLYBDATE HYDRODESULPHURIZATION CATALYSTS

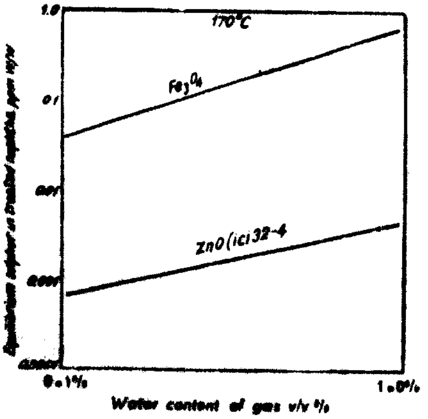


FIGURE 8. EQUILIBRIUM SULPHUR AS H_2S IN TREATED NAPHTHA FOR Fe_3O_4 AND ZnO ABSORBENTS

lysts have the same initial activity (at a fixed temperature of operation) but the non-acidic supported catalyst takes longer to become carboned up.

The rate of carbon deposition is, of course, also markedly dependent on the feedstock. In general, heavier feedstocks tend to carbon up the catalyst more readily and hence should be hydrodesulphurized using non-acidic supported catalysts whereas lighter feedstocks can be satisfactorily treated with more acidic supports.

The requirements for efficient absorption of the H_2S liberated sets a severe duty on an H_2S absorbent. ZnO is the preferred absorbent, as the equilibrium H_2S over ZnS is only about one-hundredth of that for Fe_3O_4 as can be seen from figure 8.

V. WATER GAS SHIFT REACTION

The material efficiency of the conversion of naphtha into ammonia in a modern ammonia plant is markedly dependent on the ability of the low temperature water gas shift reactor to replace CO by H_2. Every molecule of CO slipping past this reactor represents a loss of four molecules of hydrogen in the make-up gas to ammonia synthesis, together with a further loss of hydrogen in the synthesis loop purge required to remove the additional methane formed by methanating this CO. Reliable behaviour in use of the low temperature shift catalyst is, therefore, most desirable. Experience has shown that two factors which are most important in securing freedom from rapid loss of activity of copper-containing low temperature shift catalysts are firstly, correct formulation, and secondly, the absence of chlorine poisoning. Figure 9 shows clearly how important is the correct choice of preparation conditions in securing life, as two catalysts of identical chemical compositions have very different die-off curves.

The reason for this difference can best be understood by reference to the sketch in figure 10, which has been drawn up as a result of X-ray diffraction, electron microscopy, surface area and other physical investigations of the structure of these types of catalyst. Essentially, in order to secure long life the metal crystals must be separated from one another by small refractory oxide crystals.

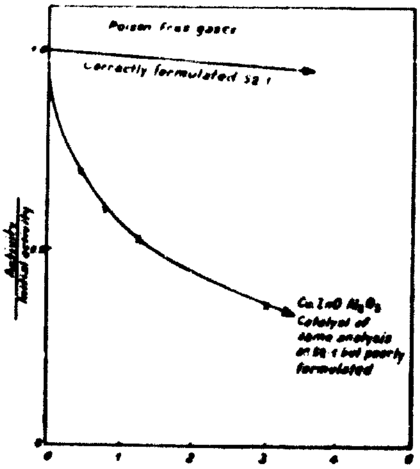


FIGURE 9. INFLUENCE OF METHOD OF FORMULATION ON THE LIFE OF LOW TEMPERATURE SHIFT CATALYST

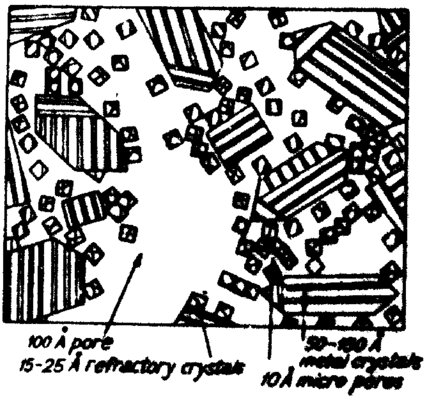


FIGURE 10. HYPOTHETICAL PICTURE OF A METAL + REFRACTORY CATALYST PREPARED BY PRECIPITATION AND REDUCTION

Furthermore, in order to secure high activity the scale of this geometry must be very small. The copper crystals in ICI 52-1 are only about 100 Å (10^{-6} cm) in diameter. The refractory crystals are even smaller, only same 20 Å in diameter. Provided a small but even separation of the metal crystals is produced, by a suitable catalyst preparation procedure, then even over-heating of the catalyst does not produce sintering of the copper and loss of activity, provided halogens such as chlorine are absent. In the presence of halogens, however, the structure of the catalyst is rendered mobile and recrystallizatoin takes place, driven by the thermodynamic differences in chemical potential between small and large crystals. The rate at which this phenomenon takes place is, for a given formulation, primarily a functian of the halogen level. Typically this recrystallization process, which is similar in principle to Ostwald ripening of precipitates, follows the law indicated in figure 11.

This type of plot of log activity against log time is very useful for predicting life from relatively short term data. Chlorine "poisaning" af the above type is, af course, nat a true poisoning but an acceleration af the structural collapse af the catalyst. It is necessarily irreversible and the only method of preventing it is to stop chlorine from reaching the catalyst by the use of a guard absorbent.

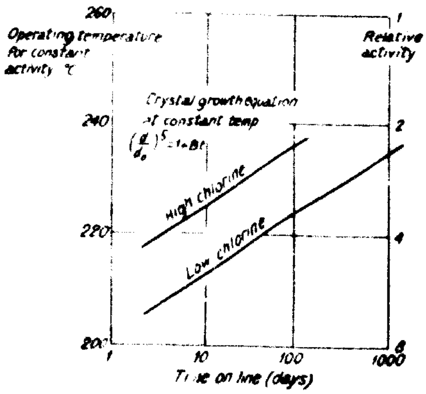


FIGURE 11. LOSS OF ACTIVITY DUE TO METAL CRYSTAL GROWTH IN A SUPPORTED COPPER CATALYST

Levels of chlorine greater than 0.01 ppm in the gas can have a serious effect on the catalyst life. Two types of guard have been devised by ICI. One (ICI 59-1) is for use where chlorine contaminatian is liable to be heavy, the second (ICI 52-1G) is for use where chlorine is less plentiful. The second type also has high shift catalytic activity and is not simply an absorbent as is the first type.

VI. AMMONIA SYNTHESIS

Very much has been written on the kinetics of ammonia synthesis from the standpoint of the chemist. Rather less has been written from the point of view of the catalyst user and the subject of catalyst life is very little discussed in a quantitative manner. Unlike most other catalysts, ammonia synthesis catalyst is available in a wide range of particle sizes, derived by different degrees of crushing and sieving of the frozen iron oxide-promoters melt. The smaller the particle size, the greater the catalyst activity (figure 12). This increased activity is only secured, however, at the expense of an inherently higher pressure drop, which increases more rapidly with decrease in particle size than does the activity. The plant operator should choose an optimum size range bearing in mind the restrictions obtaining on his plant.

The rate of loss activity of ammonia synthesis catalysts in modern ammonia plants should be much less than those in old plants because of the greater purity of the make-up gas to the synthesis loop. Catalyst life should also be longer, although the plant designer anxious to economise on capital cost will no doubt have partly offset the advantage gained by lower die-off rate by reducing the volume of catalyst in the converter.

Oxygen containing compounds are the primary cause of loss in activity in modern plants. In particular, CO slipping the methanator passes straight to the synthesis catalyst. In the modern synthesis loop both H_2O and CO_2 are finally removed by passing the make-up gas along with converted gas through the ammonia separation section of the synthesis loop. The condensing ammonia then effectively scrubs both these species from the gas stream.

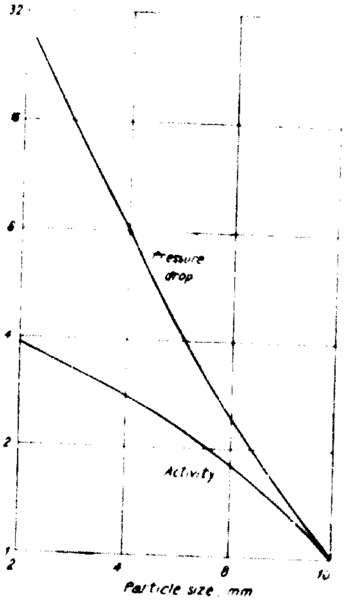


FIGURE 12. **RELATIVE ACTIVITIES AND PRESSURE DROPS AS A FUNCTION OF PARTICLE SIZE FOR NH_3 SYNTHESIS CATALYST (ICI 35-4)**

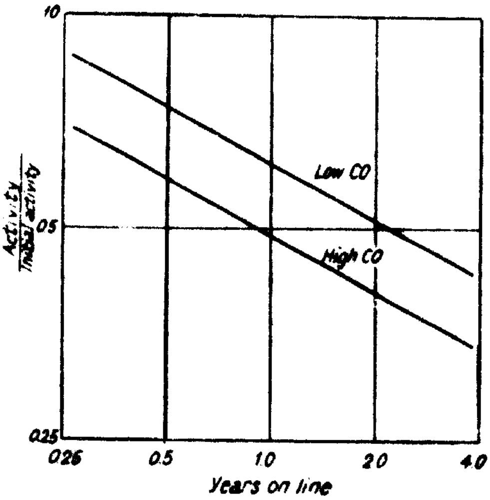


FIGURE 13. **POISONING OF AMMONIA SYNTHESIS CATALYST**

Oxygen compounds have both a temporary and a permanent effect on the synthesis catalyst. The temporary effect is due to chemisorption which is greater at lower catalyst temperatures. The permanent effect is more significant, as it results in an accelerated destruction of the catalyst surface due to crystal growth. Typical die-off plots for high and low CO in the gas entering the synthesis converter (not the make-up gas) are shown in figure 13. This figure has been plotted in the same manner as figure 11 for low temperature shift catalyst, as both die-off phenomena are the result of accelerated recrystallization. In modern plants it is desirable to reduce CO to 1 ppm or less, which corresponds to between 3 and 5 ppm exit the methanator, depending on the recirculation ratio in the loop.

VII. METHANATION

Consideration of the effects of oxygen-containing compounds, in particular CO, on the life of the ammonia synthesis catalyst thus define a required performance of the methanator. Choice of catalyst formulation for methanation in order to secure high activity is important. Even more important is a uniform charging of the catalyst in the reactor so that the catalyst bed has a uniform density. Usually methanators have a single adiabatic bed of catalyst. Gas enters containing some 3,000 ppm of CO and should leave at only 3 ppm CO, a thousand-fold reduction in concentration. Under these circumstances it is most important that the catalyst charge has a uniform voidage across the reactor cross section. The consequences of non-uniform voidage in reducing the performance of the methanator may be seen from figure 14, which has been calculated for a methanator designed to give an exit concentration of the total carbon oxides of 10 ppm. Differences in voidage of 15 per cent are surprisingly easy to achieve if the catalyst is weak or is charged in an asymmetric manner.

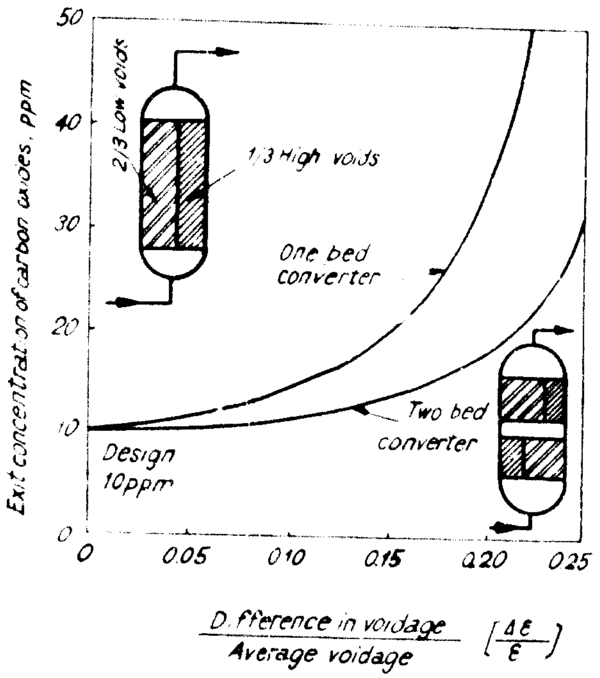


FIGURE 14. INFLUENCE OF UNEVEN PACKING OF CATALYST ON PERFORMANCE OF A METHANATOR

VIII. THE COST OF UNRELIABILITY

The modern ammonia plant process sequence, indicated in figure 1, reveals clearly how dependent the operation of this plant must be on the satisfactory performance of each of the catalysts or absorbents employed in sequence. No duplication of the major process items is normal, so that the failure of one catalyst results in the shut-down of the whole plant. It is therefore most important that, as all catalysts inevitably lose activity in time and therefore must be replaced, this loss of activity must proceed slowly and at a predictable rate, so that catalyst changes can be synchronized and unscheduled shut-downs for catalyst changes are minimized. Unscheduled shut-downs, if at all numerous, severely reduce plant availability and, in effect, increase the capital cost of the ammonia plant per ton of ammonia produced. Their economic effects are even more serious if, in addition, they reduce the output of the whole fertilizer plant through shortage of ammonia. Shut-downs and start-ups are also occasions of greater process and engineering hazard than is steady running. Shut-downs thus are liable to lead to further shut-downs. Even ignoring the indirect effects on the output of other dependent plants or the hazards associated with shut-downs, the major effect of catalyst unreliability can easily be appreciated from figure 15.

In this figure a comparison is made between the capital + catalyst cost per ton of ammonia produced for unreliable free catalysts and for

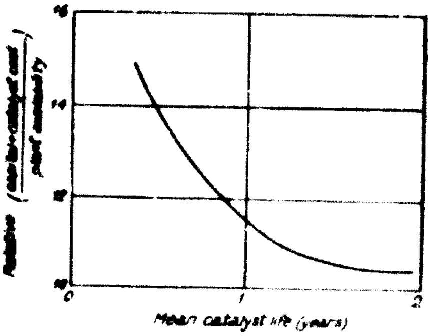


FIGURE 15. REAL COST OF "FREE" UNRELIABLE CATALYSTS RELATIVE TO RELIABLE PURCHASED CATALYSTS FOR AMMONIA PRODUCTION

reliable normal purchase price catalysts. Thus, taking a mean life of one year as an example, the free unreliable catalyst, it is assumed, might fail at any time between the first day on line and the end of the second year on line. The reliable catalyst fails at the end of one year, and it has to be purchased at the normal price. Because of the number of catalysts in sequence, unreliability leads to frequent shut-downs with the economic consequences evident from figure 15. Even when the mean life of both types of catalyst is as long as two years, the free unreliable catalyst is, in reality, more costly to the plant manager than is the purchased reliable catalyst. Reliability is worth purchasing, unreliability is expensive even if apparently free.

