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ADVISORY ASSISTANCE ON LOW- AND NON-WASTE TECHNOLOGY FOR SOME CHEMICAL PROCESSES

SI/CZE/85/801

CZECHOSLOVAKIA

Technical report: Proceedings of the Workshop on Low-Waste Technologies for some Chemical Processes*

Prepared for the Government of Czechoslovakia
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SUMMARY OF THE TERMINAL REPORT FOR UNIDO PROJECT "ADVISORY ASSISTANCE ON LOW- AND NON-WASTE TECHNOLOGIES FOR SOME CHEMICAL PROCESSES" (SI/CZE/85/801)

In the terminal report for UNIDO project SI/CZE/85/801 the technologies required for the following chemical process industries are discussed and analysed:

(a) Removal of sulphur from organic feedstocks and products;

(b) Production of sulphuric acid;

(c) Production of nitric acid;

(d) Catalytic hydrogenation as a replacement for chemical reduction.

The sulphur content of crude oil and coal used for fuel or the production of chemicals is steadily increasing. Hence there is an increasing need to desulphurize oil, coal, off-gases from combustion and/or petrochemical products.

There have been intensive investigations and developments recently in the processing of crude oils, specifically the conversion of high-boiling distillates and, above all, the residual oils to high-grade fuels and petrochemical feedstocks. Substantial progress has been achieved in the production of low-sulphur fuel oils, in coal liquefaction, and in the chemical processing of carbochemical products.

Conversion of high-boiling and residual hydrocarbon feedstocks is achieved with modern, highly effective catalytic and thermo-catalytic hydrogenation processes whereby undesirable components (sulphur, nitrogen, oxygen and metals) are eliminated from the feedstocks and quality fuel oils are produced. These hydrogenation processes also produce starting materials that lend themselves much more easily to further catalytic or thermal processing, such as the feedstocks for pyrolysis, fluid catalytic cracking and the production of lubrication oils.

The main new processes used for such purposes are catalytic desulphurization and hydrocracking of oil residues and carbochemical raw materials; mild hydrocracking; and hydrovisbreaking. These processes are highly effective technically, economical because of lower energy consumption, and also meet the ecological requirements relating to low-waste technologies.

An important complement to the modern hydrorefining and hydrocracking processes is the non-traditional use of the liberated hydrogen sulphide or of elemental sulphur produced from it. The production of sulphur asphalts and concretes, of special sulphur-containing composites, and of organic thiochemicals represents a substantial economic and ecological contribution to traditional refinery and petrochemical production.

Sulphuric acid is one of the most widely used products in the chemical industry. As to the extent of production, it ranks first in the world out of all individually produced chemical compounds. It is thus of paramount importance to the development of individual national economies and to the development of their chemical industries. In as much as the greatest share of sulphuric acid produced is destined for consumption in the production of fertilizers, it is clear that the development of sulphuric acid production has an impact on the solution of the problem of food in the developing countries.

It is clear that the selection of a specific production technology, the design and interconnection of equipment, the selection of raw materials, and the links to subsequent chemical production processes is complicated, and the specific technology must be tailored to the prevailing local conditions.

The fundamental question of minimizing sulphur dioxide pollution has currently been solved by using a double conversion technology that can yield a degree of conversion of SO_2 to SO_3 of more than 99.5%. This very high efficiency, unparalleled in other chemical production processes, can be achieved by selecting proper catalysts and optimizing the operating conditions of the commercial reactor.

From the ecological viewpoint, another problem being faced is that of disposing of and using waste solutions contaminated with sulphuric acid. This problem is successfully solved in conjunction with the use of high-sulphur residual fuel oil. Contaminated sulphuric acid solutions at concentrations higher than 50 per cent, and even sulphate solutions, can be used for thermal decomposition in furnaces fired with this kind of fuel oil.

From the economic viewpoint, a question that is essential for the sulphuric acid production plant is the utilization of waste heat for producing steam.

Processes for the effective production of sulphuric acid can be designed to suit the particular requirements of the country with due regard for protection of the environment.

Nitric acid also ranks among basic inorganic chemicals important for chemical industries, especially for the production of fertilizers.

It has been shown that the medium pressure process at 0.4-0.6 MPa is preferable for capacities up to 500 tonnes per day (tpd) of HNO_3. The NO_x concentration in the tail gas, however, is high (about 600 ppm) and selective reduction must be applied to reduce NO_x emissions.

For capacities over 500 tpd the dual process is the most economical and it also results in low levels of NO_x in tail gas. Combustion is at medium pressure with absorption at high pressure (0.5-1.4 MPa). The concentrations of NO_x in the tail gas are lower than 200 ppm, normally 125-150 ppm.

Full-scale data on the operation of 18 plants in Czechoslovakia have demonstrated that the application of low-waste technology principles can guarantee emissions below 2 kg NO_2/t HNO_3. The present average emission is 2.84 kg NO_2/t HNO_3, and the best plants produce as little as 0.35 kg NO_2/t HNO_3. Further improvement of the average figure is expected in the near future and appropriate ways and means of making such improvements are recommended in the report.

Attention was also given to the operational and environmental safety of the processes, especially to construction materials resistant to corrosion. Recent developments in energy conservation and waste energy utilization were also assessed.

The chemical methods for reducing organic compounds necessitate the disposal of the reducing agents. As a rule their use is very problematic and, mostly, such products represent detrimental wastes exerting a negative effect on the environment. From this standpoint, then, the replacement of the reducing agents by hydrogen, which acts as a reducing species in the presence of hydrogenation catalysts, is very advantageous.

The report surveys the chemical reductions of organic compounds, presenting a classification by type of group to be reduced, and indicates the appropriate method to be used in the substitution by catalytic hydrogenation. The catalyst, its specific properties, most frequent applications, and regeneration are discussed. The main producers of noble metals are listed, and the trends in prices of the precious and rare metals that have been considered in recent years for the preparation of catalysts are shown. Attention is paid to equipment for catalytic hydrogenation, the reactor types for gas as well as liquid phase hydrogenation and the methods of heating and cooling. The problems of catalyst metering and separation involving a number of practical aspects are analysed. Guidelines for safety at work with hydrogenation and sources of hydrogen use are also presented.

RECOMMENDATIONS

The Workshop on Low-Waste Technologies for some Chemical Processes, organized by the United Nations Industrial Development Organization (UNIDO) in co-operation with the Prague Institute of Chemical Technology (VSCHT), was held at Prague, Czechoslovakia, in October 1986.

The questions considered during the workshop were as follows:

(a) Are low-waste technologies ready for application in industrial processes?
(b) What technical, economic and socio-political factors must be considered when implementing such technologies?
(c) What further research is needed?
(d) How can UNIDO help with follow-up to the workshop?
(e) Should an international low-waste society be established, in order to promote the exchange of information?

A number of technical papers were presented, which are included in the proceedings. On the basis of these papers and a review of the Institute's project with UNIDO on "Advisory assistance on low- and non-waste technologies for some chemical processes", a number of recommendations were proposed for future activities to promote low-waste technologies. It was recommended that:

(a) From a technical standpoint the term "low-waste technologies" should be used in preference to "low- and non-waste technologies";

(b) The conclusions of the Institute's report should be included in the workshop proceedings and that UNIDO should consider publishing portions of the report that pertain to low-waste technologies for inorganic chemical processes separately from those for organic processes;

(c) The evaluation of low-waste technologies should be conducted collaboratively by people with theoretical and practical experience in several science, engineering, and social science disciplines;

(d) Studies should be undertaken to provide economic data and the socio-political basis for considering governmental policies concerning low-waste technologies in developed and developing nations;

(e) A handbook should be prepared that would appraise the current stage of development of specific low-waste technologies, including their technical applicability, economic viability, and potential problems;

(f) Low-waste technologies should be offered to developing countries, taking into consideration their particular circumstances and needs and including an independent evaluation of the appropriateness of the technologies. Adequate advance training of the personnel who will operate and maintain them should be ensured;

(g) An international association for low-waste technologies should be established to exchange information about the field and to collaborate with organizations in relevant disciplines in evaluating technologies and promoting those that are technically, economically, and socially sound;

(h) UNIDO should sponsor a meeting to follow-up on the initiatives of the Institute's project and of the workshop, as well as on current developments in the field of low-waste tecnologies, as soon as practicable in 1987.

LOW-WASTE TECHNOLOGY: STATE OF THE ART

Petr Grau and Peter Lischke*

INTRODUCTION

The Czechoslovak project "Advisory assistance on low-waste technology for some chemical processes", completed in mid 1986, was the first project within UNIDO to deal in detail with industrially applicable technologies that maximize the rational use and complete processing of natural resources and thus lead to the conservation of raw materials and energy and to the improvement of environmental conditions.

Specifically, the project focused on four widely used chemical technologies:

(a) Oil refining, with special attention to the removal of sulphur compounds from petrochemical raw materials and products;

(b) Production of sulphuric acid, with special attention to the minimization of SO_2 emissions and to the use of waste heat;

(c) Production of nitric acid, with special attention to the minimization of NO_x emissions;

(d) Organic synthesis, with special attention to the replacement of traditional chemical reduction by low-waste catalytic hydrogenation.

A. Terminology

International co-operation on low-waste technology dates back to the early seventies. Basic principles and concepts were formulated in 1975 by an ad hoc meeting of experts of the Economic Commission for Europe (ECE) [1].

Early documents used the term non-waste technology. From the spirit of those documents it can be seen that the term was proposed as a theoretical category and means an absolute goal that society can only approach step by step and that may not even be reached in the foreseeable future.

> "Transition to non-waste technology is a gradual and comprehensive process, the goal of which is to come to a closed system, production-consumption, that is, the creation of a non-waste economy" [1].

With the expansion of activities in this novel area and with exposure of non-professionals to new concepts, strategies, principles and goals, the use of the term non-waste technology began to be criticized as being unrealistic and misleading to the public and a new term was proposed and adopted in international co-operation: low- and non-waste technology [2].

This term has also been used in all UNIDO documents so far. The term actually suggests, however, that there are three different technologies: traditional technologies; low-waste technologies; and non-waste technologies.

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This is of course not the case. Non-waste technologies do not exist at present and whether they can theoretically exist at all depends on the definition used for the term waste.

Some support has been found in more recent publications for the use of the terms clean technologies or low-waste technologies [3].

The term pollution abatement and control technologies [4] has a broader meaning and includes not only the low-waste concept, but also the control concept, which is generally equivalent to waste treatment technology. Thus pollution abatement technology and non-waste technology are similar, but not identical or equivalent, as shown below.

For the rest of this paper, the term low-waste technology and its acronym LWT are used.

B. Definition of low-waste technology

Low-waste technology has been defined in three ways:

(a) The United Nations Economic Commission for Europe:

> "(LWT is) the practical application of knowledge, methods and means, so as - within the needs of man - to provide the most rational use of natural resources and energy, and to protect the environment";

(b) The Commission of the European Communities:

> "(LWT is) a technique to produce a product with the most rational use of raw materials and energy, at the same time reducing the amount of polluting effluents in the environment and the quantities of wastes produced during manufacturing and during the use of the manufactured products";

(c) Industry preferred definition, as advocated by de Reeder [3]:

> "(LWT is) the entire range of actions aiming at minimizing the wastage of raw materials and energy and the production of pollutants".

It is not intended in this paper to discuss the definitions, but rather to show that LWT is a broad concept not limited to good housekeeping within an existing process and technique. Various aspects of LWT were summarized and discussed in the final report of the Czechoslovak project. It appears that, as soon as a real specific technology is being elaborated, such terms as most rational use of natural resources and energy become very vague and do not offer a reliable criterion for decision making. What seemed to be perfectly rational yesterday, does not seem rational today and may be very doubtful tomorrow.

Rationality is closely related to economics. It is definitely not true that what is economical is also rational. On a company level, however, rationality is measured by economic criteria. Other components of rationality do have rather the nature of constraints or boundaries to the system, e.g. safety, environmental standards and public acceptance. When an LWT action has a positive economic result for a company, it will be adopted quite naturally.

In many cases, higher costs for the producing company are believed to be counterbalanced by lower costs to the state, region, continent or even several continents. The professionals, such as engineers, researchers and representatives of industrial companies, generally feel that they do not have enough information on development in this area. Apart from the Declaration on the employment of low- and non-waste technology and the reutilization and recycling of wastes, accepted by the high-level meeting within the framework of ECE on the protection of the environment [3], there are few international activities related to the non-company aspects of LWT.

C. Information on low-waste technology

There are three comprehensive sources of information on low-waste technology:

(a) Symposium of the CMEA countries on the theoretical, technical and economic aspects of low- and non-waste technology, March 1975, Dresden, German Democratic Republic, comprising 4 plenary papers on the social and political importance of non-waste technology, on economic aspects, on scientific and technical aspects and expected development of non-waste technology in various industries and 46 papers on various industries (12 chemical, 14 coal and mining, 12 on metallurgy, 8 on construction materials). A report of this symposium in English is contained in [4];

(b) Seminar on the principles and creation of non-waste technology and production, organized by the Senior Advisers to ECE Governments on environmental problems, held in Paris, France, December 1976, comprising 76 papers (5 on concepts and principles of non-waste technologies, 14 on national experience and policy, 24 on industrial experience, 15 case studies, 4 on cost/benefit aspects, 10 on ways and means of implementing non-waste technologies and 4 on methodological and strategic aspects of non-waste technologies. A report of this seminar in English is contained in [6];

(c) Compendium on low- and non-waste technology, published by ECE. So far, seven volumes have been published as abstracts (ECE/ENV/36) and as monographs (ENV/WP.2/5), comprising 129 industrial LWT processes at various stages of development.

D. Where are the gaps?

There are very few recent sources of data and studies to support the establishment of government legislation for LWT.

Such data and studies should elucidate the logic and efficiency of the following:

(a) Economic pressure (positive, financial incentives; negative, pollution charges);

(b) Legislative pressure (environmental standards, quality standards on recovered materials etc.);

(c) Public pressure (opinion, acceptance).