The consequences of relatively small amounts of sulphur entering the naphtha reforming catalyst, of chlorine entering the low temperature shift catalyst and of carbon monoxide entering the ammonia synthesis catalyst have been outlined above. It is worth while noticing that these levels of poison in the gas streams are not easy to measure. Frequently the plant manager only learns of the excessive levels of these poisons when it is too late and his catalyst has lost its activity and has been discharged and examined. His first defence against such a calamity must be an assurance that the appropriate purification systems, hydrodesulphurization plus zinc oxide, low temperature shift guard and the methanator have reliable catalysts in them, charged correctly, and operated in the correct manner. Poisons are not the only reasons for loss of activitiy of the reforming, shift and ammonia synthesis stages. Poor formulation of the reforming catalyst can lead to carbon laydown, poor formulation of the shift catalyst can lead to structural collapse with loss of copper surface area and activity, poor formulation of the ammonia synthesis catalyst leads to lack of stability relative to thermal sintering. These catalysts may also be damaged by mal-operation. The only sure course for the plant manager must therefore be both to choose reliable catalysts for all stages in ammonia synthesis and, having learnt the necessary conditions for optimum operation of these catalysts, to initiate operating routines which ensure, so far as is possible, that these conditions are adhered to.

IX. IMPLICATIONS FOR DEVELOPING COUNTRIES

The arguments put forward in this paper apply to all ammonia plants whatever their location. The ammonia plant operator in a developing country is, however, under greater pressure to operate his plant well because of the important place his plant occupies in the industrial sector of his country's economy. The fertilizer it produces is vital to the agricultural industry and enhances the quality of life of his fellow countrymen. Equally, while his country's technical infrastructure is developing, the plant manager is less likely to have as many highly qualified technicians and technical organizations ready to assist him in time of operating difficulties. His plant operators are often less experienced than those in an industrial country and spare parts and catalysts may not be so freely available

Because of all these factors the greatest care must be taken in selecting catalysts to be used in the ammonia plant. The choice must be made on the grounds of catalyst quality and reliability and the temptation to merely buy the cheapest catalyst must be resisted. It is the responsibility of management (and Government) to ensure that adequate funds are available for plant managers to buy the quality of catalyst they require. Any extra cost involved will be rapidly recovered in improved plant operation.

TRENDS IN THE DEVELOPMENT OF CATALYTIC PETROLEUM REFINING PROCESSES[1]

ION GHEJAN*

I. AN OUTLINE CATALYTIC PROCESSES DEVELOPMENT

The trends in the development of catalytic processes used in oil processing are a direct response to some of the major challenges facing the contemporary world: providing adequate resources to meet the steeply increasing worldwide energy demand and providing feedstocks for the great organo-chemical industry which is increasingly turning into a "petrochemical" one.

A massive growth in energy requirements is predicted for the next 10 years amounting to more than 50 per cent over the 1970 level and more than 50 per cent of these requirements are to be met by oil. In order to meet such demands, the crude processing capacity in 1980 will have to soar to 170 per cent of the 1970 figures (1).

This capacity was 2.6 billion tons/year on January Ist 1970; it will be in excess of 4.2 billion tons/year in the late 1970s (2).

Considering the present distribution pattern of oil products and the trends manifested in various countries, it may be assumed that in the future, as well developments in crude processing will vary according to the social-economic conditions and to the resources available in particular countries. This differentiation is tellingly illustrated by the oil products distribution pattern in the United States of America and in Western Europe. The comparison shown in figure 1 is significant in that two opposing tendencies prevail in the management of crude processing: in the United States, crude processing is oriented towards maximizing gasoline production, while in Western Europe it is directed towards obtaining heavier fuels (1). This is naturally reflected in the share catalytic techniques take in crude processing. In table I, a comparison is given between the capacities of the main processes in relation to crude processing capacities in Western Europe and the United States.

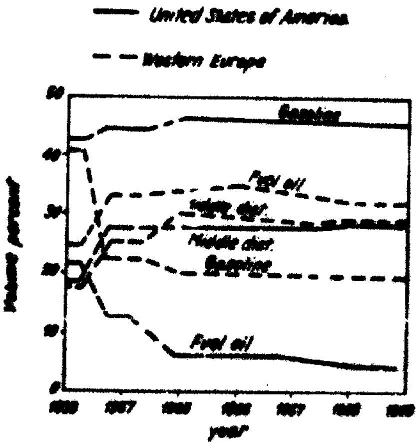


FIGURE 1. REFINING YIELDS

---

[1] This paper was issued in provisional form under UNIDO reference ID/WG.123/25.

* Romanian Research and Design Institute for Petroleum Refineries, Ploieşti, Romania

The author acknowledges the co-operation of T. [illegible] and S. [illegible].

TABLE I

PROCESS CAPACITIES IN REFINERIES IN RELATION TO TOTAL CRUDE PROCESSING CAPACITY

	Western Europe	United States of America
Crude capacity	100	100
Catalytic cracking and hydrocracking	8	51
Catalytic reforming	13	22
Alkylation	1	7
Thermal cracking	4	13

Current development trends have been computed from the capacities of the units expected to be built in various countries after January 1970. As the construction of these units may be expected to take about three years, this computation in fact offers a most up-to-date picture of the trends in the building of refineries around the world. The capacities of various processes, also in relation to crude capacities, are given in table II (1). Note that the table leaves out thermal cracking processes, as no data on their capacities were available; most of the projects refer to coking units.

TABLE II

PRESENT DAY DEVELOPMENTS IN CRUDE PROCESSING IN DIFFERENT PARTS OF THE WORLD

	North America	Latin America	Western Europe	Middle East and Africa	Japan	Asia and Australia
Crude capacity	100	100	100	100	100	100
Cracking:						
— Catalytic	17.4	28.7	8.4	17.7	13.3	0.0
— Hydro	33.1	1.6	3.8	15.1	9.5	0.0
— Total	50.5	30.3	12.2	27.8	22.8	0.0
Catalytic reforming	44.5	10.9	1.6	22.2	12.2	10.5
Alkylation	6.4	0.0	0.8	1.2	0.0	0.5

Comparing the data in table I and II, it appears that the trends previously presented for Western Europe and the United States have not changed greatly. It is noted that in North America, as well as in developing countries in Africa and the Middle East, there is a sharp increase in the application of hydrocracking processes. This is an expression of the desire to obtain higher yields from petroleum resources, thus making it possible to get middle distillates such as jet fuel, Diesel fuel or high-quality lube-oils. It should also be noted that interest for catalytic cracking and reforming processes is maintained in all areas.

Another major challenge facing the oil processing industry is that of supplying feedstocks to the chemical industry, that is to say, supporting "petrochemistry". Although such feedstocks at present make up a rather low percentage of the crude, well below 10 per cent, it is expected that their demand will more than double by 1980 compared to present day figures (1). To meet these requirements, the catalytic processes, such as gasoline reforming, hydrocracking of [illegible] products, hydrodealkylation, etc., are [illegible] used. The flow scheme of many refineries will [illegible] to suit these objectives also, resulting in so-called "chemical refineries", just as other refineries will undoubtedly continue to be oriented towards the production of lubricants.

Among the present preoccupations leaving their mark on the development of catalytic processes, mention should be made of the automation and optimization of management of such processes, and of the attempts made to avoid pollution of the environment. All these aspects affect to a considerable extent, the economics and mode of operation and construction of new units.

While aiming at higher-quality oil products, the possibility has been considered of utilizing more general terms to characterize such materials in a more comprehensive manner. Thus, it has been found that oil product characteristics are determined largely by molecular weight and hydrogen content, the former being correlated with distillation, and the latter with physico-chemical properties (3). It has been found to be of interest to use the minimum hydrogen content of materials as a criterion in certain quality requirements. This value decreases as the distillation range of the respective fraction increases, from approximately 18 per cent for liquefied gases, to less than 8 per cent for fuel oil. In the following, some examples will be given to illustrate the possibilities opened up by this approach.

Combustion or engine performance of jet and Diesel fuels can be expressed by the hydrogen content of the respective fractions. Thus, a relationship has been found between this content and the Diesel index of fuel oils. For instance, for a satisfactory Diesel fuel with an D.I.=50, the hydrogen content will be around 13 per cent.

The severe regulations regarding octane number imposed by many countries on motor gasoline, are well known. „Premium" gasolines obtained today by various techniques, especially by catalytic processes, have a content of about 14 per cent H. In order to ensure both a good performance in the motor and to meet anti-pollution requirements, this content should be no less than 13.2 per cent.

On the other hand hydrogen addition to the fractions in refining implies rather high costs. It is therefore easy to understand the interest shown for refining processes which maintain a maximum hydrogen content in the products compared to the hydrogen fed in with the crude. This „hydrogen efficiency" of processes has been continually improved, resulting in higher selectivity and a lower percentage of coke and non-saturated gases. A typical example in this respect is furnished by the recent development of cracking over zeolite catalysts.

The increasing number of cars in use poses the problem of air pollution in the great urban centres. The severity of pollution problems differs with each country, depending on the number of cars in use, their density on traffic routes and various climatic factors. Regardless of these variations, pollution problems are faced everywhere, the tendency of increasing the number of motor vehicles assuming a general character. This, no doubt, will be a major determinant in future developments in oil refining, and particularly, in the development of catalytic processes and of catalysts.

It is of interest to discuss the problem of lessening pollution in the case of spark-ignition engines in relation to the characteristics of gasolines and the trends of changes in of such characteristics.

Since lowering of gasoline volatility entails problems in cold start ignition, this cannot be pushed very far. No lowering below approximately 465 mm is expected. Neither is it expected that any modifications of distillation characteristics will be made (4).

The elimination of aromatic hydrocarbons is carefully controlled because of their toxicity and of their role as carcinogenes and smog producers. Besides, aromatics are responsible for increased deposits in engines. For these reasons, although no legislatory steps are anticipated, it is desirable to obtain gasolines with as low a percentage of aromatics as possible. It should be noted that air pollution by aromatics can be avoided by the catalytic conversion of engine exhausts.

Sulphur in gasoline is being drastically brought down today through catalytic refining processes, and the sulphur content is expected to be brought even lower through the more intensive use of catalytic hydrotreating processes, even where sulphur-rich crudes are concerned.

Olefins are quoted as producing photo-chemical smog, a problem characteristic for California, but which may become of concern for other areas of similar climate. This, along with their effect to decrease the Research Octane Number makes it likely that some limitations on their concentrations in gasolines will be introduced, e.g. max. 15 per cent.

As regards metallic additives in gasolines, especially lead, ample dispute has been heard; it has been concluded that in future, metallic additions will be greatly diminished or even eliminated altogether.

For the present, no increase of gasoline octane number is expected; it is to be noted that even in the United States, there is a tendency to manufacture lower octane engines. On the average, the research octane (RON) requirements of automobiles manufactured in the United States in 1971 was 91. Some predictions even go so far as to assume a decrease of RON down to 93 for premium gasoline and 85 for regular gasoline in the United States, after the mid-1970. However, taking into account the fact that present levels would have to be attained without additives, the average anti-knocking value of gasolines would have to be improved through increased severity of refining processes, that is to say, by introducing new flow-diagrams where catalytic processes will continue to play a predominant part.

Nevertheless, a marked decrease in fuel consumption and an increase in octane number of lead-free gasoline is expected. It is predicted that in the United States, the level of 95 RON will be attained in a first stage and then rise to 97 RON (4, 5, 6).

Based on the above considerations, in table III is given a synopsis of predictions on the quality of gasoline which will be used in the United States.

TABLE III

FUTURE PREDICTIONS ON MOTOR GASOLINE (UNITED STATES OF AMERICA)

Gasoline grades	2 minimum
R.O.N. (average)	95–97
M.O.N. (average)	min. 87
Metallic additives contained	nil
Vapour pressure (RVP)	min. 420 mm Hg
End boil point	less than at present
Sulphur content	less than at present
Olefin content	bromine index max. 30
Aromatics content	no greater than required by engine characteristics

In order to meet these trends towards higher octane gasolines, various refining schemes have been considered (4, 5, 6): C_3–C_4 alkylation, gasoline hydrotreating and reforming, catalytic cracking of heavy distillates and [illegible] processing, and thermal processes (vis-breaking, delayed coking). [illegible] are added including butane and [illegible] isomerisation, hydrocracking of various distillates, hydrogenation of cracking recycle or dehydrogenation of C_3–C_4 cut to increase olefins for alkylation, all implying various separation techniques.

In principle, a solution to the problem of producing gasolines of the required quality is offered by one of two ways (1):

1 "Aromatics" route
2 "Aliphatics" route

These two refer mainly to processes employed for the conversion of paraffinic hydrocarbons ($C7^+$). The "aromatic" route is based on the reforming process, which, besides naphthene dehydrogenation, achieves a major gain in octane by aromatization of $C7^+$ paraffins. Improvements in catalysts and reforming processes in recent years have made it possible to operate under conditions of higher severity (lower pressure, lower H_2 recycle ratio) for the production of higher octane gasolines, at a higher liquid and hydrogen yield.

In order to make the "aliphatic" route explicit, the yield and octane number potential of an average naphthenic gasoline is shown in table IV; this gasoline underwent processing by the "aliphatic" route – dehydrogenation and dehydroisomerization. If, by some process, the paraffins could be converted into their respective alkylates, an 93. 5 ON product would be obtained, with the same yield, and, finally, an 103.6 ON gasoline at a 94 per cent yield. Should such a conversion be possible, it would certainly be most advantageous.

TABLE IV

YIELD AND OCTANE NUMBER POTENTIAL OF A MEDIUM NAPHTHENES CONTENT GASOLINE (4)

	Feedstock	Yield	Octane No.
Paraffins, % vol.	50	50	93.5
Naphthenes, % vol.	40	34	115
Aromatics, % vol.	10	10	115
Total:	100	94	103.6

In order to boost gasoline production along this line, besides the production of cat-cracker gasoline, the production of C_3–C_4 olefins for alkylation would have to be augmented. This could be achieved either by more severe catalytic cracking, subjecting hydrogenated recycles to cracking, to obtain a cracking conversion as high as 98 per cent or by combining catalytic cracking and reforming with pyrolysis of some gasolines, or even of some light hydrocarbons (e.g. isobutane). A hydrocracking process has been claimed by which paraffinic hydrocarbons in the gasoline boiling range are broken virtually in the middle without methane or ethane and with little propane production (4). The feedstock for such a process can also be a heavy gasoline fraction or a raffinate derived from reformed gasoline. Figure 2 is a diagram of conventional catalytic processing. In figure 3 is shown a process flow for light fractions which yields high octane number aromatic gasoline and a paraffinic fraction which constitutes the feedstock for the catalytic or thermo-catalytic processes mentioned above.

These widely different ways to meet requirements make it necessary, to select carefully between the many variants possible taking into account, besides technical and economic factors, the types of feedstock available, the unit capacities and the additives allowed. Such a calculation has been made on a computer, assuming four additive levels, i.e., 3.0–0.5–0.25–0 expressed as TEL/gal., and four crude capacities, i.e, 4,800,

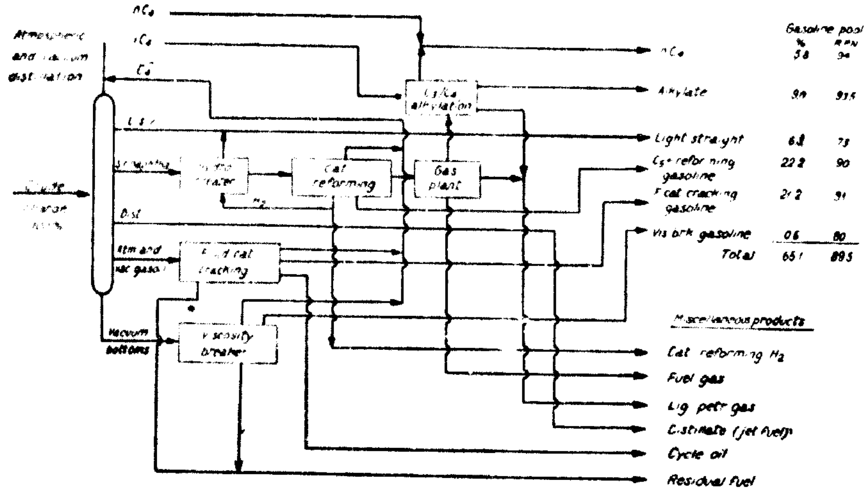


FIGURE 2. GASOLINE PRODUCTION BASE REFINERY FLOW SCHEME (4)

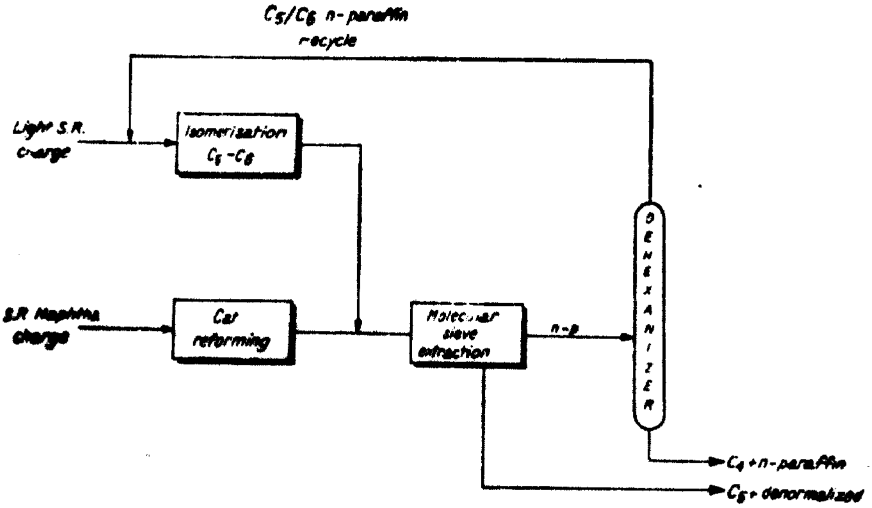


FIGURE 3. FLOW SCHEME FOR CATALYTIC REFORMING COMBINED WITH ISOMERIZATION AND MOLECULAR SIEVE EXTRACTION

9,600, 18,200 and 36,400 cu.m./day (7). These calculations have shown that the production pattern of the refineries would change drastically if the additive level is lowered, but is virtually unaffected by changes in through-put. Besides the basic processes mentioned previously, i.e., distillation, hydrofining, reforming, catalytic cracking, alkylation and delayed coking. It appears imperative that, as additives are reduced, new reforming processes should be brought into play along with the introduction of additional catalytic processes such as C_5–C_6 isomerization, hydrocracking as an additional source of isoparaffins for alkylation, C_3–C_4 dehydrogenation, as well as new hydrofining and alkylation capacities. These calculations would show on the other hand that, by maintaining a low additives level, i.e. 0.25 cc TEL/gal, sizable cuts in installed costs would be made possible. In figures 4 and 5 are shown the refining schemes mentioned, where, in dotted-line frames, are shown the processes required for lowering gasoline additives levels.

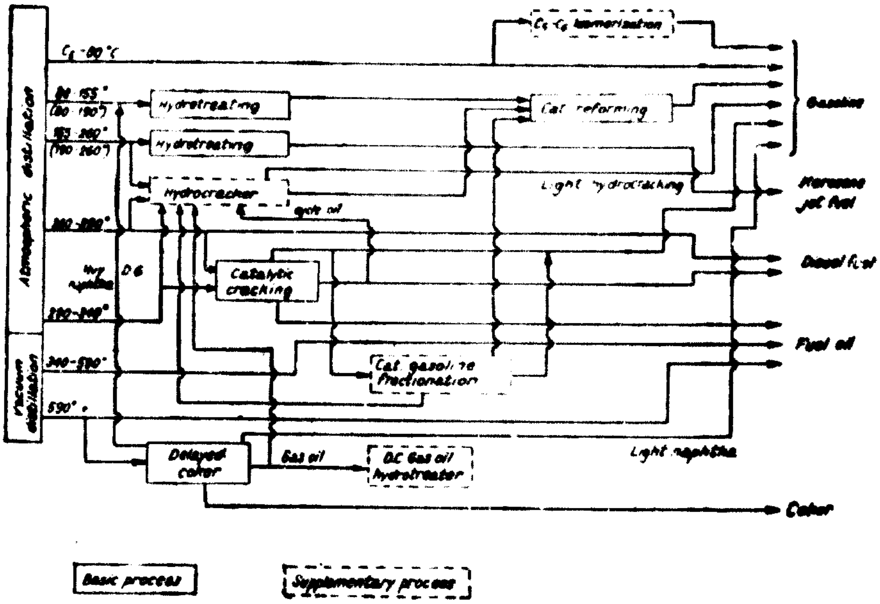


FIGURE 4. COMPLEX REFINERY FLOW SCHEME (7)

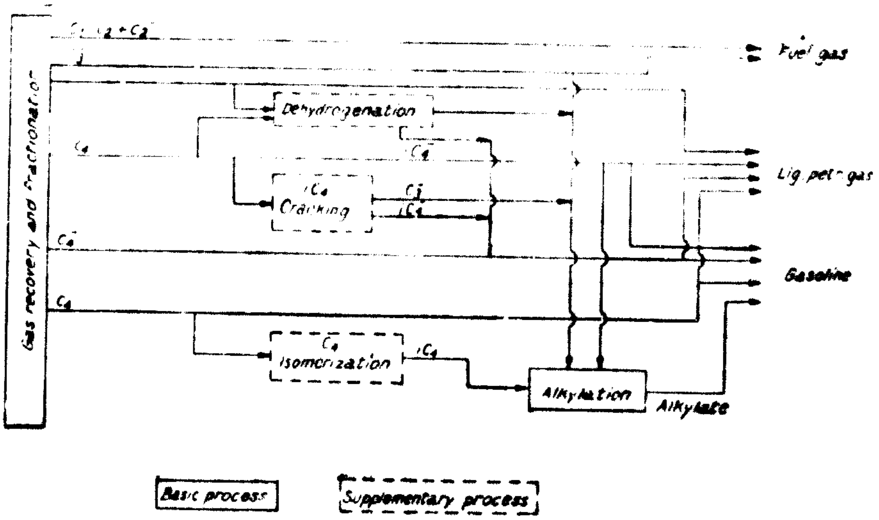


FIGURE GAS PROCESSING POSSIBILITIES (7)

The increasing emphasis laid on the building of refineries oriented towards production of feedstocks for the chemical industry, has been pointed out previously. This emphasis is explained by the higher market value thus obtained for crude, as well as by the fact that only thus can some countries cope with shortages of some products, such as benzene.

In figure 6 is given the flow scheme of a refinery based on chemical processing, in which catalytic reforming and pyrolysis are key processes (8). Besides gasolines, kerosene and fuel oils, individual aromatic and olefinic hydrocarbons are obtained as products of high value. These goals can also be achieved with other catalytic and separation processes. Among these we should mention pentane isomerization and m-xylene isomerization.

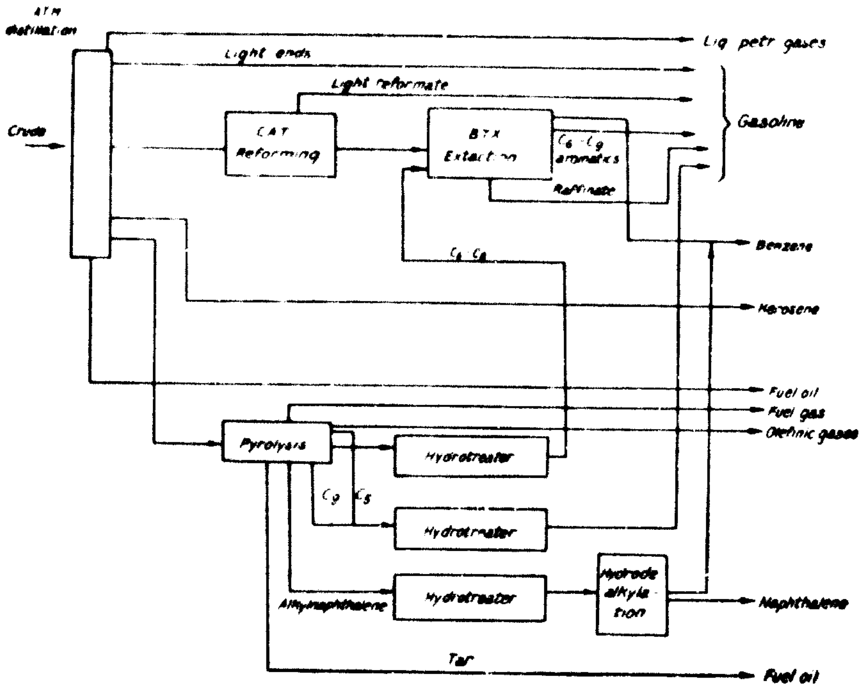


FIGURE 6. FLOW SCHEME FOR A CHEMICAL REFINERY

As an example of the actual trends, figure 7 shows the rates at which processes are being added to the United States refineries (1).

II. CATALYTIC CRACKING

Among the catalytic processes employed in crude refining, catalytic cracking looks back on a history of 30 years of steady progress. Since May 1942, when first applied in crude processing, the fluid-bed catalytic cracking (FCC) process has known a most dynamic development and has remained to this day the main way to convert heavy distillates into gasoline and petrochemical feedstocks. It can be seen from figure 8 how the significance of this process increased between 1940 and 1970.

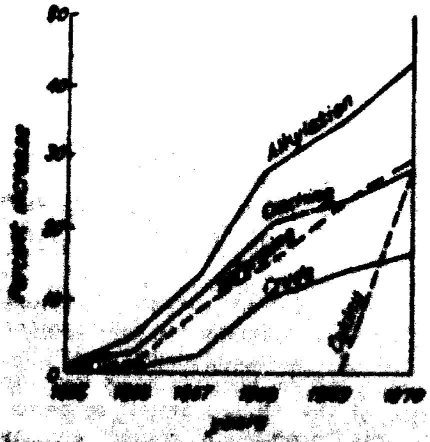


FIGURE 7. PERCENT EXPANSION IN THE UNITED STATES OF AMERICA

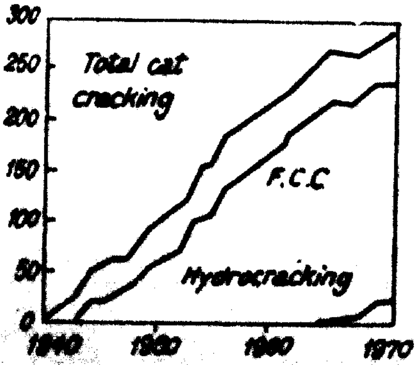


FIGURE 8. CATALYTIC CRACKING IN THE UNITED STATES OF AMERICA

In 1954 the growth rate was 18 per cent in the United States and 41 per cent outside the United States. Between 1955 and 1963, cat-cracking capacity increased by 8 per cent in the United States and by 6 per cent outside the United States, amounting to 42 per cent and 8 per cent of the total crude through put respectively (9).

Besides the other cat-cracking processes – fixed and mobile bed – the fluid bed process has gained prominence from the beginning; in 1955 it accounted for 72 per cent and 1965 for 82 per cent of the entire cat-cracking capacity in the United States and for 79 per cent outside the United States.

Following 25 years of service, in 1967, FCC was being written off by some as a tired holdover. The growth rate has settled at about 50 per cent of the total crude capacity in the United States. The leading position in the growth rate was taken over by hydrocracking. Since that time, a quickening of catalytic cracking has been brought about by the introduction of zeolite catalysts. These new catalysts, by their higher conversions and better selectivity, have led to the conservation of more than 30 million m^3 crude in the United States only.

The savings brought about by such catalysts have been estimated at 250-350 million dollars/year (10).

More recent statistic data show that between January 1st 1969 and January 1st 1971, cat-cracking capacity had increased by about 1.25 per cent/year in the United States i.e. from 923,000 m^3 SD to 950,000 m^3/SD (12). It has been conceded, however, that this growth does injustice to the true state of affairs, since FCC growth was 3 per cent but the capacity decrease in other catalytic cracking processes has brought down the total growth rate (13).

These capacities account for 50 and 47.4 per cent of the crude processing capacity respectively, and indicate a slight re-distribution of crude among various processes.

The world-wide distribution of cat-cracking capacities is evident from the data given below (1st January 1969) (11):

Area	Cat-cracking capacities m^3/SD	Percentage of crude through-put
Africa	4,050	3.4
Middle East	13,300	3.6
Asia and Pacific Area	57,600	7.2
Western Europe	109,000	5.3
South America	95,000	12.
North America	1,010,000	49.3

Owing to the decidedly leading position of fluid catalytic cracking, our further considerations will deal only with this type of process.

The application of the fluidization technique of finely divided solids renders this process more complex than the fixed-bed catalytic process.

As we have already shown, after the 1942–1954 period in which the process was brought to maturity, the main incentive for development during the next 10 years was the covering of increasing demands on the oil product market. The yields were oriented within possible limits towards maximizing gasoline production (the case of the United States) or petrochemical feedstocks and middle distillates production, respectively, as was the case for markets in Europe and elsewhere.

The main trends within this period were:

- catalyst development
- construction of larger units with capacities up to 1,600 m^3/SD.
- increases of operating cycle lengths
- constructive refinement on existing units aiming at elimination of bottlenecks
- refinement in unit design
- operating improvements

The share of synthetic silica-alumina catalysts has grown over that of the natural ones, and the 24% or 28% Al_2O_3 catalyst has claimed increasing attention as the most stable and active. At the same time, micro-spherical catalysts have brought about improved circulation, simplified unit operations and decreased catalyst losses and equipment erosion.

Setting up of larger units has brought installed costs per unit capacity down to about 1/4 of the 1946 level (9).

Mechanical sophistication, on-stream repairs and improvements of operating conditions have increased cycle lengths from 1 to 2 years to 2 to 3 years on the average, bringing down operating costs.

The catalytic hydrogenation of feedstocks improves their quality by lessening the metals, sulphur, nitrogen, Conradson carbon and aromatics contained, aiding to lower coke production and increase gasoline yield of higher lead susceptibility.

Catalytic cracking, due to its capacity of processing heavy feedstocks, has contributed to a substantial decrease of residual fuel in the United States between 1955 and 1967 from 15 to 5 per cent in good agreement with market changes (9).

PRESENT POSITION AND FUTURE TRENDS

The present position of catalytic cracking as a major process of heavy feedstock conversion should be viewed in conjunction with the introduction of hydrocracking. The great flexibility, of the latter has been welcomed as the most suitable tool for the conversion of the heavy ends of the barrel into a variety of products with remarkable marketing potentialities. Hydrocracking is at present much more expensive than catalytic cracking.