Technical, economic and government policy information on LWT is mostly contained in documents having restricted and limited circulation. There are no widely circulated periodicals (journals, magazines) and non-periodicals (books).

There are no professional societies on LWT. Support should be given to national and international seminars, symposiums etc., where LWT can be discussed among all interested parties.

There is also a lack of information on LWT concepts and approaches in developing countries. Can they afford not to use LWT?

Low-waste technology as a scientific and engineering discipline is still in statu nascendi.

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REPLACEMENT OF CHEMICAL REDUCTION BY CATALYTIC HYDROGENATION

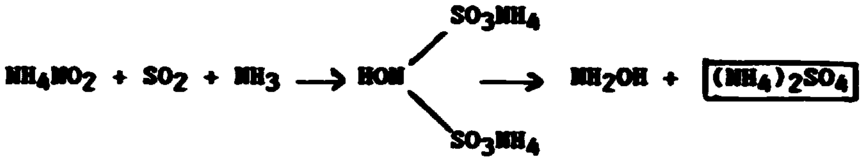
J. Pašek and L. Červený*

INTRODUCTION

In the reduction of various functional groups, the reducing agent is oxidized and the oxidation product usually represents a very unpleasant waste:

$$4RNO_2 + 9Fe + 4H_2O \longrightarrow 4RNH_2 + \boxed{3Fe_3O_4}$$

$$3RNO + 2Na_2S_2 + 3H_2O \longrightarrow 3RNH_2 + \boxed{2Na_2S_2O_3}$$



$$NH_4NO_2 + SO_2 + NH_3 \longrightarrow HON\begin{matrix} \diagup SO_3NH_4 \\ \diagdown SO_3NH_4 \end{matrix} \longrightarrow NH_2OH + \boxed{(NH_4)_2SO_4}$$

$$RCOOR' + Na + H_2O \longrightarrow RCH_2OH + R'OH + \boxed{NaOH}$$

In the production of aromatic amines, especially of dye intermediates, many different nitro- and nitroso-compounds are reduced. Hydrated iron oxides containing a certain amount of amine are usually used in the manufacture of pig iron. This raw material is not suitable, however, for use in metallurgical works. In reductions using sulphides, the waste water contains unreacted disulphide, thiosulphate, sulphate and other substances. The main product of the oxidation, the thiosulphate, cannot be separated in the required purity. Hydroxylamine is used in the manufacture of caprolactame, with large amounts of ammonium sulphate produced as a by-product. This is not a very good nitrogen fertilizer, especially for heavier soils. Czechoslovakia now has difficulties with the sale of ammonium sulphate. The problem can be solved by technological modifications in some of the processes, especially in the coking of coal.

Catalytic reduction by hydrogen does not produce such wastes and thus this process has gradually replaced chemical reductive agents over the last decade. The replacement was initially restricted to high capacity plants, although it is now used even in smaller processes.

This development has been made possible by three circumstances:

(a) Enlargement of hydrogen resources and the broad application of hydrogen;

(b) Development of selective catalysts, catalyst selectivity being in some processes the determining aspect of the applicability of hydrogenation;

(c) Development of suitable apparatus.

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This paper contains two examples from the Czechoslovak chemical industry: the reduction of nitrobenzene to aniline; and the reduction of 4-nitrosodiphenylamine to 4-aminodiphenylamine. Both processes were developed from laboratory research at the Prague Institute of Chemical Technology and are now used in large industrial plants.

A. Reduction of nitrobenzene to aniline

When using iron to produce 1 tonne of aniline from nitrobenzene, 1.8-2 tonnes of iron are consumed and 4-5 tonnes of moist hydrated iron oxides and 1-5 m^3 of waste water are produced. This process has many disadvantages when compared with catalytic hydrogenation:

(a) Transport, crushing and classification of iron cuttings are very work-consuming operations that pollute the working environment;

(b) Aniline residues cannot be completely separated from the iron oxide sludges, which must be dehydrated in open deposits where the aniline evaporates;

(c) The transport of moist sludges is very difficult;

(d) The high humidity of the sludges makes them an unusable raw material in metallurgical works;

(e) Stripping the aniline from the sludges by means of water vapour produces a large amount of aniline water. Although this can be recycled into the process, the amount of waste water is much higher than that produced in catalytic hydrogenation, where only reaction water is formed (0.4 m^3/t);

(f) The probability of aniline leaks, which cause pollution of the working environment, is higher in the process using iron.

Smaller amounts of iron oxide sludge can be used in the manufacture of pigments or abrasive materials.

Catalytic reduction of nitrobenzene is performed in various technological modifications:

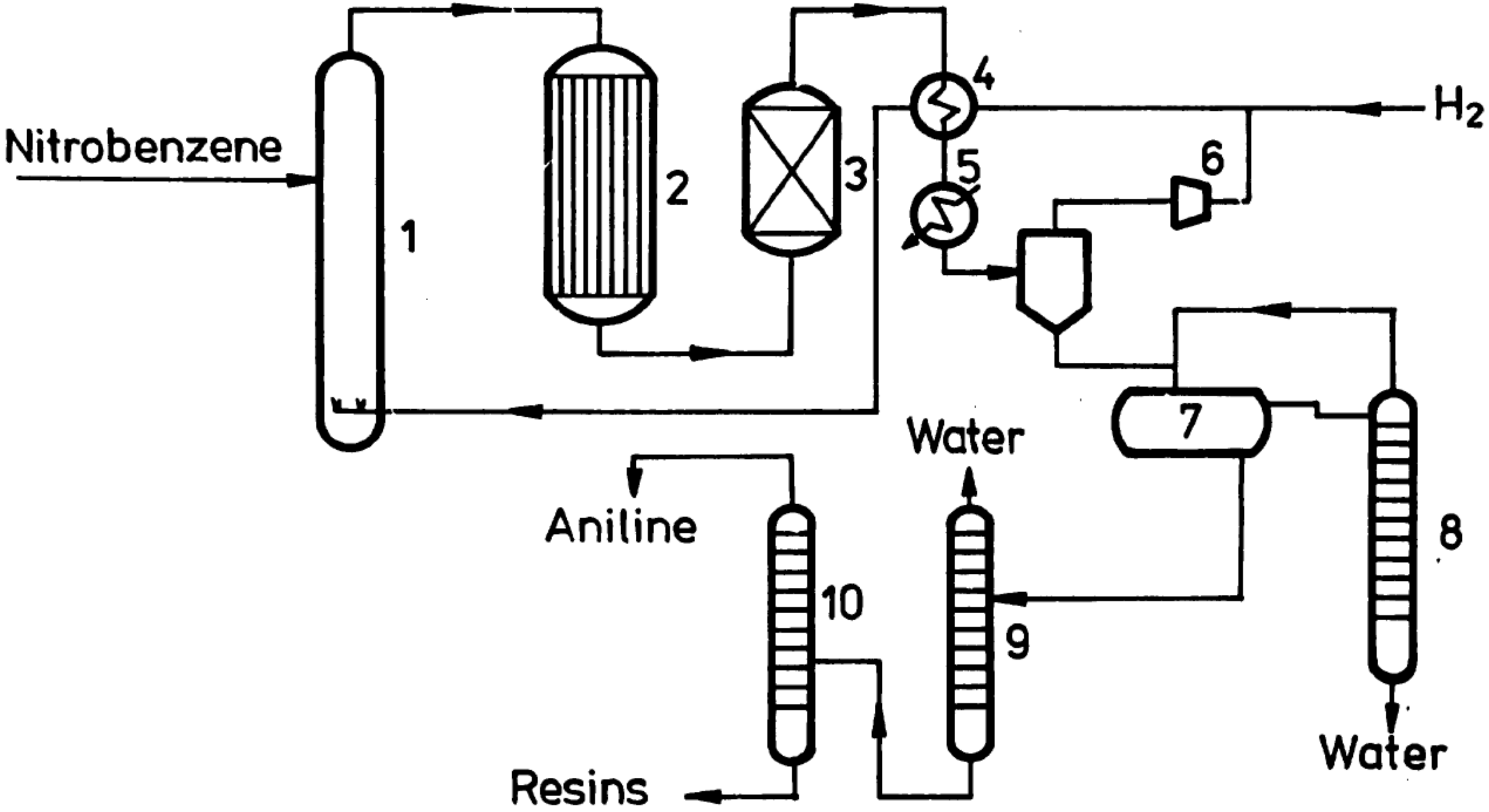
(a) Gas-phase hydrogenation in a fixed bed reactor is used by NIOPIK in the Union of Soviet Socialist Republics, by Sumitomo in Japan, by Moravské chemické závody in Czechoslovakia, and by Bayer in the Federal Republic of Germany;

(b) Gas-phase hydrogenation in a fluid bed reactor is used by American Cyanamid Co. in the United States of America and by BASF in the Federal Republic of Germany;

(c) Liquid-phase hydrogenation in a slurry reactor is used by ICI in the United Kingdom of Great Britain and Northern Ireland and by Tolo Chimie in France.

Individual processes differ in the catalyst used, the manner in which heat is uptaken, the arrangement of the rectification, the way the aniline water is treated etc. A simplified scheme of the MCHZ process developed at the Institute is shown in figure I. Technical and economical parameters of the MCHZ process (with respect to the production of 1 tonne of aniline) are as follows:

Figure I. Hydrogenation of nitrobenzene in the gaseous phase



__Key__: 1 Nitrobenzene evaporator
2 Tube reactor
3 Adiabatic reactor
4 Heat exchanger
5 Cooler
6 Recycling compressor
7 Phase separator
8 Aniline-water column
9 Dehydration column
10 Aniline column

Nitrobenzene consumption, 1,335 kg (yield 99%); catalyst consumption, 0.7-1.0 kg; heat consumption, -0.5 GJ; electric energy consumption, 150 kWh.

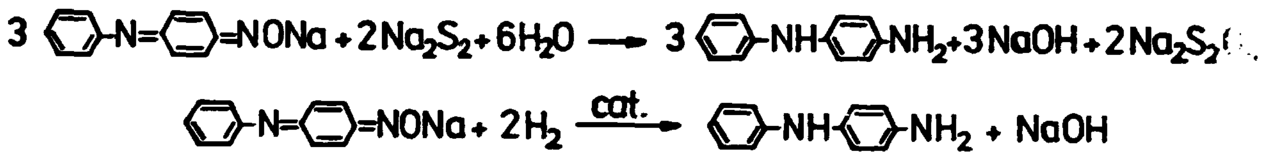
Heat consumption is a very important process parameter. The energy consumed is harmful to the environment in two ways: the production of energy always negatively affects the environment; moreover, the dissipated heat presents another harmful attack on the environment. In the MCHZ process, some heat is produced. This was achieved by exploiting the high reaction heat for steam production and the multiple heat exchange between the technological streams. The technique of multiple heat exploitation is shown in figure II.

It was not only ecological factors that forced the replacement of the chemical reduction process by one using catalytic hydrogenation: hydrogenation also reduces costs by 20%. Chemical reduction using iron is now only carried out in smaller plants. In Czechoslovakia, the manufacture of aniline by this method was abolished in 1975. The development of polyurethane and rubber chemicals required the construction of large new aniline plants that were unthinkable on the basis of the chemical method.

B. Reduction of 4-nitrosodiphenylamine

4-nitrosodiphenylamine is formed in water-methanol solution in the rearrangement of 4-nitrosodiphenylamine. The solution is suitable for subsequent treatment to 4-aminodiphenylamine, without separation of the pure substance.

There are two ways to reduce the nitrosogroup:

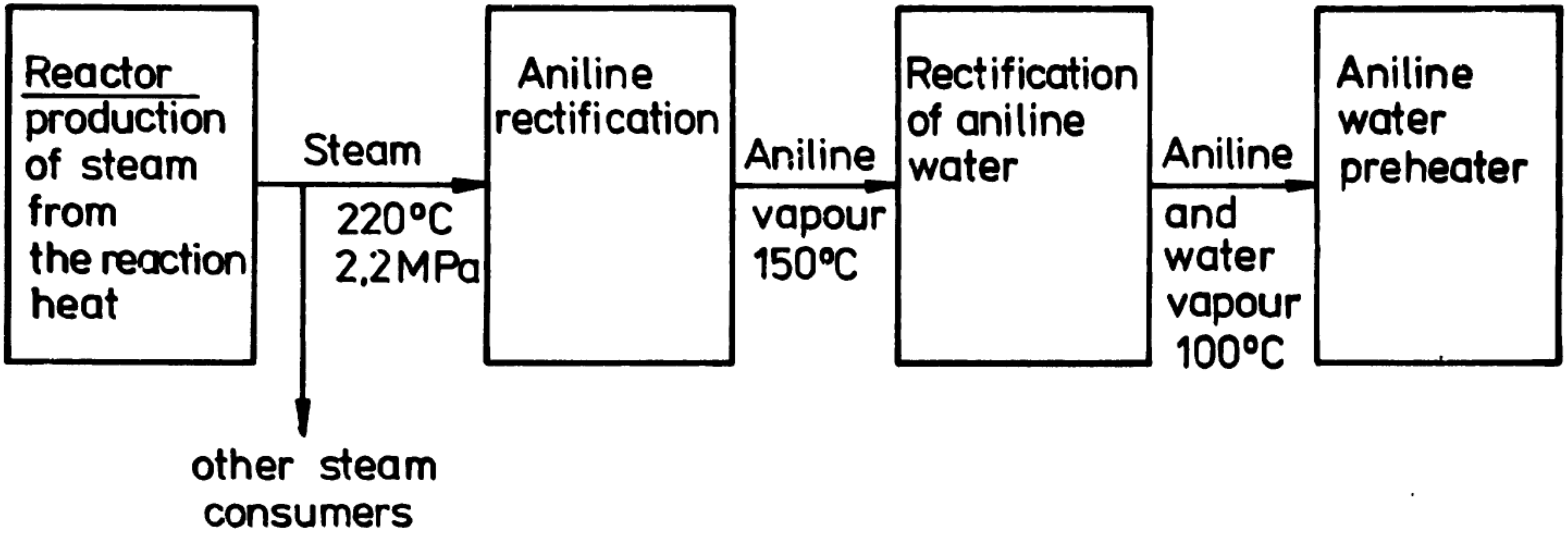


In contrast to the reduction of nitrobenzene, where the choice of reducing agent is now unequivocal, in this case hydrogenation is not so clearly preferable. The costs of the reducing agents, i.e. disulphide and hydrogen plus catalyst, respectively, are comparable. The apparatus for the catalytic hydrogenation, however, is more expensive: the plant consists of high pressure apparatus, compressor and filter for catalyst separation etc. The apparatus for the sulphide reduction, on the other hand, is very simple.