Since most of the technological improvements in catalytic cracking lately are centered around zeolite catalysts, the latter deserves closer scrutiny.

Of the great variety of crystalline aluminasilicates, known also as molecular sieves, the ones noted X and Y have gained paramount importance in the field of industrial catalysis. Certain cationic forms of these "ion-exchangers", and especially those containing trivalent rare earth ions, are remarkably stable even at high temperatures and in the presence of steam. The cracking activity of such cationic forms is higher than that of amorphous silica-alumina by several orders or magnitude and would permit the use of much smaller reactors. This development is, however, limited by two basic restrictions related to the process itself. In a thermally balanced cyclic process such as the reaction-regeneration process, the cracking reaction rate cannot exceed coke burning rate; on the other hand, the catalyst takes on the important role of a heat transfer medium between regenerator and reactor.

The problem of heat transfer has been overcome by dispersing 5 to 25 per cent zeolite in a silica-alumina gel which assumes the role of a heat reservoir. The zeolite particles, which are catalytically active, must be accessible to feed molecules, thus calling for a porous form of the matrix.

The zeolite matrix system features important synergism as tables V and VI show (10).

TABLE V

MATRIX EFFECT ON ZEOLITE STABILITY

Catalyst	Zeolite [1]		18% zeolite [2] in silica-alumina		Silica-alumina [2]	
	a	b	a	b	a	b
Conversion, % wt.	67.8	6.3	67.5	58.2	34.4	35.2
Gasoline, % wt	58.3	5.8	54.7	49.7	28.8	30.6

1) Conditions: 480°C LHSV = 16; time, 10 minutes.
2) Conditions: 480°C LHSV = 4; time, 10 minutes.
a. Air calcined for 10 hours at 550°C, then calcined for 24 hours in 100% steam at 1 atm.
b. Treatment (a) followed by 48 hours at 850°C in 5% steam air.

TABLE VI

MATRIX EFFECT ON ZEOLITE ACTIVITY

	Pure zeolite		Zeolite dispersed in silica-alumina			
			I		II	
			a	b	a	b
Conversion, % vol.	43.4	64.3	45.7	63.1	46.9	65.9
Reactor zeolite, g	7.5*	17.0*	3.1	7.3	2.9	6.7
Conversion modification, % / increase of zeolite q-ty, g	$\frac{21.0}{9.5} = 2.21$		$\frac{17.4}{4.2} = 4.14$		$\frac{19.0}{3.8} = 5.0$	

The catalysts had been diluted with quartz at 200 cm³.
I. Ion-exchanged with $(NH_4)_2SO_4$
II. Ion-exchanged with $(NH_4)_2SO_4$ + RE Cl_3 (rare earth chloride)
a. 4% zeolite; b. 10% zeolite
* Amount of zeolite to give about the sum conversion as the composite catalyst.

The stability against high temperature and steam is thus much increased by dispersing zeolite in amorphous silica-alumina (table V) and a maximum gain of conversion per gramme of zeolite in the reactor is obtained by this means (table VI).

Zeolite catalysts exhibit a remarkably high hydrogen transfer activity which is reflected in the product distribution pattern and in the very high hydrogen efficiency of cracking (table VII) (10).

TABLE VII

CATALYTIC CRACKING AT 480°C OF A WEST TEXAN CRUDE DISTILLATE

Catalyst	Amorphous		Zeolitic
	13% Al_2O_3	25% Al_2O_3	
Recycle ratio	1.0	1.6	1.0
Conversion, % wt.	58.5	66.0	65.4
Gasoline, % vol.	38.8	44.9	59.6
Coke, % wt.	5.2	3.2	2.6
Hydrogen efficiency at 60% conversion	86	89	94

The zeolitic catalysts undoubtedly point to a new direction and the fact that now more than 90 per cent of the catalyst inventories of all the FCC units in the United States is made up of this type of catalysts, constitutes proof of their operational and economic efficiency, at least for the North American area.

Maximizing gasoline production with simultaneous reduction of C_3 and C_4 olefins content does not enjoy universal acceptance. In some areas, constant shifts in product demand take place. A single type of catalyst may no longer suffice (14). Catalyst producers have developed or are studying new types of catalysts, the so-called "oriented yield catalysts", in order to meet the demands differing with season and geographic location.

The Davison Chemical Division of W.R. Grace & Co. have reported (14) the following catalysts tailored to such needs:

- catalysts for the production of C_3-C_4 olefins
- olefin producing catalysts retaining good gasoline and coke selectivity
- superactive stable catalysts for maximum production of C_5^+
- catalysts for increasing light cycle oil yield.

The catalysts of the near future should offer prospective users:

- higher equilibrium activity and selectivity by increasing the zeolite content as well as by ensuring a better accessibility of the catalyst dispersed in the amorphous matrix and minimizing the latter's cracking effect;
- higher mechanical strength and the reduction of fines (minus 20 microns) in oder to meet environment pollution regulations;
- higher insensitivity to contaminants (heavy metals, sodium, chlorides and nitrogen).

SOME FACTS ABOUT THE PROCESS

Before going on to discuss the changes in operation and construction of FCC units, it would be useful to review the main zeolitic catalyst properties which have brought about such developments:

- they crack naphthenes and paraffins quickly and very selectively;
- they crack aromatic nuclei slowly and with low selectivity;
- their cracking rate is relatively little affected by the feedstock boiling range;
- their efficiency is adversely affected by deposits limiting access to zeolite.

These properties lead to the following considerations as to the conditions under which the process should be applied:

- a contact time from 1 to 4 seconds is sufficient for achieving complete conversion of non-aromatics in the feed;
- the optimum conversion is largely dependent on the contents of polynuclear aromatics;
- cracking conditions should be selected such as to avoid gasoline re-cracking;
- regeneration should ensure lowest coke level on the catalyst entering the reaction zone.

Replacing amorphous catalysts in existing units with zeolitic catalysts has often failed to bring about the expected results as the process conditions did not allow the potentialities of the new catalysts to be used to the best advantage. Thus, for a contact time longer than 3 minutes and residual coke on the catalyst in excess of 0.5 per cent, zeolite performance is no longer evident.

The introduction of zeolite catalysts therefore poses two design problems:

1. Adaptation of existing units
2. Design of new units.

The adaptation of existing units consists mainly in going over from bed cracking to riser cracking. Table VIII gives the yield changes as a result of going over to riser cracking.

TABLE VIII

INCREMENTAL YIELDS FOR RISER MINUS BED CRACKING (18)a)

Operating conditions	Increments
Temperature, °C	+40
Through-put ratio, vol/vol.	−0.35
Conversion, % vol.	+5.0
Yields, % vol.	
C_5 −200°C gasoline	+7.6
C_3+ C_4	+1.4
iC_4	−0.7
nC_4	−0.5
C_3	+2.6
C_2+ C_1	−0.9
C_3	−0.9
C_2	−0.8
Cat. gas oil	−5.0
Total	+3.1
Coke, % wt.	−1.3
C_2 and lighter, % wt.	−0.4
Octane ratings	
Motor, clear	0 to −0.5
+ 3 cc TEL	0 to −1
Research, clear	+2 to 3
+ 3 cc TEL	+1 to 2

---

a) Orthoflow "B" unit, zeolite catalyst, 78 activity.
Charge stock inspections: sp. gravity 0.920, volume average boiling point 418°C, aniline point 77°C.

The data of the table show unmistakably that riser cracking favourably modifies the product distribution pattern. At a reaction temperature higher by 40°C, a 7.6 per cent gasoline yield increment is obtained, pointing to one of the major advantages of riser cracking – the possibility of using higher reaction temperatures without re-cracking of gasoline.

The regenerator, and especially its internals, have to allow for the high operating temperatures. Regenerator velocities must generally be increased to improve diffusion conditions. Since coke combustion rates are directly proportional to the partial oxygen pressure, higher regenerator pressures are sought [illegible]

Coke yield, reduced [illegible] by riser cracking, calls for higher feed [illegible] preheating is required [illegible] not all the old units can be [illegible] [illegible]

[illegible]

[illegible]

In table IX are given some of the design criterion.

TABLE IX

DESIGN CRITERIA FOR NEW FCC UNITS

1. *Reaction system*
   - — all riser cracking
   - — high temperatures for octanes and olefins
   - — minimal recycle
   - — feedstock preheating
   - — flexibility of product distribution pattern.
2. *Regenerator system*
   - — coke on regenerated catalyst 0.005 –0.15 per cent
   - — minimum inventory, associated with make-up and regeneration rate
   - — high temperatures, high partial oxygen pressure
   - — air distribution and catalyst circulation pattern
3. *Stripping system*
   - — minimum inventory, minimum steam
   - — stripping in disperse phase
4. *General considerations*
   - — functionality and simplicity

Keeping in mind zeolitic catalyst and riser cracking properties, high temperature, riser limited once through cracking of naphthenes and paraffins is predicted, without cracking of polynuclear aromatics or gasoline re-cracking.

Gasoline re-cracking may be diminished by less severe conditions in the riser and recycling of the material not converted in the first pass. This operational approach unfortunately does not preclude, the cracking of recycle polyaromatics and as a result coke deposits on catalyst are increased and catalyst accessibility suffers. This lowers the yield of naphthenic and paraffin cracking.

In cases where a maximum yield of middle distillate is sought, relatively mild conditions are required for the first pass as well as recycle in a proportion ensuring heavy cycle oil disappearance.

In the main requirement is to attain the maximum ratio of isobutane to olefins, FCC units could be designed with additional bed cracking. Under such conditions, the loss of some gasoline through re-cracking is unavoidable.

In table X is shown the distribution pattern of products obtained in cracking a heavy cycle gas oil from a Libyan crude, when maxima of gasoline middle distillate and C_3-C_4 cuts are sought (16).

TABLE X

[illegible] HEAVY [illegible] GAS OIL FROM LIBYAN [illegible]

[illegible]	Yields % [illegible]		
	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

The FCC process is therefore very flexible. However, this flexibility can only be attained at some sacrifice of the co-product yields and, evidently, with higher unit costs.

POLLUTION PROBLEMS

In highly concentrated industrial areas, air pollution problems affect the FCC units by:

- restrictions on particulate matter in the flue gas;
- restrictions on product and flue gas sulphur content;
- the trend to reduce lead contained in gasolines.

A recent study by the Air Pollution Central Administration at the Midwest Research Institute, Kansas City Mo. (17) has shown that FCC units in the United States release into the atmosphere about 45,000 tons/year of particulate matter. Although this is a small percentage of the total of 18 million tons/year released by all stationary sources in the United States the precautions to be taken to meet pollution standards, will subject refiners to serious non-productive expenditures. These anti-pollution measures will consist both in an increase in efficiency of solids retaining equipment and in working out catalysts with better mechanical strength and lower contents of fines (0–20 microns), as well as in the design of new units which promises to bring to a minimum the production of dust by attrition.

The restriction on sulphur content in the cat-cracker products will lead to a more extensive use of hydrogenation (18). Depending on the specific application, hydrogenation may be mild for the primary purpose of removing sulphur, or assure for intensive hydrogenation of aromatics; hydrogenation could also be applied to feedstock, cracked product or cycle gas oil.

In the production of low or lead free gasoline, fluid bed catalytic cracking (FCC) with zeolite catalysts and riser cracking will take a prominent place (15,19).

ECONOMICS

An investigation into the cost of FCC units is difficult.

Most of the units operate primarily on gasoline production. The degree of [illegible] type of the unit and on the [illegible] the rate at which [illegible] These two factors [illegible] capital and operating [illegible]

[illegible] 70 to 80 per [illegible] units, [illegible] 60 per [illegible]

[illegible]

Operating costs do not vary so widely, generally ranging from \$ 1.9 to \$ 2.5/m³. The economics of a FCC unit increases rapidly with slight improvements in conversion and yield for the case of good over-all efficiency. For this reason the prior hydrogenation of feedstock migh look attractive since it not only improves the quality of the finished product, but also has a beneficial effect on conversion and yields, usually by keeping coke down.

Although feedstock hydrogenation costs may be about \$ 1.25/m³ and more probable somewhere between \$ 1.9 and \$ 2.5/m³ such a combination may benefit over-all economics. It is attractive for those units which are bottlenecked at coke combustion.

Refinements in catalytic cracking technology and the possibility of combining it with feedstock hidrogenation have probably limited the extension of hydrocracking for gasoline production.

III. CATALYTIC REFORMING OF GASOLINES

The catalytic reforming process has undergone sudden development in recent years, which surpasses in novelty, scientific foundation or consequences, all that had been achieved in the previous 20 years of exploitation of this process. These advancements have been classified into four groups (20): improvements and optimization of the process, subsequent processing of the reformed product, new applications of the process and new or improved catalysts.

IMPROVEMENTS AND OPTIMIZATIONS OF THE PROCESS

Catalytic reforming achieves the increase of the octane rating of gasolines especially by converting hydrocarbons contained in the feedstock into aromatics. The purpose of the improvements was the manufacture of products highly concentrated in aromatics which also constitute a source of the individual aromatics – with increased octane number – about 100 clear. The use of more severe operating conditions, (increase of temperature or decrease of pressure), is limited by the increase of hydrocracking, which leads to the decrease of the liquid yield, and to coke lay-down on the catalyst. Processes operating under high severity conditions have been applied for several years using the conventional [illegible] but with cyclic regeneration of the catalyst. Thus, in the Ultraforming or Powerforming processes, one of the reactors is under regeneration, while the others are operated. The [illegible], however, implies higher operating costs and [illegible] and catalyst [illegible].

[illegible]

reactors III and IV, to obtain more advantageous thermodynamic conditions for the conversion of paraffins into aromatics. To protect the catalyst in these reactors, the hydrogen recycle ratio is increased by adding to the stream leaving reactor II, a new stream of hydrogen discharged by the hydrogen recycle compressors. Thus the hydrogen flow rate is

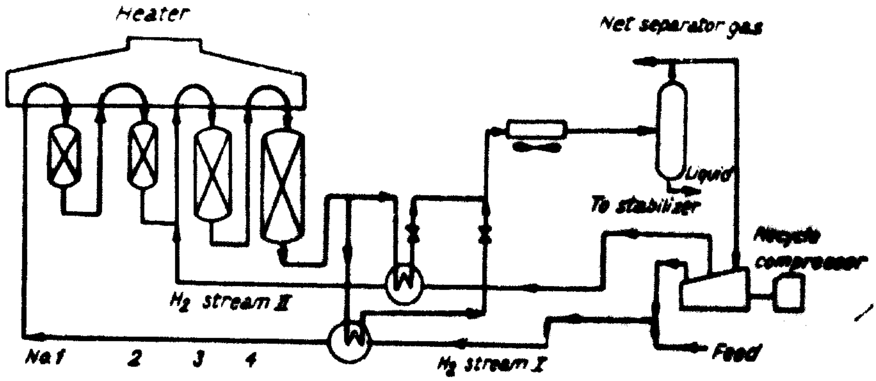


FIGURE 9. MAGNAFORMING PROCESS

doubled. It has been shown that this mode of operation leads to a gain in the gasoline yield of about 3 per cent at a high octane number level. UOP has announced a new type of reforming plant with continuous catalyst regeneration, which allows more severe operating conditions. It is reported to be thermodynamically more advantageous, avoiding high costs, and is specific to plants with cyclic regeneration. The flow sheet of this plant is given in figure 10 (24). The principle of this plant is the

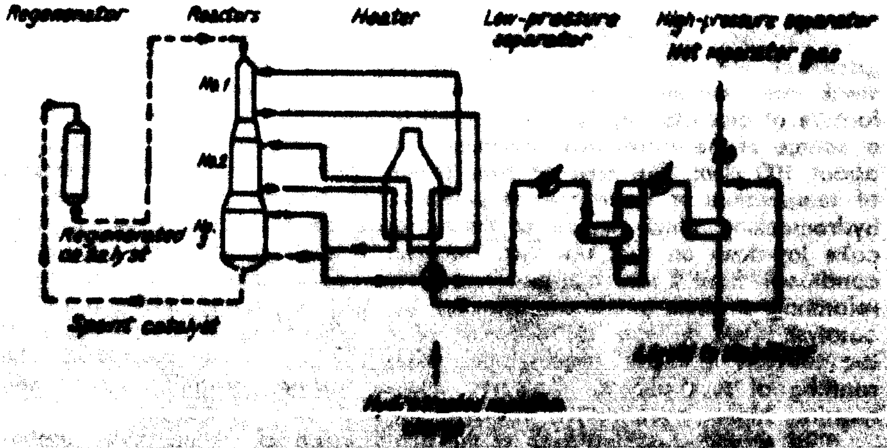


FIGURE 10. U.O.P. [illegible]

[illegible]

reactors benefits from the advantages of fresh catalyst maximum activity and selectivity. It has also been shown that the catalyst charge in the regenerator, is smaller. The volume of the catalyst in the entire plant is therefore not increased markedly.

SUBSEQUENT PROCESSING OF THE REFORMATE

Subsequent processing of the reformate has been considered in order to avoid overly severe conditions in the reforming process. In principle, an aromatic concentrate of very high octane number can be obtained by extraction, but the yield is too low. On the other hand, recycling raffinate, suggested by some older processes, seems to suffer the accumulation of the most refractory components in the feedstock, thus reducing the efficiency of the process.

Another more modern way is the separation of the n-paraffins and i-paraffins by molecular sieves. These processes are also expensive, but are justified economically when the high purity n-paraffins constitute feedstock for the chemical industry.

An interesting solution has been brought forward by the process called Selectoforming (25) in which the reformate product is processed globally under such conditions as to hydrocrack the n-paraffins exclusively. An increase of the octane rating is thus obtained with higher yields than those obtainable from more severe processing and reforming. Table XI shows a comparison of these yields when processing a gasoline to obtain ON=102 ([illegible]); the reforming process, prior to hydrocracking, was operated at two distinct degrees of severity (2). The increase in yield of depentanized product is especially noteworthy.

TABLE XI

EFFECT OF SELECTOFORMING ON YIELD

	Reforming	Reforming and selectoforming	Yield	Reforming	Reforming and selectoforming	Yield
[illegible] octane number [illegible] + 3 ml [illegible]	102.0	97.9	–	102.0	99.2	–
[illegible]	–	[illegible]	–	–	102.0	–
C[illegible] Vol -%	[illegible]	[illegible]	+6.0	[illegible]	51.3	+7.3
C[illegible] Vol -%	61.3	61.3	0	60.9	62.3	+1.4

Another way of subsequent processing, a very simple one, is applicable in the case of severe reforming conditions. The light part of the reformate [illegible] for isomerization and [illegible]

[illegible]

TABLE XII

FRACTIONATION-ISOMERIZATION AFTER TREATMENT OF REFORMATE

Total reformate octane number (research clear)	99.7
Overhead 25 vol. per cent octane number (research clear)	77.8
Bottoms 75 vol. per cent octane number (research clear)	105.1
Isomerization of overhead 25 per cent yield, vol. 25 per cent based on feed to isomerization	98.8
Octane number (research clear)	92.8
Final blend yield, vol. per cent	99.7
Octane number (research clear)	102.0

NEW APPLICATION OF THE CATALYTIC REFORMING PROCESS

The use of very acidic catalysts produces severe hydrocracking of gasoline yielding liquid petroleum gases (20). Such applications are not widely used.

IMPROVED REFORMING CATALYSTS

The most interesting and perhaps the most revolutionary improvement in recent years achieved in the field of catalysts, has been the introduction of the bi- or polymetallic catalysts.

Studies, carried out over many years on metals with catalytic activity, have shown the leading position of platinum. Platinum exerts intensive catalytic activity in the dehydrogenation of naphthenes and the hydrogenation of aromatics. The rate of these reactions is considerably higher with platinum than with any other metal, including platinic metals or non-platinic metals of the VIII-th group of the periodic system.

Where this activity is very weak or even absent, the chief reaction is hydrocracking (26).

Reforming catalysts containing one or several other metals in addition to platinum, the bi- or polymetallic catalysts, did not find use except in severe processes, at low pressures, introduced in recent years. Although most of the patents or articles claim advantages in the yield of reformed gasoline, the principal claim of the platinum-rhenium catalyst, the most frequently used of the new bimetallic catalysts, is its higher stability in comparison with conventional reforming catalysts (27, 28, 29, 30). These advantages have led to a rapid introduction of this type of catalyst so that, today, all large reforming catalyst manufacturers in the world offer catalysts or reforming processes with Pt-Re or other bimetallic catalysts. Among these are:

- Chevrom Research Co., (United States) Rheniforming process and catalyst (31).
- U.O.P. (United States) catalysts R 16 and R 20 (32).
- Houdry (United States), HR-71 catalyst (22).
- Engelhard Ind. (United States), catalysts with Pt-Re, E-500 and E-600 (21)
- Esso Research and Engineering Co. (United States), multi-metallic catalysts for Powerforming (33).
- Institut Français du Pétrole (France), bimetallic catalysts [illegible] 235 (34).
- Leuna (German Democratic Republic), [illegible]

Since all the above-mentioned manufacturers claim [illegible] the same kind of advantages, in the following, as an example, [illegible] of one of the Pt-Re catalysts will be described.

Good temperature stability, and lower fouling rate than the best platinum catalyst.

Very low yield decline with temperature. This allows working at higher temperatures. Expressed in another way, (table XIII) temperature influences the rate of dehydrocyclization and hydrocracking reactions differently.

TABLE XIII

EFFECT OF TEMPERATURE ON REACTION RATES IN REFORMING

$$\frac{d\ (\text{Rate of dehydrocyclization})}{d\,T} = A$$

$$\frac{d\ (\text{Rate of hydrocracking})}{d\,T} = B$$

Conventional reforming catalyst	$B > A$
Platinum-Rhenium catalysts	$A \geq B$

Good regeneration stability.

Another claimed quality, resistivity against poisons, or capacity of regeneration after accidental poisoning, has not been confirmed. On the contrary, certain sources indicate that the activity of the Pt-Re catalyst is conditioned by the severe purification of the feedstock (27). The conclusions of the 1970 Question and Answer Session of the National Petroleum Refiners Association (35) were similar. Thus, it has been shown that the increase of the sulphur content in the feedstock over 2 to 3 ppm produces serious declines of the operating cycle, and a significant increase of the reactor temperature. Therefore, a maximum limit of 1 ppm sulphur is recommended for feeding reforming plants with bimetallic catalysts.

Summing up the advantageous behaviour of the bimetallic catalysts, it is asserted that the operation of plants with such catalysts has the following consequences (29):

Operation at higher octane levels
Operation at higher feed rate
Operation at lower pressure
Operation at lower H_2/hydrocarbon ratios
Longer runs
Improved yields
Savings in platinum investments

To illustrate, tables XIV and XV show comparative performance data obtained with classical catalysts and with Pt-Re catalyst (30). Figures 11

TABLE XIV

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]

TABLE XV

RHENIFORMING OPERATION IN PERTH AMBOY REFINERY

	Typical operation before rheniforming		Current a) operation	
	Regular	Premium	Regular	Premium
Feed rate, bbl / oper. day	11,800	8,900	15,000	12,800
Octane, F—1 clear	86	96	93	99—100
Pressure, last reactor out, psig	500		425	
Run length between regenerations, months	3—5		3—5	
Yield decline, LV% C_5^+	5		1	

a) Operating data after three regenerations (about 115 b/lb).

Note: Refinery estimates yield improvement through lower pressure, adjusted to 95 F-1 clear average octane as:

C_5^+ 1.5 LV%

H_2 100 scf/bbl

and 12 show the change of temperature and reforming gasoline yield, when manufacturing a gasoline with ON=100 (F_1-clear) (27).

The above mentioned advantages cannot be obtained simultaneously and existing plants cannot be easily converted to operate under the most advantageous conditions recommended for bimetallic catalysts. Operation at about 10 kgf/cm^2 has been mentioned with the inherent advantages of working at very low pressures, but in new plants with the continuous system of catalyst regeneration. One can predict the possibility of operating at 7 kgf/cm^2 pressure in the case of very paraffinic feedstocks (36). Also, one cannot neglect the higher costs of the catalysts, their sensitivity towards sulphur and water (37).

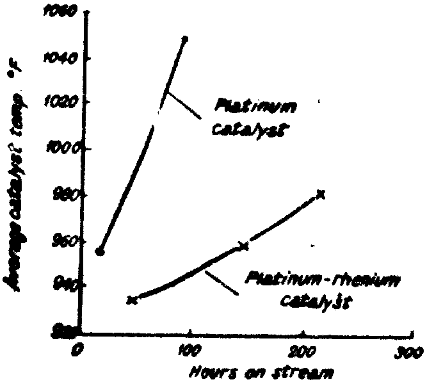


FIGURE 11. REFORMING FOR 100 R.O.N. NAPHTHA WITH Pt- AND Pt-Re CATALYSTS

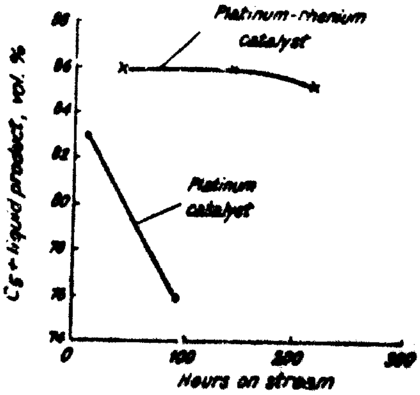


FIGURE 12. REFORMING FOR 100 R.O.N. NAPHTHA WITH Pt- AND Pt-Re CATALYSTS

It is of interest to know the mechanism by which the bimetallic catalysts operate.

Although a clear understanding of this subject does not yet exist, but it seems that one cannot speak of a different mechanism for the various reactions which occur in the reforming process. However, observations have been made and suggestions offered with respect to the higher stability of the Pt-Re catalysts. One of the causes could be the higher melting point of rhenium, 3,440°C, as compared with 1,769°C for of platinum, which is correlated with the higher resistivity against detaching of the Pt-Re alloy from the catalyst. The specific existence of the alloy about has been proved by the fact that the promoting action of rhenium is related to its concentration with respect to platinum (figure 13) (20).

Working under highly severe conditions, a larger amount of coke is unavoidably deposited on the catalyst. If, in the case of conventional platinum catalysts, a coke deposit of 3 to 10 per cent requires regeneration, the bimetallic catalysts admit much larger deposits, amounting to 20 per cent. This observation can lead to the assumption that the existence of the alloy has a dispersing effect on the coke deposits (38).

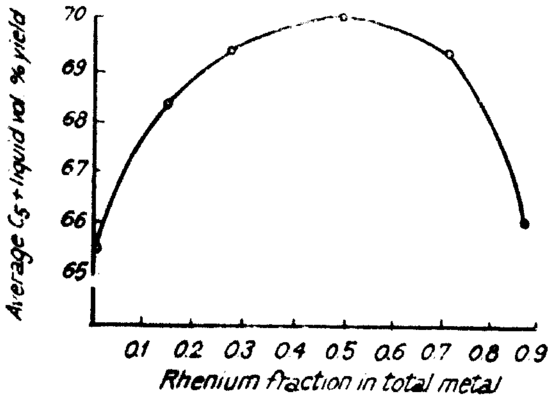


FIGURE 13. PLATINUM-RHENIUM CATALYSTS – EFFECT OF METAL COMPOSITION ON C_5^+ YIELD

The results obtained with the Pt-Re catalysts have stimulated investigations with other alloy type catalysts based on platinum. Thus with the purpose of reducing catalyst cost and the severity of feedstock purification, new types of catalysts have been announced containing additional metals with promoting effects, sometimes in combination with a sulphur compound. The subject is treated in patents, which mention palladium and iridium, group IIIA elements, such as scandium, group IVA elements, such as zirconium, group IVB elements such as germanium, tin or lead, or of group VIA. Such a catalytic system is represented by the latest UOP catalyst – R 20 – which is characterized as being polymetallic but without rhenium. This catalyst is described as having a higher selectivity than the Pt-Re catalyst, R-16, producing an additional gasoline yield of over 3 per cent (20).

Processes with bi-metallic catalysts of the semi-regenerative type, working at 15–20 atm., have also shown good performance in aromatics production (39).

ECONOMICS

The increasing demand of high octane fuel, of aromatic hydrocarbons and of hydrogen for hydrotreating processes and the progress made in recent years in the field of catalysts and processes, has intensified the spread of the reforming process. The present world capacity (excluding countries with centrally planned economies) is about 14 per cent of the crude oil distillation capacity, as compared to 13 per cent five years ago [illegible]. New construction promises an increase in the coming years. Among the countries with a highly developed petroleum processing industry, the United States reached a reforming capacity of about 175 million m³/year, in 1974, representing about [illegible] per cent of the crude distillation capacity.

[illegible] LIGHT HIGH OCTANE [illegible]

[illegible] the octane rating of clear [illegible] operation. Only considering especially of C_5 and C_6 hydrocarbons, to obtain the largest possible amounts of isoparaffins. There are, in principle, three ways of increasing the isoparaffin concentration: alkylation, isomerization and isomer separation.

Alkylation, as a process for manufacturing, light gasoline cuts with clear octane numbres close to 100, is applied today on a large scale in the countries with free market economies, especially in the United States. Less interest has been shown for alkylation in Western Europe and in developing countries. Being a relatively expensive process, other processes have been preferred. However, trends toward diminishing or eliminating gasoline doping could stimulate interest for alkylation in these countries too.

Of the two commercial alkylation processes, the capacity of sulphuric acid alkylation plants is about double that of HF acid alkylation plants. Efforts devoted to the improvement of the alkylation process refer to mechanical aspects of corrosion, acid recovery, product purification, etc. This is, however, beyond the purpose of this paper, which refers to processes using solid catalysts and to the catalysts themselves.

The isomerization processes, especially of n-pentane and hexanes, although representing a small capacity with respect to the total processing capacity, recently has become of interest for the increase of the antiknock properties of light gasoline cuts. These light gasoline cuts, representing 10 to 15 per cent of the total gasoline, usually have an octane number between 65 and 70, markedly lower than that required. Reforming processes, even modern ones working at low pressures, are not fed with these cuts since no satisfactory isomerization is obtained. Only mild aromatization of the C_6 hydrocarbons occurs. Even the light top of reformate might constitute the feedstock for isomerization.