In spite of slightly higher costs for catalytic hydrogenation, this process was preferred for use at the Institute because it produces a cleaner waste water. The following table shows the composition of the waste water resulting from the production of 1 t of 4-nitrosodiphenylamine.

	Sulphide reduction	Hydrogenation
Waste water (m^3)	7	5
NaCl (kg)	500	500
NaOH (kg)	350	350
Na_2S_2 (kg)	70	-
$Na_2S_2O_3$ (kg)	600	-
Organic substances (kg)	25	25

Figure II. Block diagram of multiple heat exploitation



The waste water from the hydrogenation can be treated after neutralization, by a biological purification procedure. Waste water from the sulphide reduction contains a lot of bonded sulphur, which requires high oxygen consumption in the biological treatment. It is therefore necessary to separate the sulphur before biological treatment of the waste water. The sulphur dioxide formed during the neutralization presents another problem. Sodium disulphide increases the content of sodium ions in the waste water, producing an increase in the salinity of effluent water.

The simpler waste water composition from hydrogenation allows some of the minerals to be exploited. Sodium hydroxide, for example, may be converted into the insoluble bicarbonate, which can be separated by filtration. Its calcination leads to the carbonate, which is a valuable by-product. Moreover, the amount of salts in the effluent water is decreased.

The hydrogenation of 4-nitrosodiphenylamine is carried out continuously in a series of bubble columns. The amount of suspended catalyst in the feed solution of the nit :ocompound is 0.04%.

C. The choice of the hydrogenation arrangement

The selection of the hydrogenation apparatus is discussed in detail elsewhere. Only the question of the size of the production capacity is mentioned here.

A special apparatus is necessary for the hydrogenation. The economical effectiveness of its use markedly increases with increasing size of the production capacity. Many organic compounds, however, are manufactured in relatively small amounts. This discrepancy can be solved by setting up larger multi-purpose plants.

Not all the reactor systems for hydrogenation are equally suitable.

There are four main types of hydrogenation reactor:

(a) Gas-phase hydrogenation in a fixed bed reactor;

(b) Liquid-phase hydrogenation in a trickle bed reactor;

(c) Continuous liquid-phase hydrogenation in a slurry or expanded bed reactor;

(d) Batch hydrogenation with a suspended catalyst.

The first and third types of hydrogenation should be carried out in a special apparatus and are not convenient for the production of multiple compounds. The trickle bed reactor and stirred autoclaves, on the other hand, are convenient for this purpose. In continuous hydrogenation in a trickle bed reactor with a layer of a granulated catalyst, it is not necessary to manipulate the catalyst in the case of slurry hydrogenation. Trickle bed reactors are therefore relatively simple.

The introduction of a fine catalyst powder into the autoclave and then catalyst separation by means of filtration are not only very unpleasant, but also hazardous operations, because many catalysts are pyrophoric.

However, the use of a simple trickle bed reactor is limited by several factors of which two are of major importance:

(a) Fast catalyst deactivation;

(b) Decrease in selectivity caused by a shift of the kinetic régime into the region of internal diffusion.

In the area of hydrogenation, the Department of Organic Technology at the Prague Institute of Chemical Technology investigates:

(a) The synthesis and properties of hydrogenation catalysts;

(b) Certain types of hydrogenation reactions;

(c) Chemical engineering of trickle bed reactors;

(d) Control of reactors;

(e) Development of industrial hydrogenation processes.

In co-operation with industrial companies, the Institute has developed and set up 14 processes in the area of hydrogenation and hydrogenative (reducive) amination: gas-phase hydrogenation, 4 processes; hydrogenation in a trickle bed reactor, 3 processes; batch hydrogenation in an autoclave, 5 processes; continuous slurry hydrogenations, 2 processes.

REMOVAL OF SULPHUR COMPOUNDS FROM PETROCHEMICAL RAW MATERIALS AND PRODUCTS BY HYDROGENATION AND EXPLOITATION OF THE RECOVERED HYDROGEN SULPHIDE FOR FURTHER CHEMICAL SYNTHESES

O. Weiser* and H. Schulz**

INTRODUCTION

The refinery, carbochemical and petrochemical industries have been considered for many years to be serious sources of industrial waste that have a very negative influence on the environment. However, over the last few years the situation has improved substantially, and some processes that produced undesirable wastes are, in their modern versions, low-waste technologies (a typical example is the latest commercial fluid catalytic cracking process).

Fossil fuels consist not only of hydrocarbons but also of compounds that incorporate heteroatoms, e.g. sulphur, nitrogen, oxygen and even metals. These non-hydrocarbon components are generally detrimental to the quality of final products, and if disposed of, for example by combustion, have an adverse effect on the environment.

The higher the boiling point of the hydrocarbon feedstock, the higher is the heteroatom content and the more difficult is its removal. The refining of the high-boiling and residual feedstocks represents, therefore, one of the greatest challenges, both technically and economically, faced in the industrial processing of fossil fuels, and also concerns a fundamental ecological problem that has to be solved.

High-boiling and residual hydrocarbon fractions can be refined by means of physical methods, such as extraction, adsorption, de-asphalting, special distillation and thermal diffusion. These processes have two basic disadvantages: they are not universally applicable and they produce substantial quantities of wastes, which can frequently only be converted further with great difficulty.

Hydroprocessing is a universally applicable method for refining high-boiling and residual fractions. Many hydroprocesses have been developed in which the undesirable components are removed and refined products with desirable properties are obtained under various degrees of severity of reaction conditions.

Hydroprocesses are also very effective from the ecological point of view: they are of a low- or even non-waste technology nature. Undesirable components are transformed into valuable hydrocarbons and heteroatoms are removed as their hydrogen compounds or as pure metals.

From the economic point of view, the intensity and productivity of the hydrogenation processes must be maximized. Catalytic processes are therefore generally used (if it is technically and economically possible). For highly contaminated feeds, however, the application of catalysts is not feasible and other methods for ensuring an adequate hydroprocessing rate must be sought.

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Because of these interrelations, some of the above-mentioned problems, mainly those of ecological importance, have been treated in more detail elsewhere. Only the most important facts are discussed here.

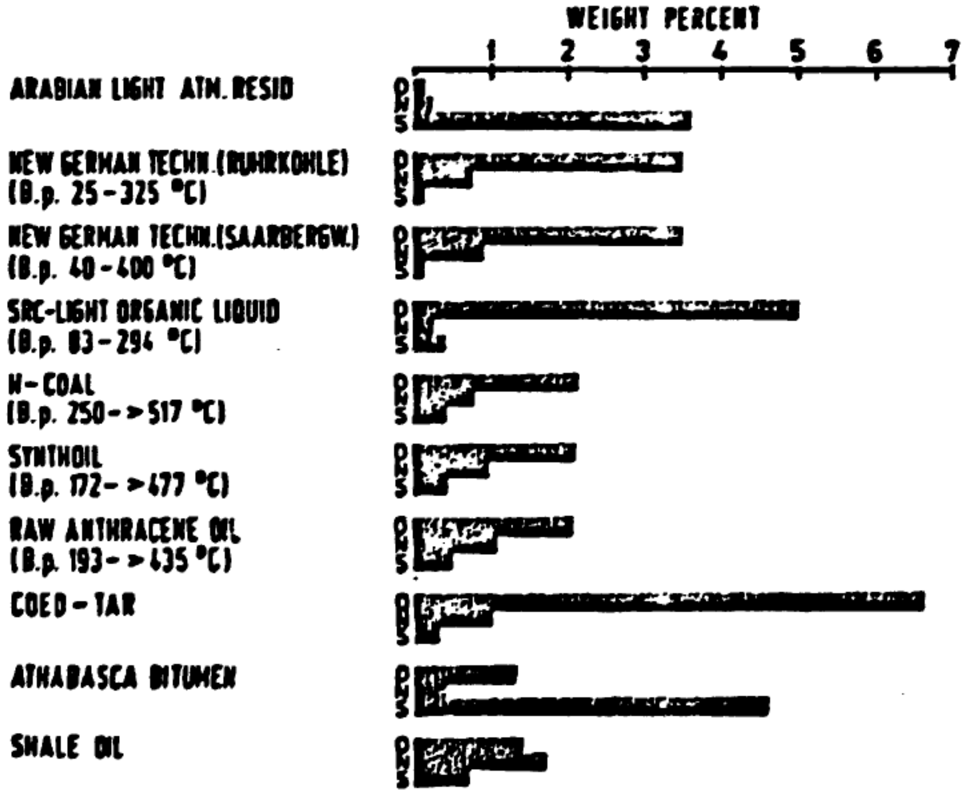
A. Characteristics of heavy oils

Heavy oils are rich in carbon and poor in hydrogen. Correspondingly, their hydrocarbon composition is primarily aromatic and less aliphatic and naphthenic.

All the crude oils, even the light ones, contain a certain fraction of residual oil, which has to be processed for final use specifications. As the resources of light oils become increasingly exhausted, the heavy oils will be the main feedstock for both high quality fuels and chemicals in the future. It is therefore very important, and must generally be recognized, that modern heavy oil processing and usage should approach the "non waste" principle as closely as possible.

The percentages of heteroatoms (sulphur, nitrogen and oxygen) in selected liquid fuels are given in figure I: petroleum oil from coal hydrogenation; tar from high temperature coal carbonization; shale oil; and oil from tar sand. Petroleum can be particularly rich in sulphur. Although the sulphur content in coal-derived oils is relatively low, Athabasca bitumen, which is extracted from a tar sand, is particularly rich in sulphur. The reactivity of sulphur compounds to hydrodesulphurization is relatively high, but residual oil desulphurization is complicated by catalyst contamination from the deposition of metals and coke.

Figure I. Content of oxygen, nitrogen and sulphur in selected liquid fuels



Nitrogen, as a constituent of liquid fuels, has less environmental impact because of its lower concentration. On closer inspection, however, it is seen that nitrogen can be a more problematic contaminant than sulphur. Emissions of NO_x, which can be particularly harmful to needle trees in special situations, result both from nitrogen in the fuel and from reaction with atmospheric nitrogen during high temperature combustion of the fuel. In addition, nitrogen compounds are much more stable towards hydrorefining, requiring more severe reaction conditions, which results in higher costs owing to increased hydrogen consumption, increased reaction pressure and temperature and poorer selectivity towards the end products.

Metals (such as nickel and vanadium), as constituents of heavy petroleum derived oils, are largely responsible for the complexing capability of nitrogen compounds such as porphyrins. The complexes formed are soluble in crude oil and are rather stable. Demetallization is mainly achieved by hydrogenation of the conjugated system of double bonds of the ligand and its denitrogenation. The metal is then deposited on the catalyst. Partial demetallization can also be achieved by de-asphalting residual oils. Ni and V are typical constituents of petroleum residues but are not present in heavy liquids from coal as tars and pitches.

With respect to the environmentally most favourable uses of heavy oils, a second major route, which is not the subject of this study, should be kept in mind: gasifying the oil with oxygen and steam and purifying the synthesis gas before its further use in the production of methanol, ammonia, gasoline and other products. By analogy, the production of fuels and chemicals from coal via gasification is environmentally particularly favourable.

B. Catalytic and non-catalytic processes for conversion of petroleum and coal-derived oils to fuel oils and feedstocks for further deep conversion or refining

Recent trends in the petroleum industry exhibit substantial reductions in crude oil consumption and in the production of petroleum residues to be used as fuel oils. The changes in the consumption of petroleum products and especially of fuel oils can be derived from the data in table 1. It is clear from these data that, in the countries concerned, the rate of consumption of petroleum products will drop in the period from 1980 to 1990 and that this trend should be strongest for fuel oils.

Table 1. Development of consumption of petroleum products in the period from 1980 to 1990

	Total oil products (10^6 m^3/d)				Residual oil products (wt.)			
Country	1980	1985	1990	1980/1990	1980	1985	1990	1980/1990
Czechoslovakia				-14				-14
France	0.293	0.247	0.201	-31	27.7	22.1	14.1	-49
Germany, Federal Republic of	0.347	0.319	0.307	-12	18.6	9.5	9	-52
Great Britain	0.212	0.208	0.197	-7	28.8	23.5	22.5	-22
Italy	0.264	0.287	0.262	-1	47.7	47.6	41.3	-13
Japan	0.327	0.322	0.316	-4	38	33	28.4	-25
United States of America	2.22	2.10	1.97	-11	18.1	13.4	11.9	-34

At present, nearly 50 processes are known that aim to utilize residual oils, of which about 40% are commercial. Their classification is shown in figure II. The individual processes result in different degrees of conversion, as illustrated in table 2.

Table 2. Residual oil conversion achieved in technical operation of different processes

Process	Conversion range (%) depending on severity of process conditions
Hydrorefining	0-33
Visbreaking	5-30
Hydropyrolysis	25-67
Coking	50-70
Hydrovisbreaking	55-70
Hydrocracking	60-95
FCC	70-88
Pyrolysis	75-85
DSV	82-92
Partial oxidation	97-100

The following general conclusions can be made with regard to the individual processes and development trends:

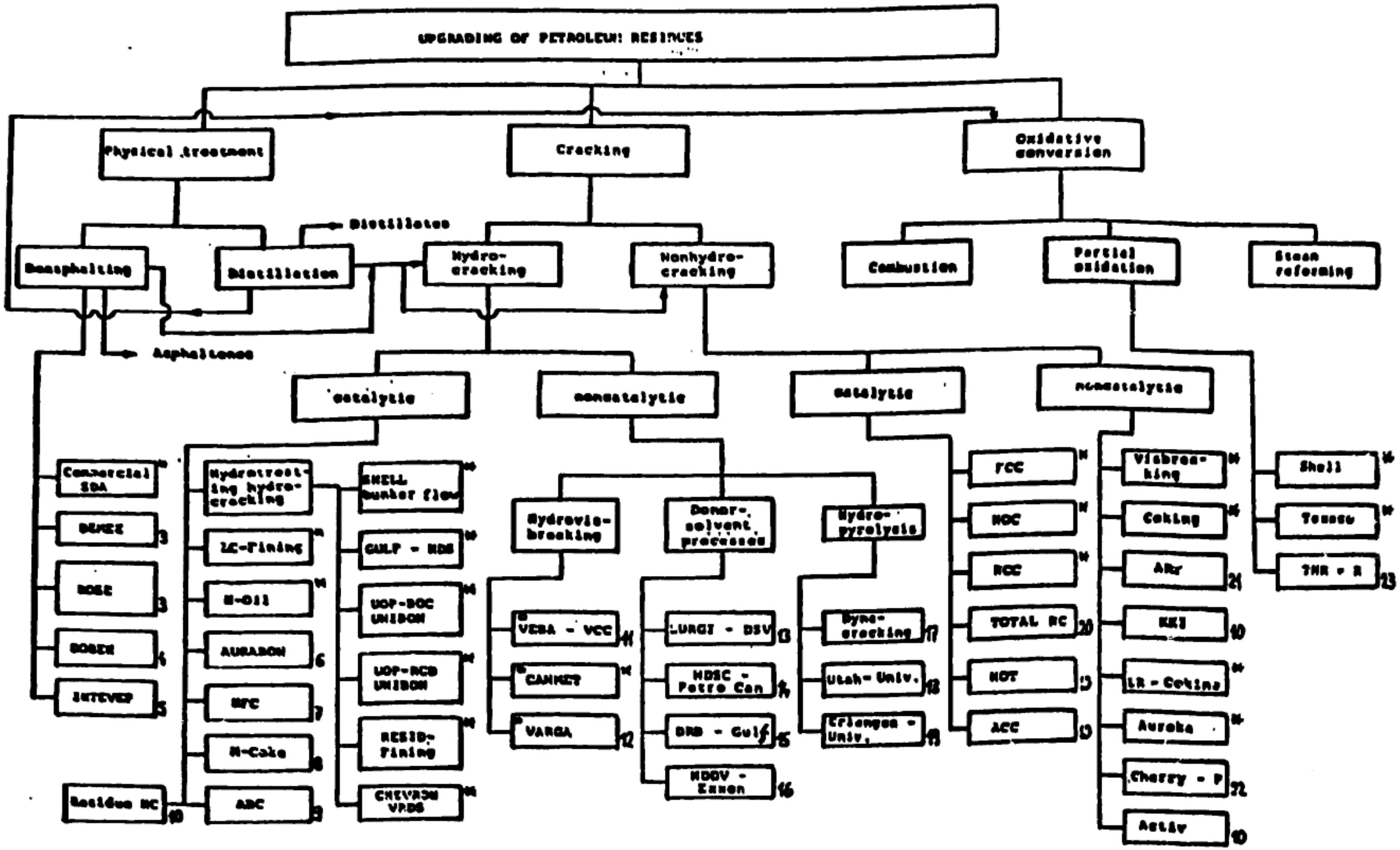
(a) The fundamental difficulties faced in direct catalytic processing of residual oils, which are due to the presence of asphaltenes and organometallic components in the case of hydrogenation processes, can be overcome by using special catalysts that exhibit, among others, the following important properties: very high metal retention power; very low coking tendency; very large active areas; appropriate porosity distribution; and moderate hydrodesulphurization (HDS) and hydrodenitrogenization (HDN) activity.

The combination of hydrodemetallization (HDM) and HDS catalysts is advantageous in the hydroprocessing of residual oils. A suitably selected ratio between HDM and HDS catalysts can regulate the degree of conversion and desulphurization.

Direct hydrodesulphurization of residual oils produces low sulphur fuel oils in the simplest technological way. Owing to intensive deactivation of the catalyst, however, the process is very challenging, both technically and economically. Indirect processes for residual oil desulphurization are therefore used, where the basic principle is to limit the contact between the major contaminants present in the residual oil and the hydrodesulphurization catalyst, to which only the prerefined oils are fed (figure III).

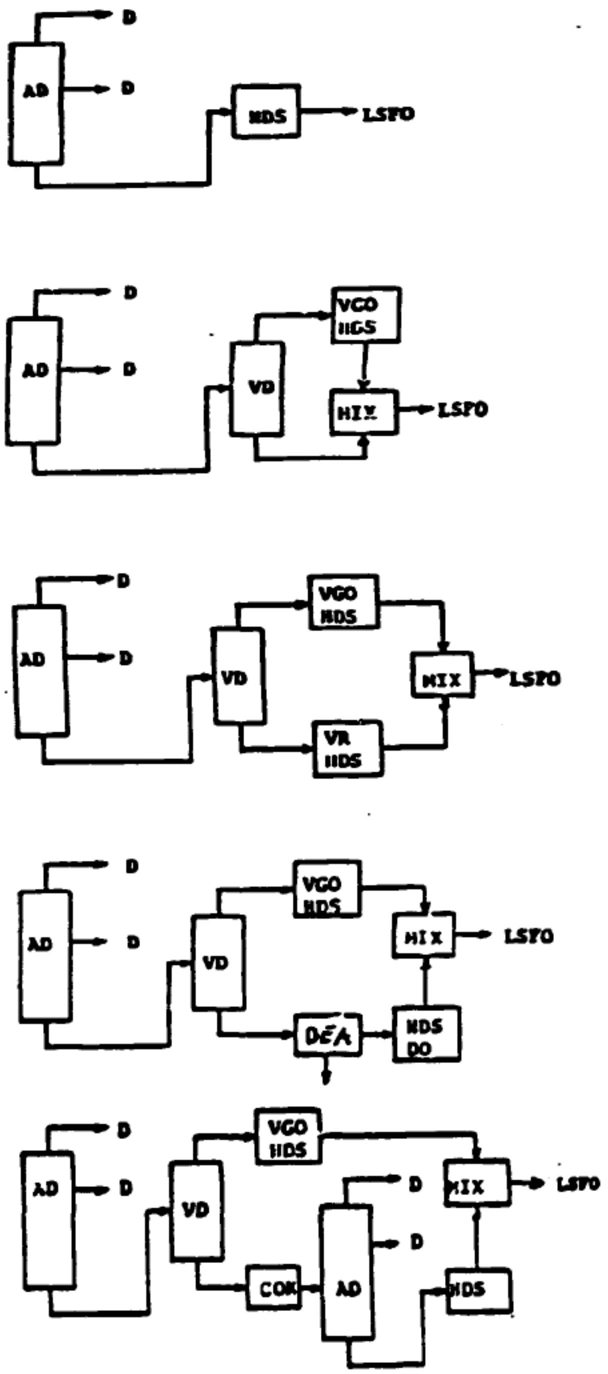
(b) Because of the fundamental problems involved in the direct catalytic conversion of residual oil, the commercial tendency is to favour more widely the thermal route. The purely thermal variant is improved by the application of additives that exhibit only a minor catalytic effect and whose main function is to act as discharges for coking deposits. The coke precursors and other contaminants deposit preferentially on their surface and not on the apparatus walls.

Figure II. Upgrading of petroleum residues



Key: * Commercial scale processes
o Addition of once-through additives (catalysts) that improve the conversion of thermal processes
2-23 Reference numbers

Figure III. Examples of the most important schemes for producing low-sulphur fuel oils



Key:			
AD	atmospheric distillation	SE	solvent extraction
VD	vacuum distillation	COK	coking
D	distillates	MIX	mixing of fuel oils
HDS	hydrodesulphurization	LSFO	low-sulphur fuel oil
VGO	vacuum gas oil	DEA	de-asphalted oil

(c) Hydrogenation processes proceed more easily when solvents with hydrogen donor properties are used. These produce hydrogen radicals required for the chain reaction of thermal cracking or the saturation of unstable intermediates.

(d) In catalytic hydrocracking processes, a number of reactor-engineering means are applied to slow down catalyst deactivation. The most important means are as follows:

(i) Protective catalyst layers (guard reactors) are used for hydrodemetallizing the feedstock (this is done in a separate reactor or in the first layer of the hydro-cracking reactor);

(ii) Catalyst tailoring, i.e., optimization of chemical composition and texture, such as wide pores for the top layer and narrow pores for the bottom layer of the catalyst in the reactor;

(iii) Use of moving catalyst particles so that the catalyst can be continuously regenerated or replaced;

(iv) Catalysts highly resistant to deactivating metals and coke-forming components are applied, e.g. special supports are used (such as special zeolites) that are highly resistant to deactivication by metals;

(v) Special reactors are used, such as trickle phase with perfect distribution of the liquid phase and with wall effect elimination, reactors with ebullating or pseudofluid beds, and slurry reactors.

(e) For non-hydrogenation processes, the following typical trends can be noted:

(i) For wider chemical use of heavy oils, the classical visbreaking has been modified to hydrovisbreaking;

(ii) Coking processes are being optimized, for example the Flexicoking process, which has outstanding thermal efficiency owing to the gasification of a part of the coke being produced so as to produce synthesis or fuel gas. The ART process is a modification of fluid coking, with an inert carrier on which metals and coke deposit. The Japanese EUREKA process is a modification of delayed coking in which the formation of coke is inhibited by means of superheated steam and tars of high aromaticity are formed;

(iii) Efforts to extend the application of FCC to cover residual oil processing have led to catalysts that are passivated against the deactivating effect of metals (Sb additives). Further progress made concerns the regeneration of catalysts that have been deactivated by metals (e.g., in the DEMET III process). In subsequent work, efforts have been made to replace the FCC catalysts based on aluminosilicates by more resistant catalysts. For instance, the Japanese process HOT (10), which is under development, makes use of iron as a catalyst;

(iv) Processes are also under development in which residual oils are used as feed for pyrolysis to produce basic olefinic chemicals.

Coal and other carbonaceous materials such as tar sand and oil shale are important raw materials for industrial chemistry. The transformation of bitumen to high quality fuels or chemicals is one of the most challenging industrial processes, both as a technical and economical goal. Such processes are very important, particularly as reserves of oil and natural gas will be nearing exhaustion within the medium term.

C. Examples of modern processes of heavy oil conversion and their major ecological and economic relevance

The deep conversion of petroleum is based on the hydrogenative or nonhydrogenative cracking of the high-boiling and residual fractions for obtaining maximum yields of lower molecular weight products. The main reasons why numerous deep conversion processes are used in modern refineries are:

(a) Crude oil savings are maximized;

(b) High-quality products are produced that can be used without polluting the environment;

(c) Substantial increases are possible in overall economy and flexibility.

The following are typical processing routes, which are of high technical and ecological importance:

(a) Mild hydrocracking (MHC) of high-boiling petroleum fractions as an efficient and flexible process for producing different fuels and petrochemical feedstocks;

(b) Hydrovisbreaking of residual petroleum fractions for obtaining higher conversion rates and better product qualities than via visbreaking;

(c) Desulphurization of residual oils, especially the combined process of solvent deasphalting and hydrorefining of deasphalted oil;

(d) Direct coal liquefaction as the most important process for producing fuels and carbochemicals from substitute petroleum resources.

Technical details of these selected processes are discussed elsewhere, with only the most important facts covered in the present paper.

Mild hydrocracking is a very flexible process with a relatively extensive area of application, especially for the following:

(a) Production of low-sulphur components of fuel oils;

(b) Production of high-quality components of lubricating oils;

(c) Production of diesel fuel and jet fuels of excellent quality;

(d) Production of FCC feeds;

(e) Production of steam-cracker feeds.

It is particularly attractive that MHC allows the use of existing HDS units, which means that there is a possibility of improving substantially the economy of a refinery when VGO-HDS overcapacity exists. The use of an existing HDS plant for MHC requires only low capital expenditure and slight engineering modifications. Table 3 gives a comparison of the cracking yields for the two feedstocks. The recycled oil has a substantially lower sulphur content owing to hydrogenation of the feed.

Table 3. FCC yields
(Wt. %)

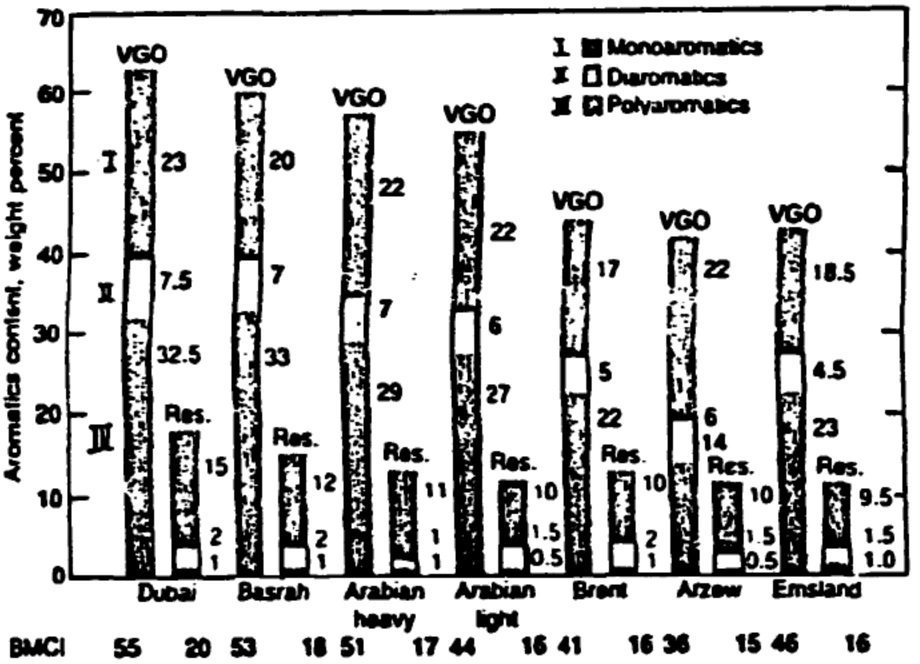
Type	Hydrotreated VGO	Unhydrotreated VGO	Hydrotreated-unhydrotreated
Capacity (tons/day)	3 400	3 200	
Gasoline EP 205 °C ASTM	57.3	49.0	+8.3
C_2 minus	3.9	5.2	-1.3
Propane	1.4	1.4	0
Propylene	4.8	4.3	+0.5
i-Butane	1.9	2.2	-0.3
n-Butane	0.4	0.6	-0.2
Butenes	2.3	3.8	-1.5
LCO, EP 390 °C ASTM	18.4	20.4	-1.9
Clarified oil	4.4	7.7	-3.3
Coke	5.2	5.5	-0.3
Conversion 750 °C			
Vol. %	78.7	74.4	+4.3
Wt. %	77.2	72.4	+4.8
Gasolene selectivity			
Vol. %	88.4	81.2	+7.2
Wt. %	74.2	67.7	+6.5
LCO selectivity			
Vol. %	82.8	75.3	+7.5
Wt. %	80.9	73.6	+7.3
Gasoline + LCO			
Wt. %	75.7	69.3	+6.4

The profitability of catalytic cracking is comparatively high with hydrotreated feedstocks. For instance, at the petrochemical works at Schwechat, Austria, there was an increase of 28.5% in the total daily profit owing to the use of hydrogenated FCC feedstocks.