The isomerization of light paraffinic cuts produces an increase of about 13 to 15 octane units, the increase depending on the nature of the feedstock and on the isomerization process applied. With recycling, almost total conversion to isoparaffins is obtained, and the octane number of the cut reaches 83 (95 with lead). Table XVI gives the motor and research octane numbers of the main C_4, C_5, C_6 and C_7 paraffins (41).

TABLE XVI

OCTANE NUMBERS OF PARAFFIN HYDROCARBONS

	Motor method	Research method
n-butane	90	94
isobutane	99	100+
n-pentane	62	62
isopentane	90	92
n-hexane	26	25
2-methylpentane	73	73
2.2-dimethylbutane	93	92
n-heptane	0	0

To understand the limitation and present trends in developing the isomerization process, it is useful to consider the thermodynamics of the isomerization of C_5 and C_6 paraffins. Figures 14 and 15 show the change of the equilibrium composition of the C_5 and C_6 cuts as a function of temperature. The advantage of isomerizing at the lowest possible temperatures is clear; the proportion of isoparaffins increases with the decrease of the temperature. In the case of n-hexane the slope of the curve is less abrupt.

It is interesting to note the steep increase with temperature of the concentration of 2.2-dimethylbutane an interesting component due to its high octane number.

Isomerization occurs through an ionic mechanism, by formation of carbonium, on intermediates, which undergo structural changes. The active catalysts in this reaction can be classified into two groups:

— catalysts based on $AlCl_3$ or other Friedel-Crafts catalysts;

— bifunctional catalyst containing a hydrogenation-dehydrogenation function in addition to the acid function.

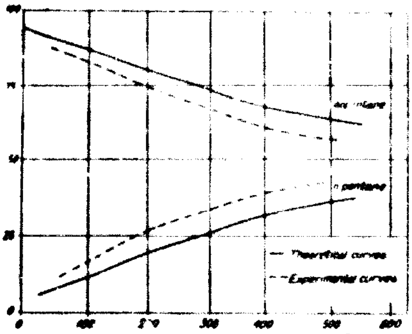


FIGURE 14. ISOPENTANE AND n-PENTANE EQUILIBRIUM

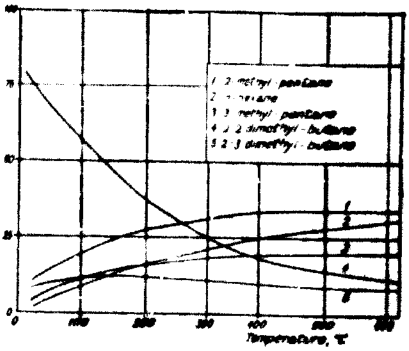
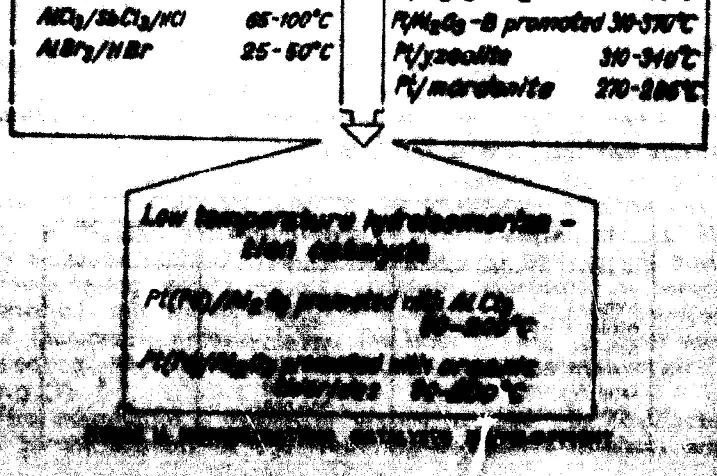


FIGURE 15. C_6 ISOMERS EQUILIBRIUM

Early commercial isomerization processes, working with Friedel-Crafts type catalysts, suffered a number of difficulties such as high reactant requirements, losses through formation of residual products, strong corrosion, pipe fouling and difficulties in product purification. Subsequent development, led to processes using bi-functional catalysts at high temperatures. Although operated with increased safety and without corrosion, these processes require high working temperatures. Due to the relatively low conversion into isoparaffins, the costs are relatively high, as a consequence of the need to recycle n-pentane and sometimes, n-hexane.

Working temperatures have been reduced by increasing catalyst acidity by incorporating strongly acid promotors or by the very modification of the carrier. The most interesting results in regard to the latter were obtained by introducing molecular sieves type – or mordenite. By this means, the working temperature was decreased to about 300°C.

Combining the advantageous characteristics of bifunctional catalysts with the strong acidity of Friedel-Crafts catalysts, even more effective cata-



[illegible]

lysts have been achieved, which today are used in low temperature processes (42). The developments which led to this solution are outlined in figure 16, in correlation with the temperatures of the respective processes (43).

The low temperature isomerization processes, which work below 200°C, employ a fixed bed of noble metal catalyst deposited on an acid alumina carrier to which a strongly acid Friedel-Crafts type promoter is added.

A derivative process uses an organic chlorinated compound as promoter together with the hydrogen-hydrocarbon feed. The organic compound decomposes in contact with the catalyst forming HCl, generating **in situ** a catalyst with high acidity. Though the system involves HCl, it is not very corrosive due to the lack of humidity (44, 45).

The low temperature isomerization processes have the advantage of deep conversions coupled with high product yield, stability and excellent catalyst regenerability. As a consequence of these advantages it is expected that they will be applied in future capacity increases.

V. HYDROGEN TREATING

A series of catalytic hydrogen treating processes have been developed, whose common characteristic is the improvement of the quality of certain hydrocarbon cuts.

The removal of heteroatoms like sulphur, nitrogen and oxygen, the saturation of double bonds in various olefinic structures, and the removal of the heavy metals and asphaltenes are the main targets of these processes.

Recent literature has treated the wide field of industrial applications in detail. The VII-th World Petroleum Congress, held at Mexico City in 1967, devoted considerable time to the analysis of the status of hydrogen treating processes. Therefore, in the following, only tendencies which seemed to us most significant for the future development of this field, will be reviewed.

The themes discussed at the VII-th Congress (1–5), indicated a tendency (borne out in the subsequent years) to widen the applications of hydrogen treating. Thus, besides progress in distillate desulphurization, innovations have been claimed in residue desulphurisation, catalytic cracking feed hydrotreating, lube hydrotreating and pyrolysis naphtha hydrofining.

Hydrogen treating capacities are increasing in the United States at a yearly rate of over 7 per cent, representing today over 35 per cent of the crude oil processing capacity. This puts hydrogen treating processes in second place, following catalytic cracking.

The following data show the distribution of hydrogen treating capacities in the world in January 1969 (11).

Region	Capacity, [illegible]	% of processed crude
Africa	[illegible]	10
Middle East	[illegible]	11
Asia-Pacific	[illegible]	[illegible]
Western Europe	[illegible]	[illegible]
Latin America	[illegible]	[illegible]
North America	[illegible]	[illegible]

Table XVII shows the distribution of processes and their dynamics in the last two years, in the United States

TABLE XVII

HYDROGEN TREATING OF VARIOUS PETROLEUM CUTS (12)

	Feed	Capacity m³/sd				
		Jan. '70	Δ%/year	Jan. '71	Δ%/year	Jan. '72
1	Reforming feed	343,000	+ 12	392,000	+ 8	423,000
2	Middle distillates	168,000	− 7	156,200	+ 6.5	166,000
3	Catalytic cracking feed and cycle oil	42,000	+ 0.5	42,500	0	42,500
4	Naphtha saturation	39,200	− 1	38,800	+ 13	44,000
5	Lube oils	21,500	− 7.5	23,300	+ 0.5	23,500
6	Heavy gas oil hydrofining	14,800	− 18	12,100	+ 18	19,600
7	Residue desulphurization, etc.	16,200	+ 15.8	25,500	0	25,500
	Total	644,700	+ 8	690,400	+ 7.5	744,100

The yearly increase of the capacity of hydrogen treating processes surpasses the rate of increase of catalytic reforming in most of the geographical areas of the globe.

The main purpose of hydrofining remains the removal of sulphur and nitrogen from the feed, as well as of metals such as arsenic and lead. The tendency to blend reforming feedstocks with increasing amounts of naphthas from thermal decomposition (coking and vis-breaking), has supplemented the duties of hydrofining with the saturation of olefins and diolefins.

Recent advances in reforming catalysts, which led to the commercial use of promoted platinum catalysts, raised new possibilities for the hydrofining of naphthas. Improvements have been achieved both in the process technology and catalysts.

Thus, thermally cracked naphthas can be successfully hydrofined in two stages, avoiding the fouling of the reactor with gums resulting from diolefins. It is preferable to operate the first stage under very mild conditions to saturate diolefins selectively. Space rates (LHSV) of 10 to 15 and temperatures of 150 to 200°C are used. The second stage is operated under the conditions required to achieve the desired degree of desulphurization (51).

Complete exclusion of air, by feeding the discharge of the coker naphtha directly to the hydrofining reactor, seems also to be a solution to prevent fouling of the reactor with gums (51).

In hydrogen treating of lube stocks, two processes can be applied depending on the operating conditions and on the goal. Hydrogen treating under mild conditions, at temperatures between 315 and 370°C and pressures of 30 to 40 atm, aims at the improvement of the colour and stability of the oils, and represents the hydrofinishing process. This successfully replaces the finishing operation with clay both for oils and waxes.

More severe treating not only completely eliminates the hetero-atoms from the oil, but the hydrocarbon skeleton is modified, leading to a marked increase in viscosity index. The latter process is sometimes called hydrotreating (49), and may be considered an alternative to mild hydrocracking (9).

The advantages of hydrogen treating in lube oils manufacture, are shown by the increase of the processing capacities of plants employing it from 5,500 m^3/sd in 1961 to 23,500 m^3/sd in 1972 (12, 53), representing about 70 per cent of the total capacity of finished lubricants (53). Its success is due to the increased yield of the finished oil, in comparison with the corresponding extraction processes, for an equal viscosity index (49, 54). The inherent losses of acid treatment are avoided, and the by-products of the process (naphtha and gas oil) have a good commercial value (49).

The replacement of the acid and clay treatment by hydrogen [illegible] is of importance in the elimination of [illegible] which [illegible].

A few comparative data [illegible] oils and conventional clay [illegible] that the major advantages of the [illegible] and higher [illegible]

[illegible]

7. the presence of organo-metallic compounds (with Ni and V) in residues which form deposits on the catalysts, giving troubles during regeneration.

To solve these problems, catalyst formulations were, and still are under investigation. Few data are disclosed in the patent literature. From data published at the last two World Petroleum Congresses, it appears that in most cases the catalysts contain the usual active elements of the VI-th and VIII-th group of the periodic system (Mo, W, Co, Ni), deposited on alumina or alumina-silica carriers, with a large variation in pore-size distribution (57).

The contacting of [illegible] by decreasing the [illegible] in the [illegible]

The total world capacity is distributed among the continents as follows:

	m³/day	% of total
North America	159,000	[illegible]
Europe	10,000	[illegible]
Asia	4,140	2.3
Africa	1,600	0.9
Latin America	4,000	2.2

The distribution of the capacities among feedstocks in the United States is given in the following figures (10):

[illegible]	[illegible]				
	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Total	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Jet fuel is another important target of hydrocracking. In 1968–1975, doubling of the requirements predicted in the United States (65), increased from 89,000 m³/day to 178,000 m³/day.

By hydrocracking a wide gas oil cut (275 to 500°C), in a one stage process with extinction recycling, one can obtain 88% vol. jet fuel, 23.5% vol. gasoline with a volume yield of C_4+ of 115.4% and a chemical hydrogen consumption of 280 Nm³/m³ (65). For a 260°C end point, according to ASTM specifications, the freezing point was −59°, as compared with the specified ASTM requirement of −40°C for intercontinental flights.

New recent plants have also been erected to manufacture naphthas by [illegible] vacuum gas oils. A typical feed for [illegible] 17 per cent sulphur and 150 ppm [illegible] yield of C_4+ of 120% vol. [illegible] (80–180°C) containing about [illegible] for the manufacture of xylenes (67).

[illegible] less valuable [illegible] oils, adding [illegible] by a [illegible] in three [illegible] considered useful to saturate the jet fuel cut in a separate plant, and to reform the gasoline cut (72).

Comparing the relative advantages and disadvantages of hydrocracking and catalytic cracking on zeolitic catalysts, the conclusion seems to indicate that combining both processes is economically favourable. This combination leads to the most advantageous balance of the use of butanes and ensures a great processing flexibility (61).

A main problem of hydrocracking is the catalyst. The versatility of the process requires catalysts with optimal composition and texture for each particular application. The literature is however very poor concerning information about the catalysts. In a communication at the last World Petroleum Congress a survey of the literature, including patents, was given, the conclusions being the following (67):

— The catalysts for the manufacture of LPG and gasoline are bifunctional with relatively high acidity, having as hydrogenation component Ni/Mo or Ni/W [illegible] in alumina-silica carrier.

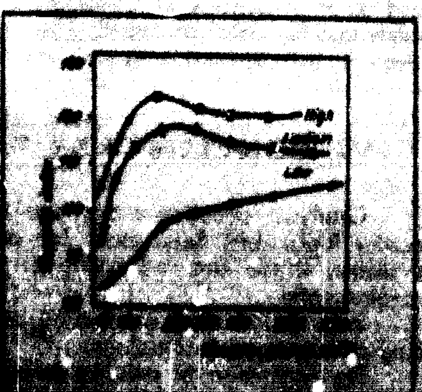
— [illegible] associated with hydrogenating [illegible] metals, such as platinum or palladium.

— [illegible]

— [illegible]

able equilibrium for the hydrogenation of aromatics at the relatively high reaction temperatures (410–430°C) and to obtain good colour stability of the oil.

Viscosity indexes of 125 (ASTM D 567) can be obtained starting from a feed with viscosity index of 25 (52). The distribution of the viscosity indexes is a function of viscosity and depends strongly on the nature of the feedstock, especially at low process severity. However, the differences diminish gradually with increased severity, especially for inferior feedstocks, due to structural changes which cancel the influence of the initial composition (figures 17 and 18).



pass even the cost of the feedstock. Though hydrocracking is now more expensive than other process alternatives, with technical development and the erection of larger plants one can expect a decrease in operating costs to about 60 per cent of current levels (19,

Capital charges are estimated at 5,000 to 7,500 dollars/m^3 sd. or even higher.

In the cracking of heavy cuts and residues, hydrocracking competes with thermal cracking and coking processes. The recent combination of coking and hydrocracking has been announced. By the relatively deep coking of the most refractory feedstocks a large amount of the sulphur and other impurities is concentrated in the coke. The coker gas oil, too sulphurous for catalytic cracking, becomes a suitable feed for hydrocracking. Over-all costs are moderate.

VII. CONCLUSIONS

Catalytic processes are the main tools of manufacture for high quality fuels and feedstocks for petrochemistry. When sour crudes are available, these are necessary to obtain products meeting the market requirements.

Even in lube oil production catalytic processes are gradually replacing conventional techniques.