Hydropretreatment of FCC feedstocks also turns out to be important ecologically: sulphur emissions are reduced when these products are used as motor fuels or the cycle oils are used as a fuel. Catalyst regenerators in cracking plants are also important, as they enable substantial reductions in the levels of SO_2 emissions to be made.

Analogously, the MHC of VGO substantially decreases the content of polyaromatic hydrocarbons and thus increases the yields of ethylene and decreases the yield of pyrolysis fuel oils when VGO serves as a feed for steam cracking. This is shown in figure IV, where the following MHC conditions were applied:

Figure IV. Yields of products, aromatics reduction and group composition changes obtained from MHC processing of different VGO feedstocks (results obtained by BASF).



Catalyst	Ni-Mo/aluminosilicate
Hydrogen pressure	8-13 MPa
Temperature	643-693 K
WHSV	0.6-1 kg/liter/hour
Gas/oil	1-2 m^3/kg

Typical yields (wt. %) obtained are as follows:

C_1-C_4	2.0-4.0
C_5-353 K (light gasoline)	2.0-3.0
353-458 K (heavy gasoline)	7.0-13.0
458-553 K (kerosine)	9.0-14.5
458-623 K (diesel oil)	20.0-29.0
Residue >623 K	60.0

Hydrovisbreaking, in the pure thermic version, in the version with additives or as the donor-solvent modification, seems to be very attractive for upgrading residual oils and making their application ecologically much more acceptable. In addition, this process will certainly play an important role in the chemical utilization of coal. Hydrovisbreaking can also be used to upgrade mixtures of petroleum and carbochemical feeds, for example in the joint processing of vacuum residues and coal tars. Thus, hydrovisbreaking could be a basic process in the future petroleum-coal refinery, which is very topical and attractive for those countries with large coal reserves but where petroleum must be imported.

Coprocessing of coal and residual petroleum fractions is one method of enabling the partial substitution of petroleum by coal. Cohydrogenation of bituminous coal, coke oven tar and residual petroleum oil increases the yields of distillate oil and lowers hydrogen consumption. There is no doubt that this is a very progressive course that will also have great environmental importance.

Another important problem of modern petrochemical combinates, that of optimal chemical utilization of sulphur and hydrogen sulphide, which are produced in relatively large quantities, is discussed elsewhere.

At present, about 90% of the sulphur produced is used to produce sulphuric acid, which is used mainly to increase the production of fertilizers required to boost agricultural yields in developing countries. Substantially larger quantities of sulphur will become available for use in other branches of the chemical and consumer industries: primarily for the sulphur asphalts and concrete; various sulphur composites; special sulphur-containing polymeric substances; and, in particular, special thio-chemicals.

Figure V shows various possibilities for the production of the technically most important thio-chemicals via catalytic synthesis from H_2S. The production of special sulphur products thus represents a substantial economic and ecological contribution to the traditional oil refining and petrochemical industry.

D. Conclusion

The amount of sulphur being recovered from crude oils and coal is generally increasing. Simultaneously, there is an intensification of the necessity for removing it, either from emissions and exhausts after combustion or, alternatively, prior to combustion from the fuels being used for power generation, transportation and chemical feedstocks.

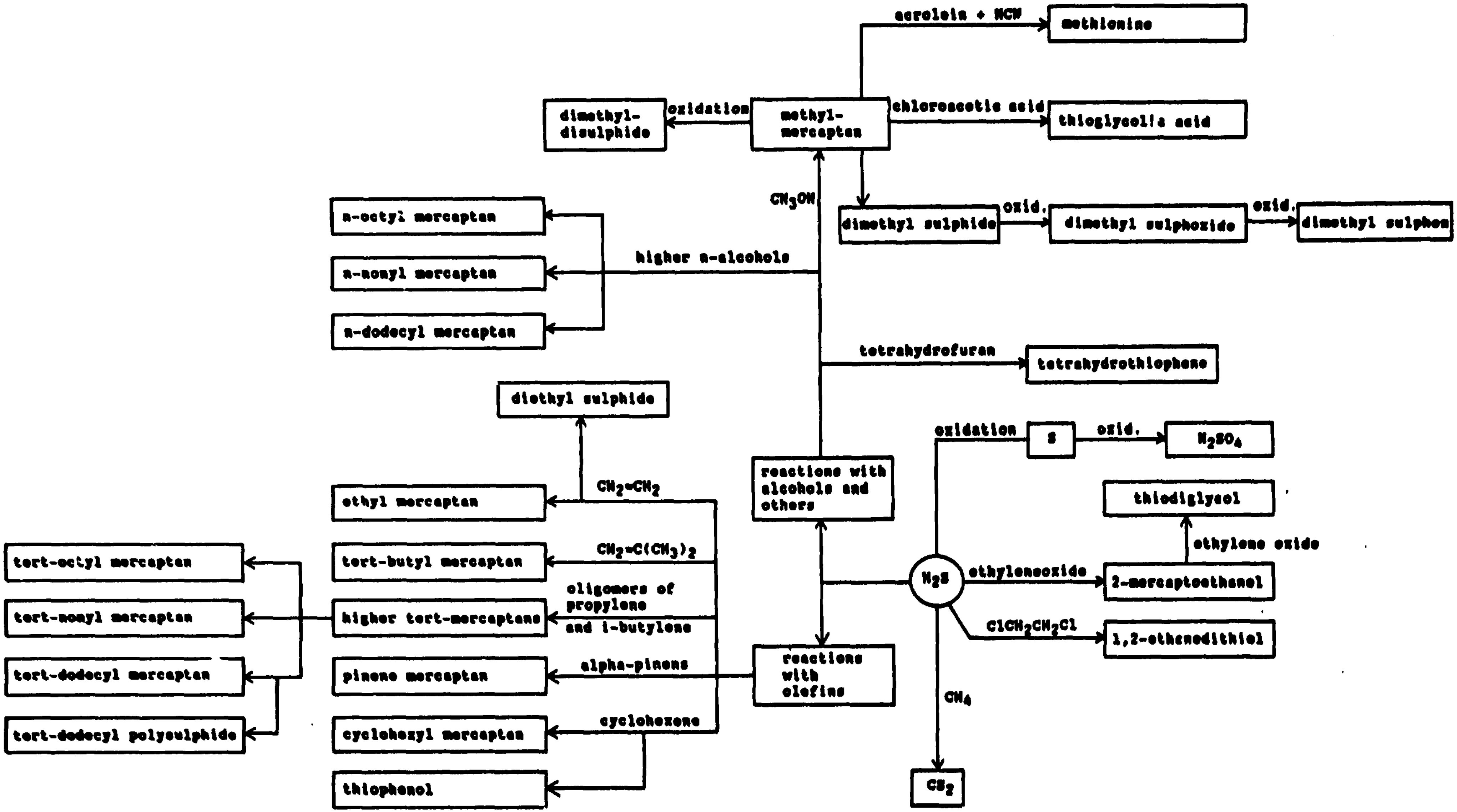
There have been important recent developments in the deep conversion of crude oil, where high-boiling distillates and residual oils are used as a source of high grade fuels and petrochemical feedstocks. Substantial progress has been achieved in the production of low-sulphur fuel oils, in coal liquifaction, and chemical processing of carbochemical products

Conversion of the high-boiling and residual petroleum feedstocks is obtained via highly effective catalytic and thermo-catalytic hydrogenation processes in which the undesirable elements (sulphur, nitrogen, oxygen and metals) are eliminated and upgraded fuel oils are produced, which can also be more easily processed in catalytic or thermal conversions, such as pyrolysis, fluid catalytic cracking and the production of lubrication oils.

The most important new processes are catalytic desulphurization and hydrocracking of residual oils, mild hydrocracking and hydrovisbreaking. These processes are highly effective technologically, they are more economic because of reduced energy consumption, and they meet the ecological requirements of low-waste technology.

An important complement to modern hydrorefining and hydrocracking processes is the non-traditional use of hydrogen sulphide and elemental sulphur. The production of sulphur asphalts and concretes, of special sulphur-containing composites, and of organic thio-chemicals presents a substantial economic and ecological contribution to the traditional oil refining and petrochemical industry.

Figure V. Survey of the technically most important thio-organic chemicals



OPTIMIZATION OF FUEL OIL PRODUCTION FROM VACUUM RESIDUE

R. Kubička*

Fuel oil production takes place in most refineries. The fuel oils produced can be divided into two groups. One group consists of lighter petroleum fractions, for example, distillate fuel oil, corresponding to gas oil. The other group is made up of residual petroleum oils, the main component being atmospheric and vacuum residue.

Among the important quality indicators of the manufactured fuel oils are their sulphur content and viscosity. Significant pressure is being applied to decrease the sulphur content in fuel oil. It is easier to conform to this demand when producing fuel oil made up of petroleum distillates. Enlargement of the hydro-treating capacities and higher production costs have to be taken into account here. This subject was recently considered for the countries of the European Economic Community. It follows from the final report that, technically, sulphur contents can be reduced and that it is only necessary to release the financial means for the completion of the refining equipment. The desulphurization efficiency could be increased from 69% in 1982 to 80% in 1990 [1].

Residual fuel oils are now produced in decreasing quantities. For Western Europe the following figures in millions of tonnes per year are given for the period 1980-1990 [2]:

	1980	1985	1990	1996
Amount of crude oil processed	606.4	527.4	505.6	477.9
Amount of residual fuel oil	200.0	115.1	106.7	90.4
Percentage of crude oil	32.9	21.8	21.1	18.9

The production of residual fuel oil is expected to decrease from about one third to one fifth of the processed crude oil. A similar development can also be expected in other areas. The desire to maximize the utilization of petroleum for the production of motor fuels and petrochemicals is principal in this development, the first result being a decrease in fuel oil production. At the same time, restricting or even ceasing to use atmospheric distillation residues can be taken as the main change in petroleum processing. Up to now, however, residual fuel oils have been produced primarily by that process. Thus vacuum residue is becoming the new basic feedstock for the production of residual fuel oil.

Vacuum distillation enters the crude oil refinery's flow sheet and vacuum gas oil and petroleum vacuum residue are obtained. There are many technological variants for a refinery [3]. When producing fuel oil it is then necessary to start from vacuum distillation residue. Frequently applied alternatives for further processing of vacuum gas oil and vacuum residue are shown in figure 1.

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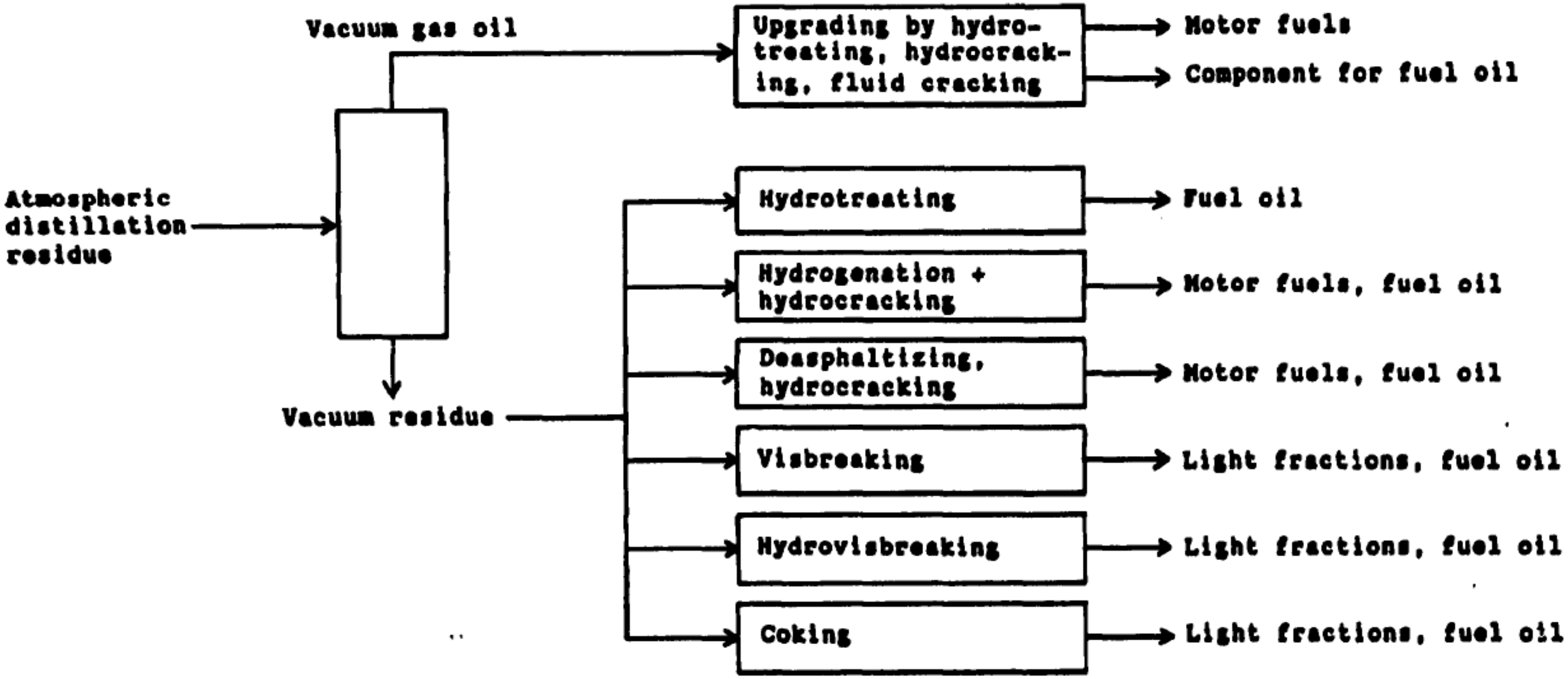
*Chemopetrol, Litvínov, Czechoslovakia.