[illegible]

13. Farrar, G.L.: Oil Gas J., Oct. 24, (1944), 89—114.
14. Baker, R.W.: Paperp resented at the Davison-Crosfield Catalyst Symposium, Scotland, April 10—11, 1969.
15. Murphy, J.R.: Oil Gas J., Nov. 23, (1970), 72—77.
16. Morrison, J.: Oil Gas Intern., 10, 11, (1970), 110—117.
17. Aalund, L.R.: Oil Gas J., March 22, (1971), 73—75.
18. Haflin, W.S.: Oil Gas J., April 1, (1968), 119—125.
19. Stacy, M.J.: Oil Gas Intern., 10,2 (1970), 38—47.
20. Pollitzer, E.L., Haensel, V., Hayes, J.C.: 8-th world Petroleum Congress, Moscow, 1971, Panel Discuss. PD 14 (3).
21. * * *: Oil Gas J., Dec. 20, (1971), 48—50.
22. Pfefferle, W.C.: USP 3.392.102, (1968).
23. Kopf, F.W., Decker, W.H. et al.: Oil Gas J., May 19, (1969), 141—152.
24. * * *: Oil Gas J., Dec. 20, (1971), 50—53.
25. Chen, N.Y., Hamik, J.: Oil Gas J. Nov. 18, (1968), 154—157.
26. Muller J.M.: Gault, F.G.: 4-th Intern. Congress on Catalysis, Moscow, 1968, paper 11.
27. [illegible], H.E.: USP 3.418.727, ([illegible]).
[illegible]

IMPROVED ECONOMICS IN CATALYTIC REFORMING[1]

C. J. OBADITCH*, J. A. NEVISON**, H. H. DALSON***

The use of platinum catalysts to reform gasoline boiling range naphthas to produce high octane blending stock, aromatics and hydrogen quickly became a major refining tool following its introduction about [illegible]. A number of competitive process designs are presently operated on a variety of distillate fractions, generally boiling within the limits of [illegible] 200 °C, ASTM, derived from crude as well as from other refinery processes (thermal cracking, catalytic cracking and [illegible]). The severity of operation, usually expressed as [illegible] reformate, varies quite widely from unit to unit [illegible] unit objectives. The directional effects of [illegible] variables upon performance [illegible]

[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

TABLE II

INDUSTRY TRENDS WORLD CAPACITY, SEVERITY, CATALYST LOADING ESTIMATES

Year	Tons/day	Severity range RON clear of reformates	Catalyst loadings Kg/MT Daily capacity
1950	Initial	—	—
1960	313,000	85 — 100	26
1970	722,000	90 — 102	21
1975	1,000,000	95 — 103	15
1980	1,200,000	95 — 105	13 — 1

mated for the years 1975 and 1980 in table II. Reforming capacities of China and the Union of Soviet Socialist Republics are not included. The estimated severity ranges and catalyst loadings are approximations; however, the trends with time are believed to be realistic. For the over-all severity range of 85 to 105 research octane clear reformates, the aromatics in reformates are correspondingly 45 to 68 volume per cent. Of the estimates of future years, that for 1975 is most probable; that for 1980 could be [illegible], depending upon changes in automotive engines. [illegible] The increase in reforming severity over the years has [illegible] in catalyst loadings per unit of feed [illegible] per unit of feed [illegible] will be [illegible] and [illegible] dent upon chloride content. It follows that maintenance of good activity depends upon water and chloride partial pressures over the catalyst. A definite relationship has been determined for these two agents specific to the individual catalyst and the conditions of use. The benefit of environment control as related to moisture level in a specific unit is shown in figure 1. The moisture content of circulating gas is shown for a period

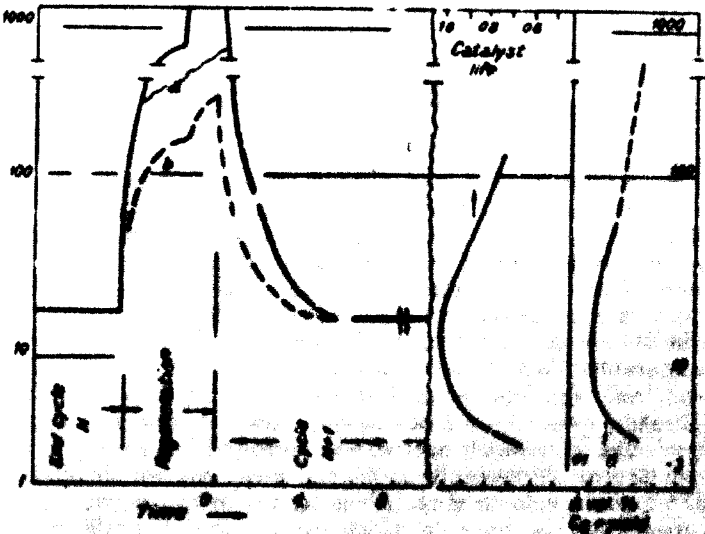
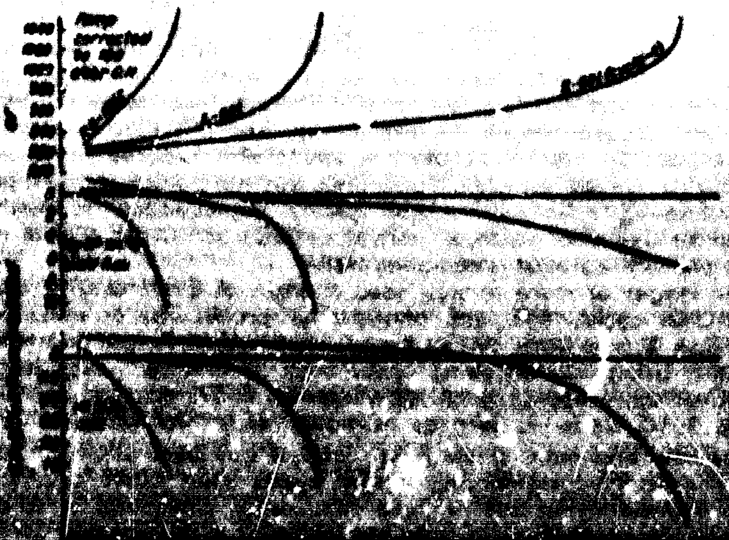


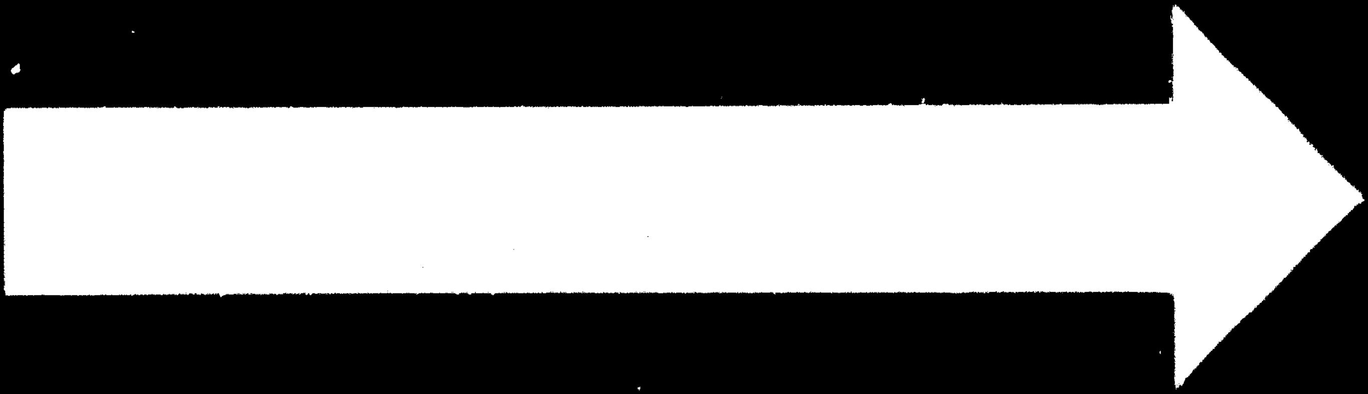
FIGURE 1. ENVIRONMENT EFFECT ON YIELD AND LIFE

at the end of a cycle, over through the [illegible] and last through the start of cycle [illegible] declines to a controlled level in [illegible] system. This controlled level is not [illegible] clean feed [illegible]; it [illegible] as shown by the two [illegible] contractual arrangements with Chevron, Engelhard first introduced a platinum-rhenium catalyst, E-501, in March 1969. A following and improved Engelhard platinum-rhenium catalyst, E-601, was put into commercial use in mid-1971. Other platinum plus supplemental metal catalysts have been announced and introduced by others into commercial trials in the past two years.

New catalysts are typically first evaluated in accelerated or high severity tests to determine their relative yield selectivities and cycle length capabilities. These bench scale, small unit tests provide selectivity and relative ageing results which can be directly related to commercial performance.

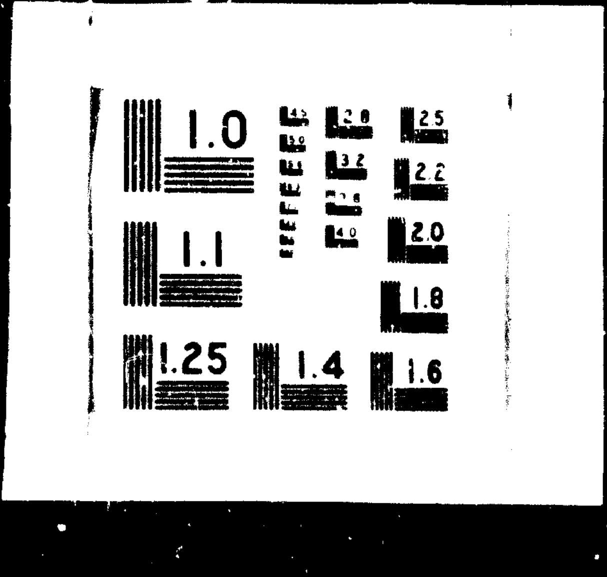
The comparative high severity test results for our platinum catalyst, RD-150C; our platinum-rhenium catalysts, E-501 and E-601, are shown in figure 2. These tests are at constant space velocity and 100 research





4 OF 4

06639



Commercial experience with the catalysts compared in figure 2 is, of course, proportional to the time since they were introduced. RD-150C and RD-150 catalysts (of 0.35 and 0.6 wt.% platinum respectively) came into use in 1954–1955. With the use of the optimum procedures in reforming and in in situ regeneration-reactivation these catalysts run very long ultimate lives, 5 to 10 years being reached frequently. Feed naphtha hydrotreating and stripping to prepare a clean reformer feed has been, and is, widely recognized as a requirement for longest reforming catalyst life. Earlier operations on these catalysts were characterized by successively shorter cycles following the succesion of in situ regenerations. As the significance of procedural steps were better understood and applied, cycles of catalyst use were not only lengthened but have come to be closely reproduced in successive cycles.

The E-501 catalyst first used in commercial units in 1969 is operating in 27 units amounting to about 32.000 t/day in capacity. These loadings have been made using from 100 to 65 wt.% as much catalyst as had previously been used. Depending upon forward operating circumstances with the individual units, these changes in operation, in different combination, have been the experience: (i) increase feed rate; (ii) increase severity and reduce octane additive (lead) use; (iii) reduce pressure to gain in yields; (iv) reduce recycle concurrent with reduced pressure and, in addition, to reduce recycle utilities. Thus, the more stable catalyst permits better reforming economics and/or quality improvement. In new units designed for use of a platinum catalyst, as little as 40 per cent of design loading as E-501 catalyst is operating well.

The longer or more severely used charges of E-501 catalyst are now in their sixth cycles. Instances of improper procedures or abnormalities resultig from upsets have caused a few short cycles. Proper regeneration-reactivation brings the following cycles back to their projected length or better. Over-all, these cycles of operation on E-501 catalyst are running 2 1/2 to 3 1/2 times as long as estimated cycles for platinum catalyst.

The new and more stable E-601 catalyst has been shown in laboratory testing to give significantly longer cycles than E-501 catalyst. This catalyst is presently in use in three commercial units and is scheduled as the next replacement catalyst in several other units. The first use cycles started six and seven months ago are still in progress.

Unit designs require restudy from time to time to adapt to improvements in procedures and catalysts. Engelhard and Atlantic-Richfield Company collaborated on the Magnaformer design concept to get best reforming economics at higher severities with the RD-150C platinum catalyst. This concept is based on optimizing catalyst distributions, reactor-inlet temperature, and gas recycle ratio for a given feedstock, and operating pressure. The primary object of this optimization is improved yield selectivity and catalyst utilization. Recycle gas flow is split for maximum increase in cycle life relative to compression costs.

As shown in the flow sheet, figure 3, a typical Magnaforming design consists of a four-reactor system using a highly skewed catalyst distribution and gas recycle introduced ahead of the first and third reactors. The reactor-inlet temperature pattern is ascending with inlet temperatures of the first two reactors held constant throughout the process cycle.

Due to the initial rapid rate of naphthene dehydrogenation and associated temperature drop, the aromatic/naphthene equilibrium is closely approached at high space velocities. As temperature decreases and equilibrium is approached, additional catalyst is ineffective and may actually contribute to over-all loss of selectivity. It is, therefore, most advantageous to utilize catalyst in the terminal reactors where it can be used at higher temperatures. Use of low reactor-inlet temperatures minimizes paraffin and

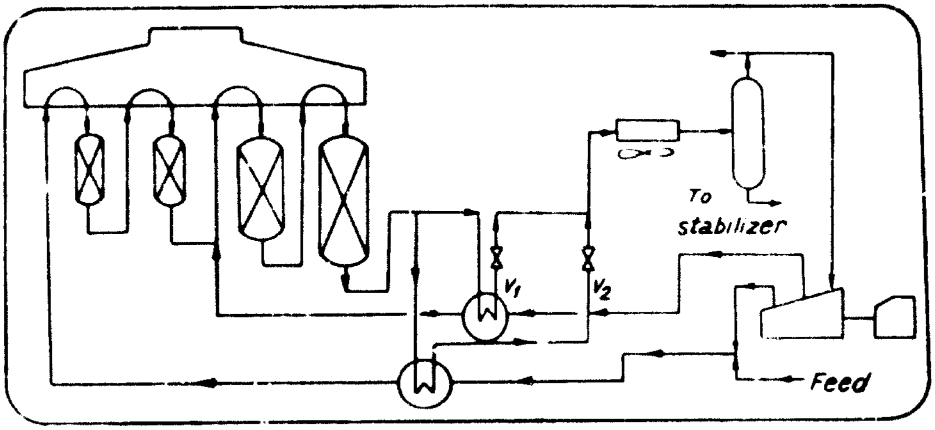


FIGURE 3. MAGNAFORMING FLOW DIAGRAM

naphthene cracking and contributes to the improved selectivity. Low reactor-inlet temperature also makes it possible to operate these reactors at very low hydrogen-recycle ratios without significant catalyst deactivation. The use of low temperature in the lead reactors results in a slightly lower conversion. However, the use of an additional reactor, relative to conventional design, and the catalyst which has been shifted to the terminal reactors when operated at a slightly higher temperature provides the necessary compensation.

Pilot-plant and commercial-unit operation show that reformate yields up to 3 per cent over those from conventional designs are possible with Magnaformer designs. The greatest yield advantages are obtained on paraffinic stocks, with the least improvement shown by heavy products obtained through hydrocracking.