Figure I. Flowsheet for upgrading petroleum residue



The processing of vacuum residue to motor fuels, pyrolysis feedstock and fuel oil is demanding, both from the process and investment points of view. Alternatives to vacuum residue processing are therefore being investigated, some of which are shown in figure II.

The production of fuel oil containing 25-30% water can be taken as a typical alternative [4].

The manufacture of fuel oil of a satisfactory viscosity by adding lighter petroleum fractions is common. The manufacture of asphalt is also fully known and used.

A useful method of producing hydrogen and synthesis gas at sites with suitable conditions is by the partial oxidation of vacuum residue.

A. The hydrodesulphurization of petroleum distillation residue

The hydrodesulphurization of atmospheric and vacuum residue was introduced in the 1980s, and can be used to desulphurize the entering feed from 2 to 5% to a rest value of 0.5-1%, the working periods being 6-12 months. Twenty-one units with an overall capacity of about 25 million tonnes per year have been constructed [5]. Of these units, 13 were built in Japan, 4 in the United States of America, 2 in Kuwait, 1 in Mexico and a small plant in Sweden. In Europe, petroleum residue is not yet desulphurized.

When hydrodesulphurizing petroleum distillation residue, 60-80% of the metal compounds are removed. This is completely satisfactory for the production of low-sulphur fuel oil. It is not sufficient, however, to produce desulphurized material that can be used as feed for fluid catalytic cracking. In that case, values of 10-20 ppm rest for the metal content, less than 5% for the Ramsbottom carbon content and below 2,000 ppm for the nitrogen content are required [6]. Although the necessity for increases in capacity is being emphasized, further desulphurization units are no longer being constructed [7].

B. Residual fuel oil production in Czechoslovakia

In Czechoslovakia, the direct desulphurization of petroleum atmospheric residue was developed. Particular attention was paid to the production of low-sulphur oil, which required for its manufacture that vacuum gas oil and vacuum residue deasphaltized by light naphtha be separately hydrotreated.

The deasphaltization was developed in the Union of Soviet Socialist Republics, and checked in a commercial size plant in Czechoslovakia. The information obtained was used to work out the project documentation for the production of 1.5 million tonnes per year of low-sulphur fuel oil. The project has not been implemented [8, 9].

The production of fuel oil is also decreasing in Czechoslovakia. The manufacture of atmospheric petroleum residue is being reduced and moreover the vacuum gas oil produced is hydrocracked to motor fuels and to pyrolysis feed for the production of ethylene.

A schematic flowsheet of the crude oil processing in the Litvinov refinery is shown in figure III.

Figure II. Possibilities for direct upgrading of vacuum residue

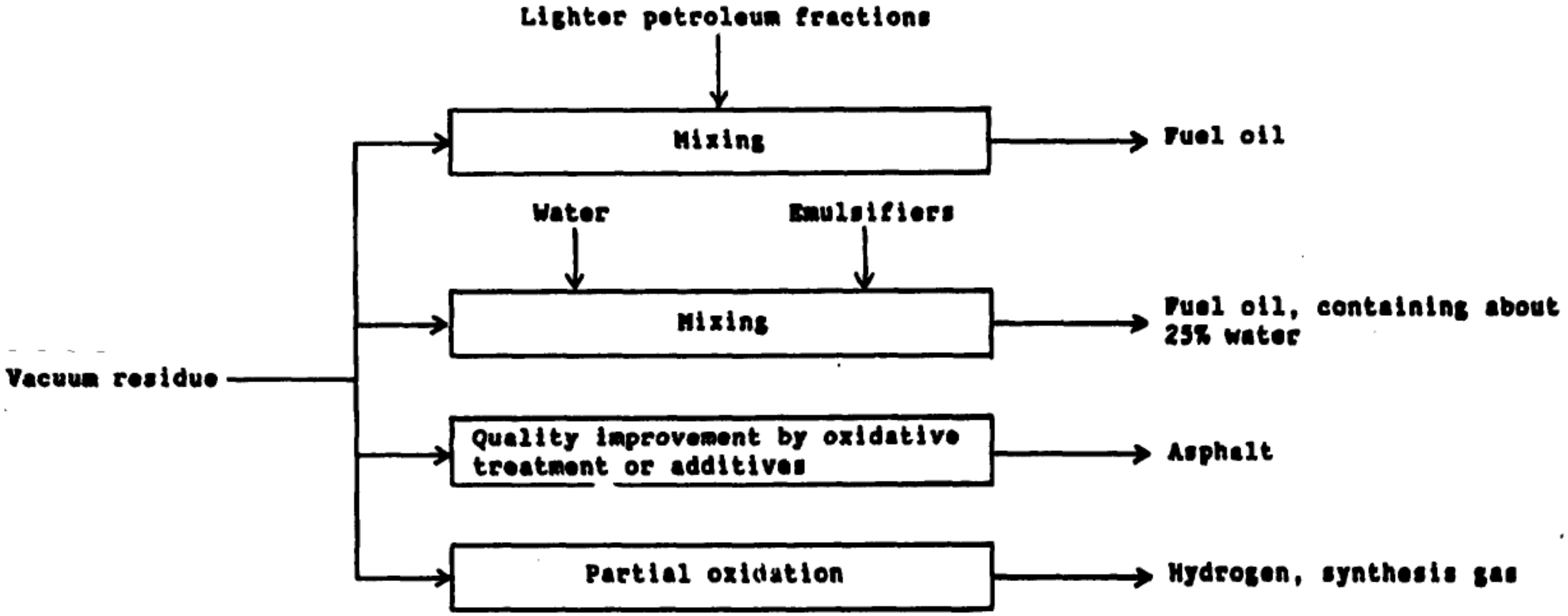
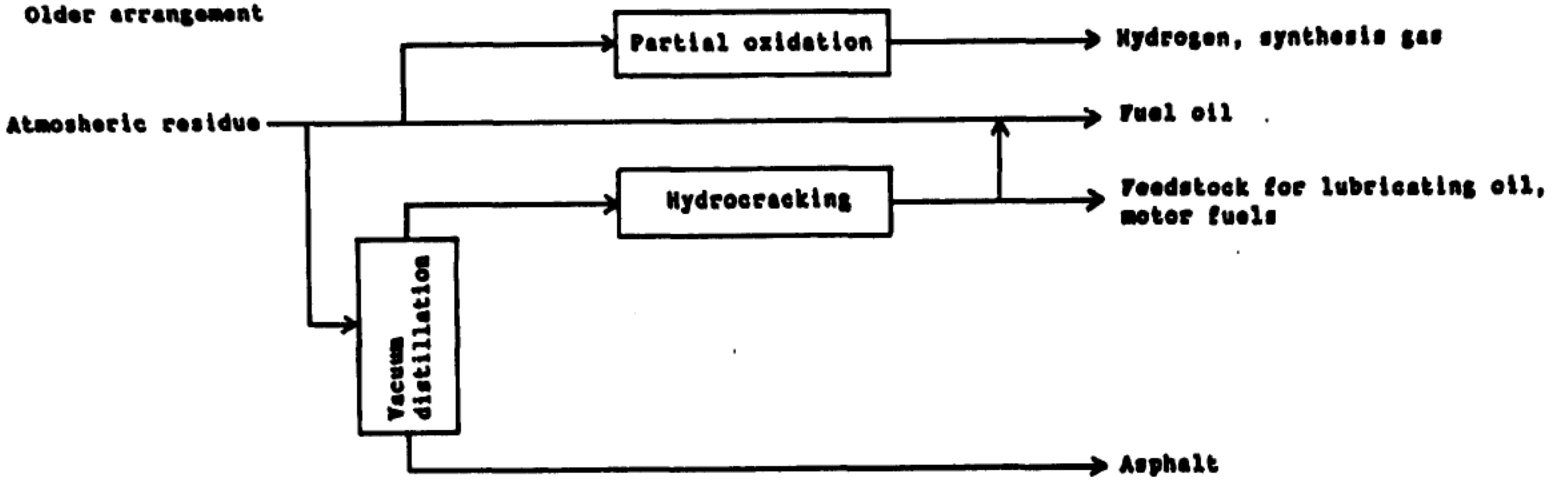
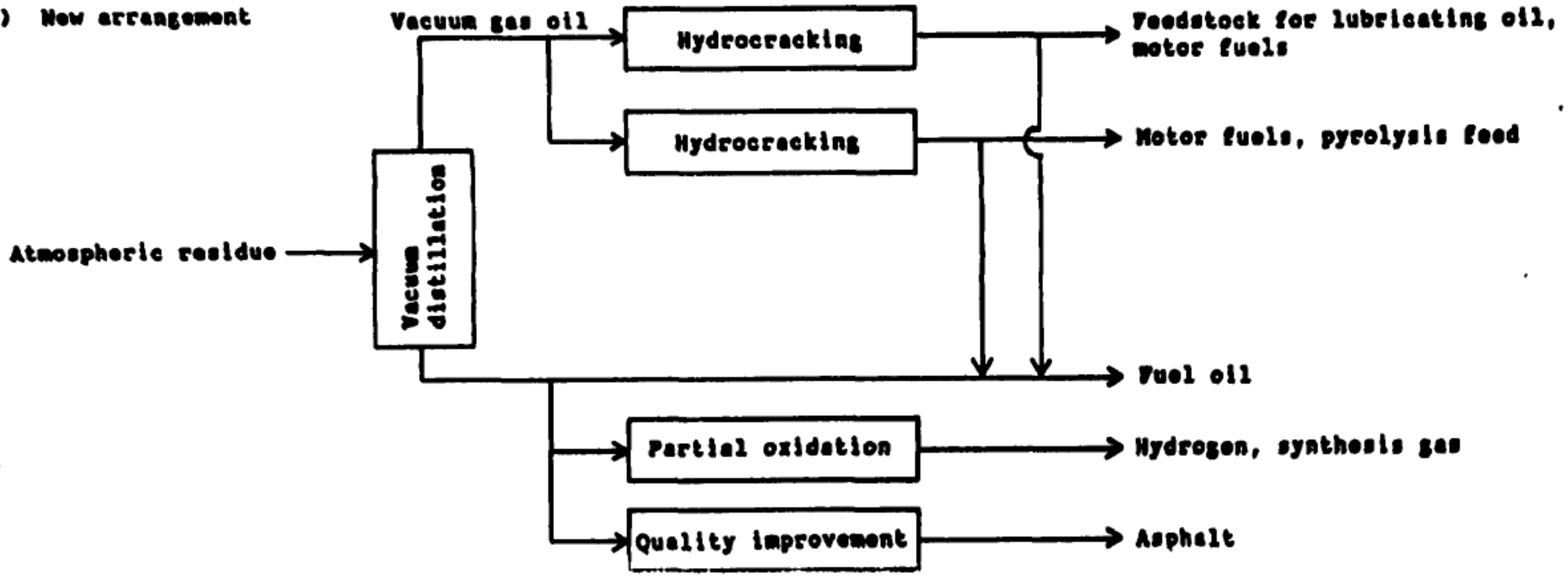


Figure III. Residual fuel oil in the Litvinov refinery

(a) Older arrangement



(b) New arrangement



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PRINCIPLES OF THE LOW-WASTE PRODUCTION OF NITRIC ACID

Jan Vosolsobě and Antonin Šimeček*

INTRODUCTION

Nitric acid is one of the most important inorganic acids, being used in the production of fertilizers, dyestuffs, resins and explosives. Further applications include stainless steel pickling and metal etching. About three-quarters of the nitric acid produced is used in the fertilizer industry, mainly for the production of ammonium nitrate and compound fertilizers. The nitric acid needed in the fertilizer industry is usually dilute nitric acid at a concentration of 50-60%. For most other applications, such as nitration reactions, 90-100% nitric acid is used.

Nowadays, nitric acid plants all over the world use the same basic process, consisting of the gas-phase oxidation of ammonia in air over a catalyst of platinum-rhodium gauze to form nitric oxide:

$$4NH_3 + 5O_2 \overset{850\text{-}920\ ^\circ C}{\rightleftharpoons} 4NO + 6H_2O \ ; \ \Delta H < 0 \qquad (1)$$

In the presence of further oxygen nitric oxide is converted to nitrogen dioxide:

$$2NO + O_2 \longrightarrow 2NO_2 \ ; \ \Delta H < 0 \qquad (2)$$

Part of the nitrogen dioxide formed is then dimerized to dinitrogen tetroxide:

$$2NO_2 \rightleftharpoons N_2O_4 \ ; \ \Delta H > 0 \qquad (3)$$

Nitric acid is produced by the reaction of nitrogen dioxide and dinitrogen tetroxide with water by a process of absorption:

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO \ ; \ \Delta H < 0 \qquad (4)$$

In addition to the main reaction (1), a number of competing and complementary reactions can also occur. To avoid the undesirable reactions, a highly selective platinum-rhodium catalyst is used.

The catalyst almost universally used consists of a fine wire, 0.05-0.09 mm in diameter, made of platinum alloyed with 5-10% rhodium and woven into a gauze. Several catalyst gauzes arranged in a pack are used in each ammonia burner. The heat released by the reaction raises the temperature of the gas and the catalyst to 850-950 °C. At these high temperatures, a significant amount of the precious metal is lost from the wire by vaporization and by erosion.

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The efficiency of the ammonia oxidation process falls slightly with increased operating pressure. The nitric oxide oxidation and the absorption reactions, however, are favoured by increased pressure, permitting the use of much smaller equipment for a given capacity plant with the production of a higher concentration of nitric acid.

Since, in general, high pressure plants are expected to lose more platinum than low pressure plants, as they operate at higher temperatures, methods must be used to reduce losses or improve the recovery of platinum catalyst.

The recovery of platinum was considerably improved by the development of a process using palladium-nickel catchment gauzes. The system now generally adopted has two or more of these gauzes installed immediately downstream from the platinum-rhodium gauzes. They are arranged in a pad with each gauze separated from its neighbour by a stainless steel mesh.

With the increasing cost of platinum in recent years, efforts were directed toward the development of non-precious metal catalysts for ammonia oxidation. Several installations of a combination of Pt-Rh gauzes and a layer of non-platinum catalyst have shown excellent results.

After oxidation the reaction gases are cooled, energy is recovered and additional air is introduced to give an excess of oxygen. The nitric oxide is oxidized to nitrogen dioxide, which is in equilibrium with its dimer.

Nitric acid is formed from nitrogen dioxide and its dimer. Whilst three molecules of nitrogen dioxide are removed in this reaction, one molecule of nitric oxide is regenerated. This NO is re-oxidized by the remaining oxygen in the gas phase and the acid-forming sequence is repeated, which means that only two thirds of the NO_2 formed is converted to nitric acid in each cycle. During this procedure, the partial pressure of NO and hence the rate of its oxidation to NO_2 decreases constantly.

Thus the absorbers, where the bulk of these reactions occur, must be large to provide sufficient residence time and also cooled to favour the equilibria as well as to increase the rate of NO oxidation, which is the limiting reaction and one of a few reactions in which the reaction rate decreases with increasing temperature. The absorption reaction never goes to completion, and some nitrogen oxide always escapes in the stack gases.

A. Nitric acid processes

It is clear from the above that both temperature and pressure influence, at different stages, the nitric acid process. The role of temperature can be controlled, and is intimately linked with the recovery of energy, whereas pressure affects, on a simple level, the efficiencies of oxidation and absorption.

In recent years, three process schemes have dominated new nitric acid plants: the medium-medium single pressure, medium-high dual pressure, and the high-high single pressure processes.

In the medium-medium pressure process the air-ammonia mixture is oxidized at a pressure of 0.4-0.6 MPa and the reaction gases pass after cooling into two absorption towers, operating at the same pressure.

Processes employing combustion (oxidation) of ammonia and absorption at lower pressures are obsolete, because at pressures lower than 0.3 MPa the waste gases contain more than 2,000 ppm NO_x, which causes serious environmental problems.

The NO_x content in the tail gas of the medium-medium pressure process operating at 0.4-0.6 MPa can be reduced to less than 600 ppm; to reach the current generally accepted emission limit of 200 ppm, however, catalytic reduction of the oxides is required. This type of process is economic for units with daily capacities up to 500 tonnes of nitric acid.

The combustion section in the medium-high dual pressure process is identical to that in the medium-medium single pressure process. After the nitric oxide containing gas has been cooled in the condenser, however, it is compressed in a radial compressor to the absorption pressure 0.7-1.4 MPa. The NO_x content of the tail gas is normally less than 200 ppm, usually 125-150 ppm. A separate treatment stage to meet current environmental specifications is thus not required. This process is the most economical for daily capacities over 500 tonnes of nitric acid.

The process scheme employed in the high-high pressure process is essentially the same as in the medium-medium single pressure process, except that the initial compression of the gases is greater. The pressure employed is usually 0.8-1.0 MPa. As a result of the high pressures, all the equipment can be made smaller, and hence cheaper, so that this type of plant is favoured where a quick return on capital is required. The main difference in the actual plant equipment required is that only one absorption tower is needed. The concentration of nitrogen oxides in the tail gas may be reduced to less than 200 ppm.

B. Methods for reducing NO_x emissions

Until recently, there was little objection to emissions of NO_x from nitric acid plants. Older plants, in partiular, are recognizable even today by their tail gas, which generally has a colour that varies between intense yellow and reddish brown due to the presence of nitrogen dioxide.

The requirement of a colourless stack gas is difficult to achieve; it can be achieved in a new plant by means of high pressure absorption or in medium-medium pressure plants by, for example, selective catalytic reduction of NO_x.

Among the methods available for reducing the NO_x emissions in existing plants, the following may be mentioned: improved acidic absorption; alkaline absorption; catalytic combustion or selective reduction of the waste gas; and adsorptive methods.

Improved acidic absorption

Improving acidic absorption is achieved primarily by extending the absorption volume and also by using the highly effective sieve trays technique and efficient cooling.

An existing plant can be equipped either with a newly-built high pressure absorption tower, or extended by one additional absorption tower.

Owing to improved recovery of the energy from waste gases, it has become possible to increase the pressure in the absorption towers. An NO_x content of less than 200 ppm can be achieved at pressures over 0.8 MPa and by increasing the number of absorption trays. An extended absorption process is economic up to 130-150 ppm.

The availability of highly effective trays allows plants operating even at medium absorption pressures to reduce NO_x emissions below 700 ppm, which facilitates further treatment of waste gases in additional equipment.

Alkaline absorption

Downstream alkaline absorption of waste gas is the oldest method of reducing emissions and has proven useful in practice. The solvents used are aqueous solutions of hydroxides or carbonates of sodium, potassium, magnesium or calcium. A precondition to making this method attractive is that there is a use for the resulting nitrite solution.

In plants where the absorption pressure is above 0.5 MPa, an NO_x content of 200 ppm can be obtained at the end of the sodium hydroxide scrubbing.

Another possibility is to use urea solutions as scrubbing liquids. Because of the high cost of urea and the need for large equipment volumes this method has not been industrially accepted.

Adsorptive methods

Adsorptive methods include pressure-swing and temperature-swing adsorption on molecular sieves. This method is expensive and desorption of nitrogen oxides requires an additional expenditure of energy.

Catalytic reduction processes

The most effective method of removing nitrogen oxides is catalytic reduction to elementary nitrogen. Reducing agents such as hydrogen, natural gas, or ammonia can be used.

The method using hydrogen or natural gas is known as catalytic combustion or total reduction and the method using ammonia as a reducing agent is called selective reduction.

The main distinction between the two processes is that hydrogen or hydrocarbons react primarily with oxygen. When the oxygen in the tail gas is burnt the excess fuel reacts with NO_x and forms N_2.

Under suitable conditions and in the presence of vanadium catalyst, in the selective reduction process ammonia reacts preferentially with nitrogen oxides to form N_2 and water.

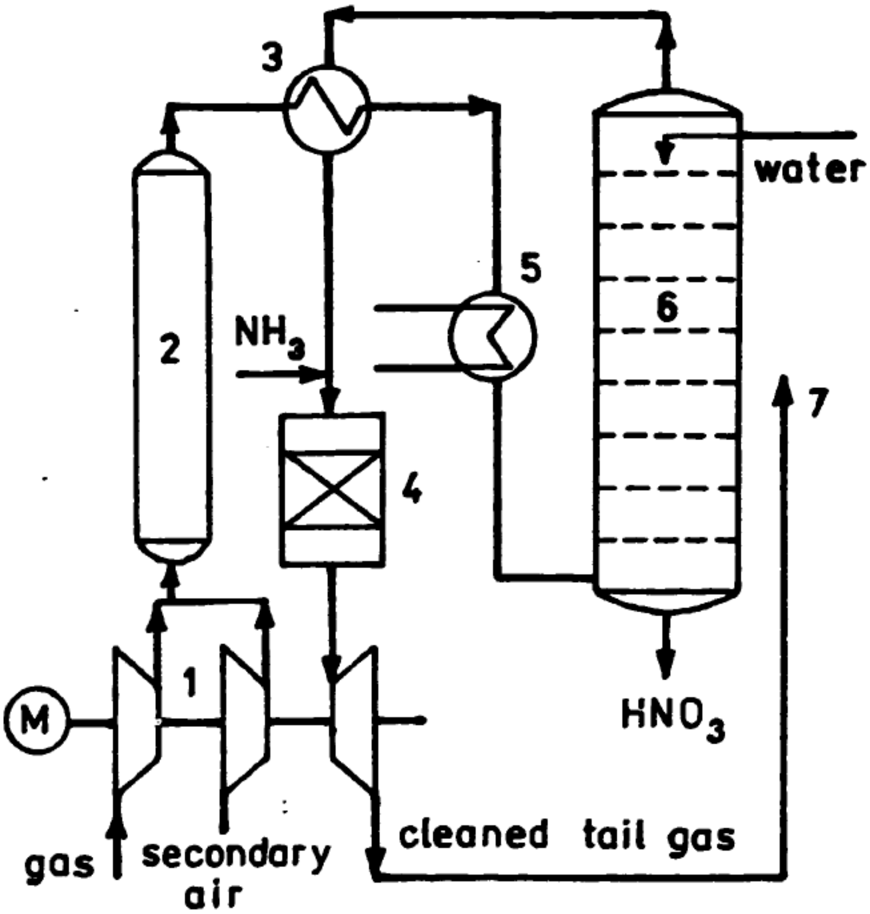
The total reduction process takes place in the presence of palladium catalyst at temperatures in the range 500-800 °C. This process is used in the United States of America.

Apart from the substantial consumption of fuel there may be problems of secondary emissions of carbon monoxide and unburnt methane when natural gas is used. Because of the high fuel cost and high emissions of hydrocarbons, this process is not acceptable in many European countries.

In this method, nitrogen oxide emissions are decreased but hydrocarbons are discharged into the atmosphere. Although both are harmful, the hydrocarbons are not visible.

The installation of the selective waste gas treatment unit in a nitric acid plant absorption system is very simple (see figure).

Installation of the selective catalytic reduction system in a nitric acid plant



Key: 1 Compressor with motor and tail gas turbine
2 Oxidation tower
3 Heat exchanger
4 Reactor
5 Gas cooler
6 Absorption tower
7 Stack

Gaseous ammonia is fed to the mixing device and heat exchanger in a controlled stream. The temperature required for the selective reduction is 220-350 °C. The highest NO_x inlet concentration in the plants is 3,000 ppm, while the lowest NO_x outlet concentration is 60 ppm. For waste gas with 400-800 ppm of NO_x a tail gas containing 60-150 ppm of NO_x is achieved.

In the selective reduction process, ammonia reacts on a vanadium catalyst with nitrogen oxides according to the following equations:

$$6NO + 4NH_3 \rightleftharpoons 5N_2 + 6H_2O \qquad (5)$$

$$6NO_2 + 8NH_3 \rightleftharpoons 7N_2 + 12H_2O \qquad (6)$$

$$NO + NO_2 + 2NH_3 \rightleftharpoons 2N_2 + 3H_2O \qquad (7)$$

The reaction of ammonia with oxygen, which is also present in the waste gases, occurs only to a small extent. The consumption of ammonia is thus lower, by an order of magnitude, than that of other reducing agents like natural or town gases.

In addition to the low consumption of reducing agent, the advantage of this process lies in its low capital costs and in the independence of the equipment on the technological parameters of the nitric acid plant. The lifetime of the vanadium catalyst is more than 10 years.

C. Conclusions

Methods have been developed that allow nitric acid to be produced on an acceptable economic basis without pollution of the atmosphere. There are processes that can be incorporated in both new and old nitric acid plants to reduce emissions of nitrogen oxides below legislated limits. Which process to employ depends on individual circumstances.

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CZECHOSLOVAK EXPERIENCE IN NITRIC ACID PRODUCTION

Rudolf Šubrt*

Nitric acid was first produced in Czechoslovakia at Lovosice, in 1954. The combustion section of the plant operated at atmospheric pressure and the absorption section operated at 0.3 MPa. As demand increased, new plants were brought on stream, and the current annual output is just under 1 million tonnes of pure (100%) nitric acid, most of which goes into fertilizers (largely in the form of ammonium nitrate and compound fertilizers), dyestuffs, resins and explosives. The selling price is Kčs 1,000 per tonne.

There are 18 nitric acid plants in operation at present. Sixteen of them were designed and built by Czech engineering groups; two units were imported. With one exception, the plants are more than 10 years old.

Three process schemes have been used. In one, combustion is carried out at atmospheric pressure and absorption is carried out at 0.3 MPa. In the second, the plants operate at 0.4 MPa in both sections, combustion as well as absorption. Such units are rated at 160-240 tonnes of nitric acid per day. In the third scheme, a dual (medium/high)-pressure system, the ammonia is oxidized at 0.3 MPa and the nitrogen oxides are absorbed in water at 0.9 MPa. The plants based on this scheme have a capacity of about 700 tonnes of nitric acid per day.

All three processes are employed to make highly concentrated nitric acid. However, since nitric acid forms an azeotrope with water at about 68.8%, it cannot be concentrated by simple distillation. Instead, the dilute nitric acid is mixed with concentrated sulphuric acid, which acts as a dehydrating agent and allows the nitric acid to be distilled off in concentrated form.

In addition to the classical HOKO process, one unit based on the Sabar process, including rectification and final physical absorption of the nitrogen dioxide, was imported last year.

Because new-generation ammonia plants have cut the cost of ammonia in half, it is unlikely that other raw materials for nitric acid will become competitive in the near future. As no substantial change in the technology of nitric acid manufacture is anticipated before the end of this century, efforts to improve nitric acid production have focused on two areas: reducing the amount of nitrogen oxides discharged to the atmosphere in the tail gas and minimizing the loss of precious metal catalyst during oxidation of the ammonia.

Good progress has been made in reducing environmental pollution. In 1978, the average nitrogen oxides emission was 12.6 kilograms NO_2 per tonne nitric acid, but by 1985 this was down to 2.8 kilograms per tonne of nitric acid. Overall improvement is summarized in table 1.