The gas-recycle split is provided by use of two compressors, or more typically, a single side-takeoff centrifugal machine. Since the quantity of gas which must accompany the fresh feed through exchange and preheat is significantly reduced, the savings in compression cost can be applied to supply additional gas recycle to the terminal reactors. As a result, higher recycle in the terminal reactors and thus better catalyst life is obtained at no increase in utility cost over a lower over-all recycle ratio in a conventional single-recycle-loop design. Since reactor-inlet temperatures to the lead reactors are not raised over the cycle, the additional heat, obtained from exchange as terminal-reactor temperatures are raised, can be diverted by use of valves V_1 and V_2 to supplement the No. 2 interheat requirement.

Seventeen Magnaformer design units are operating or in stages of construction or design. They total about 31,000 t/day reforming capacity and include four expansion revamp units.

The Magnaforming operation with E-601 catalyst was evaluated in a multiple reactor adiabatic pilot unit with the results shown in figure 4. Initial operation was at equal reactor inlet temperatures and a single recycle gas flow. After a period of conventional operation, the inlet temperatures and recycle flows were adjusted to Magnaforming conditions. The yield selectivities showed an immediate increase. A cycle of conventional operation on RD-150 catalyst is shown for reference. This illustrates that improved yield selectivity derived from the Magnaforming operation and from improved catalysts are compatible, the two being complementary.

Should it be necessary to maintain continuous onstream operation or if the feedstock or severity be such that semi-regenerative operation is not practical because of short cycle length or poor stream efficiency, a

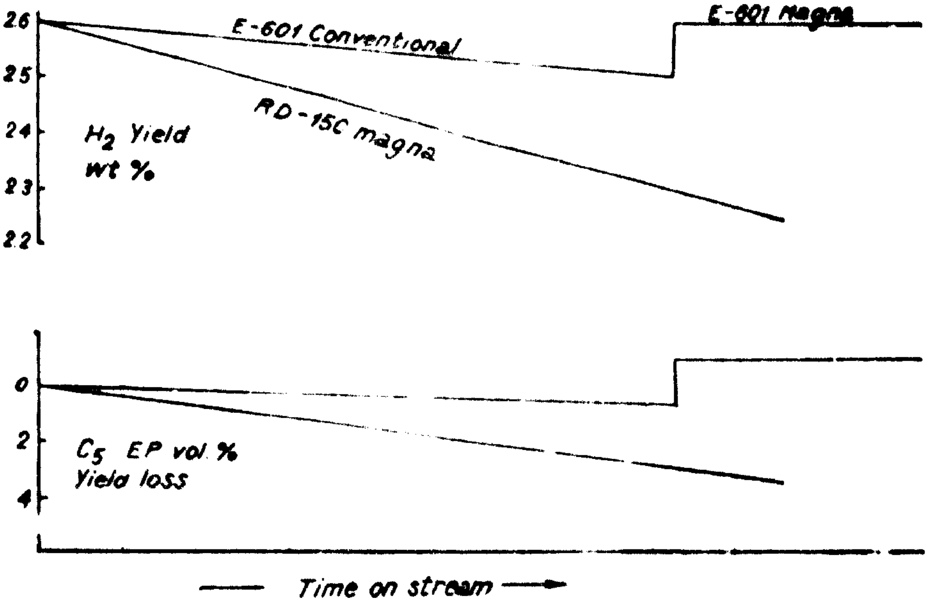


FIGURE 4. MAGNAFORMING WITH E-601 CATALYST

swing-reactor design may be employed. Since the lead reactors operate at very low average catalyst temperature over the entire process cycle, their deactivation rate is extremely low. Cycle lives much greater than one year have been established. Thus, in a swing-reactor design, the lead reactors would be regenerated after about 24 months operation when the unit is brought down for maintenance.

An external regeneration loop and additional reactor can be provided to allow continuous operation while a portion of the catalyst in the terminal reactors is being regenerated. Should the swing-reactor operation not be required for initial operation of the unit, provisions can be made to add the regeneration loop and additional reactor when required.

An optimization study of Magnaforming design for most economic use of E-601 catalyst has been carried through a multiplicity of cases based on a specific feed reformed to 103 clear research octane number. An exemplary case using anticipated 1975 United States product values is shown in table III. The recycle loop pressure drop shown is a safe

TABLE II

SEMI-REGENERATIVE MAGNAFORMER — OPTIMUM ECONOMICS

BASIS	
Mid-continent (United States of America) naphtha feed	2,600 t/day
C_5 plus reformate, RON, clear	103
Cycle length, months	5
Catalyst	E-601
CONDITIONS FOR BEST 10-YEAR ECONOMICS, ALL COST INCLUDED	
Average reactor pressure, kg/cm² gage	11.0
Weight hourly space velocity	2.2
Terminal reactor recycle gas / feed mol ratio	9
Recycle loop pressure drop, kg/cm²	4.5

minimum practical for low pressure circuits as demonstrated by experience to date.

In developing the conditions for optimum economics in this case, the incremental total dollar values varied with the inter-related process conditions as shown in figure 5. Total dollar value increased but slowly with change in cycle length, WHSV, and pressure at a constant gas recycle ratio.

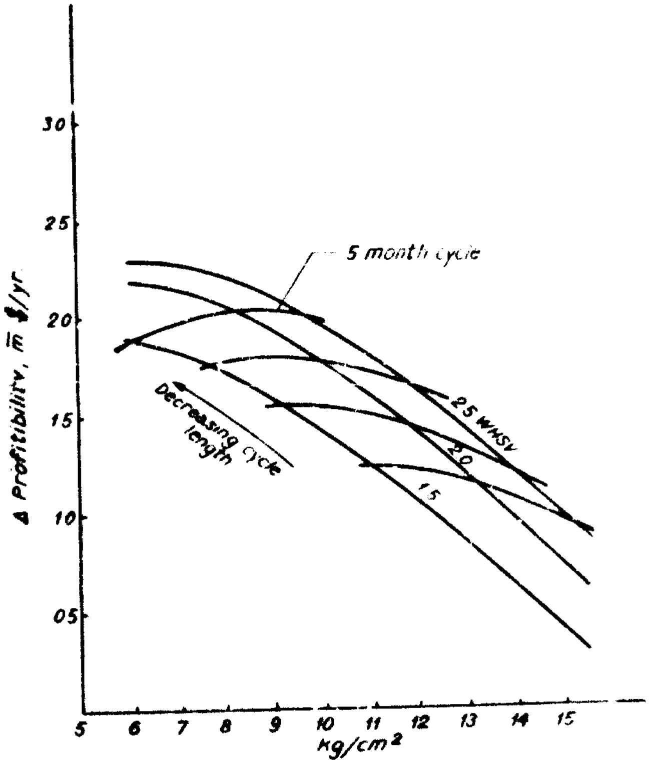


FIGURE 5. MAGNAFORMING DESIGN OPTIMIZATION CONSTANT H_2/HC

For a constant cycle length, say five months, the maximum dollar values can be determined with change in recycle gas ratio, in space velocity, and in system pressure. A plot of incremental total dollar values vs system pressure for the different optimum cases is shown in figure 6.

Definitive design and pricing of a Magnaformer as described previously in table III shows capital requirements to be lower by about 20 per cent for a 2,600 t/day unit than for other current unit designs requiring continuous catalyst regeneration. An intermittent terminal reactor regeneration system to permit a Magnaformer to supply hydrogen continuously for up to 24 month periods is estimated to increase the capital requirement by about 15 per cent for this size unit.

The present state of catalytic reforming (improved catalysts, procedures and unit designs) prompt a comparison of reforming result using earlier technology as compared to that going into use in new units today. Such a comparison, covering the change in industry severity approximated in table II, 1960 to 1975, is shown in tables III-A and III-B. The pre-1960 design operation on the feedstock shown produces 92.0 research octane clear with an 82.5 volume % yield of C_5 plus reformate. The current

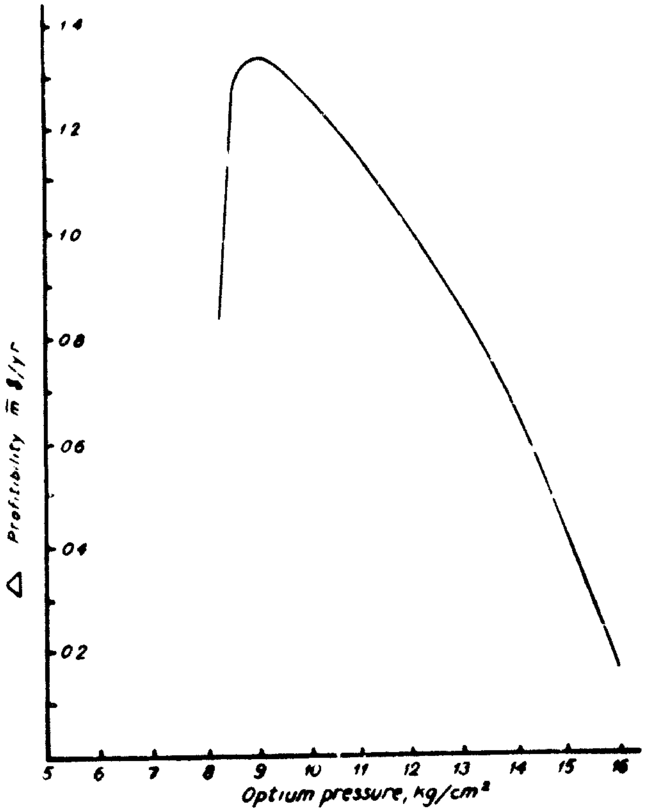


FIGURE 6. MAGNAFORMING DESIGN OPTIMUM PRESSURE (FIXED CYCLE LIFE)

design is shown to produce the same reformate yield, 82.5 volume %, but these supplementary advantages are obtained:

a) reformate research clear octane is up by 7 numbers, 99.0 compared to 92.0

b) aromatics yields are greater by 1.3 times

c) hydrogen yields are greater by close to 2.0 times.

In summary, catalytic reforming has progressed with these significant attainments:

a) Semi-regenerative, lower cost unit designs can produce the probable maximum quality products required with acceptable operating cycle lengths of 6 to 12 months;

b) Operating pressures for these units will be increasingly in the 7.0 to 15.0 kg/cm² gage range with correspondingly high yields of reformate and hydrogen;

c) While catalyst costs per unit weight will trend upward, due to increasing complexity in preparation and reduced volume of sales, costs to refiners per unit of product will be reduced due to use of less catalyst and its greater useful life.

TABLE III-A

COMPARATIVE REFORMING CURRENT AND PRE-1960 DESIGNS

Feedstock	
API	53.8
ASTM distillation, °C	
IBP	101
10	119
50	142
90	169
EP	185
Paraffins, Vol. %	47
Naphthenes	45
Aromatics	8

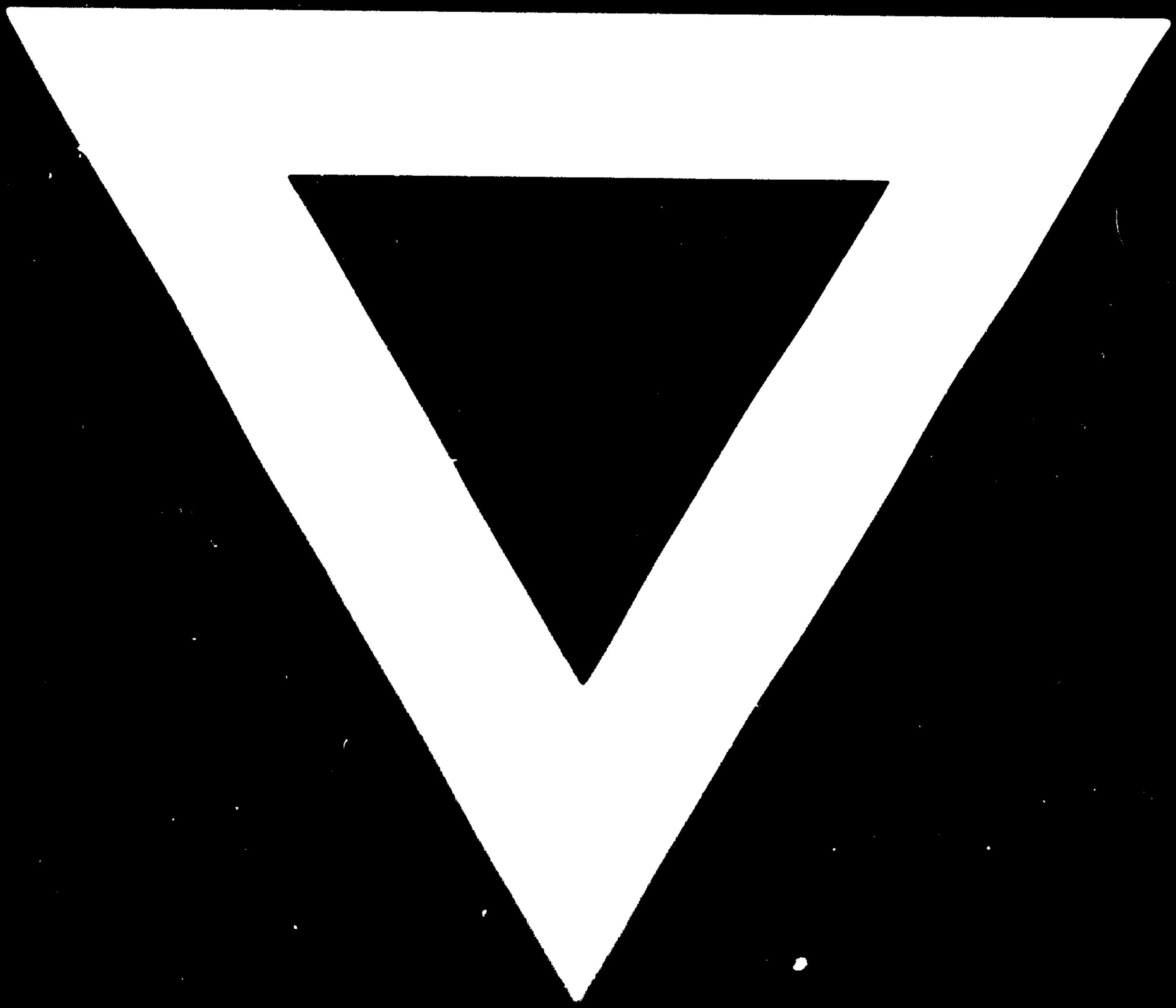
TABLE III-B

COMPARATIVE REFORMING CURRENT AND PRE-1960 DESIGNS

Operating conditions and yields	A current design E-601 catalyst magneforming at low pressure		A design pre-1960 RD-150C catalyst conventional reforming at intermediate pressure	
C_5-EP, Res on clear	99.0		92.0	
C_5-EP, Res on + 3 CC tel	103.0		98.5	
YIELDS, %	Wt.	Vol.	Wt.	Vol.
H_2	3.1		1.6	
C_1	1.1		1.9	
C_2	1.6		2.8	
C_3	2.3		3.8	
iC_4	1.0	1.4	1.7	2.2
nC_4	1.5	2.0	2.6	3.3
C_5^+	89.4	82.5	85.6	82.5
C_5-EP REFORMATE				
API	39.5		47.5	
Paraffins, vol. %	21.5		35.5	
Naphthenes, vol. %	2.5		5.5	
Aromatics, vol. %	76.0		59.0	

Printed in Romania

ID/WG. 123/28
April 1975
English Only



75. II. 20