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Table 1. Emission of nitrogen oxides from nitric acid plants in Czechoslovakia

	1978	1980	1985
Number of plants	19	19	17
Production of HNO_3 (tonnes)	1 017 619	1 010 480	970 532
Average emission (kg NO_2/tonne HNO_3)	12.6	9.4	2.8
Total emission (tonnes NO_2)	12 822	9 390	2 760

Regulatory limits for nitric acid plant discharges in Czechoslovakia now stand at 2 kilograms NO_2 per tonne nitric acid for new plants and 10 kilograms per tonne for old plants. To meet these limits on NO_x (expressed as NO_2), an original catalytic system has been developed in Czechoslovakia and put into practice in plants at Lovosice and Pardubice. The system, which is a modification of the selective reduction process, uses two layers of two different catalysts. One catalyst is highly selective for the reduction of nitrogen oxides, while the other decomposes the unreacted ammonia. This system reduces ammonia consumption and improves the reliability and safety of the process.

The NO_x emission rates of individual plants are given in table 2.

Table 2. Nitrogen oxide emissions of individual plants in Czechoslovakia, 1985 (kg NO_2/tonne HNO_3)

Plant	Emission rate
Lovosice I-IV	1.89
Lovosice V	0.89
Duslo Šala I-IV	1.45
Duslo Šala Krebs	2.0
Semtin	18.85
RY	0.85
Chemko Strážske I	7.35
Chemko Strážske II	0.35
Ostrava	5.50
Average	2.84

Alkaline absorption has been carried out in two of the units, and total catalytic combustion is carried out in two other units. There are plans to improve the efficiency of the absorption units operating at high pressure.

With the rising cost of platinum, efforts have been made to further reduce platinum losses and improve the recovery of platinum catalyst. A United States company [1] has reported the re-introduction of a pelleted cobalt catalyst. Other organizations [23] have announced their development of base metal catalysts for ammonia oxidation.

In one medium-, single-pressure plant, the suitability of the Degussa system of platinum recovery has been tested. This system was able to catch about 70% of the platinum-rhodium particles on palladium-nickel gauze arranged in a compact pack. If this method of platinum recovery can be combined with the use of the non-noble metal catalyst developed in Czechoslovakia, platinum losses could be reduced by 15%.

Conclusion

Enough experience has been gained to enable Czechoslovak engineers to design as well as build and operate all types of nitric acid plants. Two original catalytic systems have been developed. One allows most of the platinum-rhodium gauzes to be replaced by non-noble catalyst and substantially reduces the losses of platinum. The other reduces the amount of NO_x emitted from nitric acid plants, keeping it below the legislated limit.

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ENVIRONMENTAL PROTECTION IN THE PRODUCTION OF SULPHURIC ACID

Jaroslav Poživil and Jiří Michálek*

INTRODUCTION

This paper is concerned with environmental protection in connection with sulphuric acid production and is intended to enable developing countries to appraise the installations being offered and to select those systems that will meet the standards laid down for environmental protection. It also considers the recovery of energy from waste, the selection of catalysts and the special criteria that would influence the choice of a technology for developing countries.

Sulphuric acid ranks among the principal products of the chemical industry. The extent of its production and consumption is one criterion by which the overall state of a country's chemical industry can be judged. Estimates of global sulphuric acid production run as high as 120-130 million tonnes per year.

The large volumes of sulphuric acid produced and the relatively low costs of the raw materials have led to plants that are technologically advanced, so that even the operating costs are rather low. This is due not only to the high degree of utilization of the feedstock (98-99.5%), but also to the high recovery of reaction heat as steam and hot water and to the reliability and dependability of the process equipment. Since the operating modes of the individual apparatuses of the production line are relatively stable, it is not difficult to apply simple regulatory loops or even control computers, and with a minimum of servicing, the operation can approach the economic optimum.

There are a number of process variables from which to choose, including variables with respect to feedstock, but perhaps the most important choice lies in the way potential pollution problems are handled. In the case of sulphuric acid, there are two points at which the environment can be affected. The first point is during production and involves mainly pollution caused by unreacted SO_2 emissions and by H_2SO_4 mist. The other point is during sulphuric acid consumption and involves the eventual disposal of sulphuric acid waste solutions.

Although it may be claimed that the problems encountered in production have been mastered and that it is merely a matter of economics to decide how far to go with abatement, the same cannot be said of the problems engendered by sulphuric acid consumption. At present, the processing of waste sulphuric acid streams is a major challenge that will have to be dealt with in the very near future. For this reason, this paper also goes into the question of waste H_2SO_4 regeneration and reprocessing. Closing the loop of H_2SO_4 production-consumption-regeneration not only would solve the matter of protecting the environment but also would settle the issue of the raw materials base and of production methods.

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A. Raw materials for sulphuric acid production

Historically, many different raw materials have been used to make sulphuric acid. Indeed, any sulphur-containing substance may be used, as long as it can be converted into SO_2 or SO_3. The material that at present best satisfies all the requirements is elemental sulphur. The other sulphur compounds that had once been used have gradually fallen out of favour, at least for the direct production of sulphuric acid. Where they are still used, it is mainly because they serve as an outlet for waste SO_2.

The use of sufficiently pure elemental sulphur, which is the most expensive of all the sulphur raw materials, allows the entire processing line of the sulphuric acid plant to be greatly simplified. In practice, this leads to lower capital outlays, better operating reliability, and easier process control. By contrast, the use of cheaper raw materials complicates the entire process, makes it more prone to defects, and necessitates more demanding inspection and control. For this reason, it has become less economical to produce sulphuric acid from inexpensive sulphur raw materials than to produce it from relatively expensive elemental sulphur.

The economics can be quite different, however, if there is a supply of waste sulphur dioxide (from, say, the roasting of polymetallic sulphidic ores or the desulphurization of combustion gases) that would otherwise have to be disposed of, or if waste sulphuric acid and sulphates are available for which no suitable use or disposal method can be found. Indeed, the economics are relatively attractive where it is possible to dispose of several sulphur-containing wastes or low-value substances simultaneously. For example, the thermal decomposition of waste H_2SO_4 or waste sulphates uses as a fuel a high-sulphur heating oil, coke or coal that could not otherwise be burnt. In this case it is also the sulphur contained in the fuel used for H_2SO_4 production which is utilized.

B. Technology

There are plants in the industrially advanced countries that can produce between 50 and 2,500 tonnes per day of sulphuric acid. The raw material - sulphur of at least 99.9% purity - is brought to the production site in either solid or molten form. It is then oxidized in furnaces similar in design to the steam boilers in which heavy oil or other liquid fuels are burnt. The only difference is that the sulphur is oxidized in dry air. The combustion temperature may reach 1200 °C. The sulphur/air ratio is maintained such that the sulphur dioxide gas produced contains 9-12% SO_2 and 9-11% O_2. The sulphurous gas is cooled at the preheater and at the water banks of the steam boiler to the working temperature of the vanadium catalyst, which is 400-420 °C. Between 0.9 and 1.2 tonnes of steam at 4 MPa can be produced for every tonne of sulphuric acid output.

The oxidation of sulphur dioxide to sulphur trioxide proceeds very slowly if unaided, so a vanadium catalyst is used to speed up the reaction. The converter section, which consists of catalyst beds and the auxiliary equipment required to maintain the desired temperature, is the most critical part of the equipment as far as process control is concerned, for only if it is operating properly can the necessary conversion of SO_2 to SO_3 be achieved. With so-called single-stage conversion, the yield of SO_3 from SO_2 reaches 98%.

Since sulphur trioxide absorption carried out in the presence of water or in aqueous sulphuric acid solutions - having a certain water vapour pressure - would yield H_2SO_4 in the form of a hard-to-retain mist, it is instead generally carried out in concentrated H_2SO_4. The off-gases from the absorption tower pass first over filters (demisters), where entrained H_2SO_4 droplets are retained, and then to the stack, where they are vented to the atmosphere. The off-gases contain approximately 0.2% sulphur dioxide, which means that 2% of the sulphur dioxide processed ends up in the atmosphere, there to be gradually oxidized to sulphuric acid and to return to the earth as acid rain. Thus, a sulphuric acid plant having a capacity of 1,000 tonnes per day emits sulphur dioxide in quantities that produce 20 tonnes per day of sulphuric acid in the atmosphere.

C. Control of sulphur dioxide emissions from sulphuric acid plants

A conventional sulphuric acid production facility makes use of no more than 98% of the sulphur raw material; the remaining 2% becomes sulphur dioxide pollutant. A number of methods for controlling these emissions are theoretically possible, but only some of them have been put into practice.

Alkaline washing

This is a rather simple unit, technologically. A packed column absorbs the sulphur dioxide residues in NaOH, Na_2CO_3, or NH_4OH solutions. When properly designed, this absorber reduces the sulphur dioxide content of the exit gas to 0.0001%.

Double conversion method

The principle of the method is very simple: the catalytic oxidation is discontinued once 90-94% sulphur dioxide conversion has been reached, whereupon the gas is cooled and the sulphur trioxide produced is removed in a so-called "intermediate" absorber. The sulphurous gas containing up to 1% sulphur dioxide is then heated to the catalyst working temperature and the reaction is allowed to continue. The theoretical conversion is 99.99%, and 99.5% is attained in practice. The sulphur trioxide produced is absorbed again in the final absorber.

Sulphur dioxide oxidation in the liquid phase

These methods trap the residual sulphur dioxide in water and then oxidize it.

D. Conclusion

The selection of a technology for making sulphuric acid, as well as the design and interlinking of the process equipment and the choice of raw materials, is a complicated matter. Many factors, including the availability of inputs, manpower skills, and waste heat utilization, must be considered, and different combinations will be optimal under different conditions. Nevertheless, a number of observations can be made:

(a) The pollution problems associated with a sulphuric acid plant based on elemental sulphur have been overcome by the use of an intermediate absorption system that achieves a total sulphur dioxide conversion of greater than 99.5%. If the facility is to be located in a densely populated area, the Peracidox process can reduce the sulphur dioxide emissions even further, to the point where they have little effect on the environment. Proper operation of the contact reactor, the key piece of equipment for obtaining a high SO_2 conversion, is contingent on proper selection of the catalyst;

(b) The problems associated with waste heat can be alleviated by substituting it in part, for the combustion, e.g., of solid fuels, thus alleviating pollution from those sources. While the use of high-temperature heat sources for heating steam is common, we have recommended the use of lower-temperature heat sources by adequate consumers. The related engineering requirements are outlined in the final report of the Czechoslovak project SI/CZE/85/801;

(c) Many ecological problems are created by sulphuric acid wastes. One means of coping with these wastes appears to be thermal decomposition, with the decomposition products being recycled into fresh acid production;

(d) It is important to developing countries that the process they select be a reliable one and that it require little or no maintenance and service. It is for this reason that plants based on elemental sulphur can be recommended for the developing countries. Unlike plants that use other sulphur-containing raw materials, the plants that use elemental sulphur are simple and reliable, their operation is stable, and they are not maintenance-intensive. Process control is not difficult and can be achieved using either manual controls or simple computerized control systems.

It can be said, in conclusion, that it is possible for a sulphuric acid production facility to be operated without unduly burdening the atmosphere with sulphur dioxide emissions and other pollutants. Such a facility can at the same time generate steam for use in the adjoining units of the chemical complex.

LOW-WASTE TECHNOLOGY IN THE PRODUCTION OF ORGANIC INTERMEDIATES

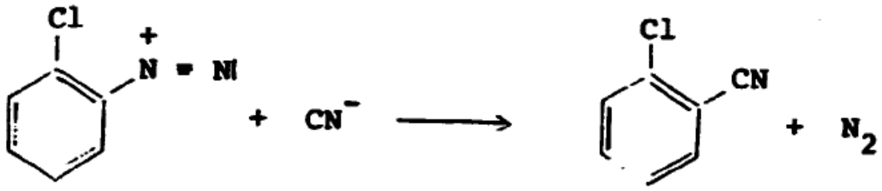
I. Zelenka and J. Hojer*

INTRODUCTION

The Research Institute of Organic Syntheses specializes, as its name implies, in research and development in the field of organic synthesis, especially the synthesis of dyes and their intermediate compounds. Both of the processes that are described here - the ammoxidation of aromatic compounds and the ion exchanger-catalysed condensation of phenol with acetone - have been carried out in full-scale plants.

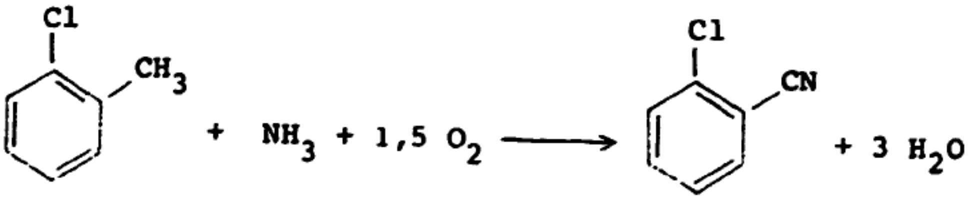
A. Ammoxidation of aromatic hydrocarbons

Aromatic nitriles -- for example, o-chlorobenzonitrile and p-chlorobenzonitrile - are often used as starting materials for the manufacture of dyes. A classical method of introducing a nitrile group into an aromatic ring is the Sandmeyer reaction:



The CN⁻ ion is usually added to the reaction mixture as a complex solution of cuprous cyanide, which is prepared in a parallel step. Of course, the Sandmeyer reaction itself is preceded by diazotization of the parent amino compound. All three steps - diazotization, cuprous cyanide preparation, and the Sandmeyer reaction - generate waste.

A new method, catalytic ammoxidation, which was originally developed by the Institute for the purpose of ammoxidizing chlorinated aromatic compounds, achieves the same result in a one-step procedure:



The reaction, which takes place at 300-350 °C, minimizes the production of waste:

	Waste generated (kg/tonne product)	
	Sandmeyer	Ammoxidation
Organic compounds	500	10
Inorganic compounds	7,500	3

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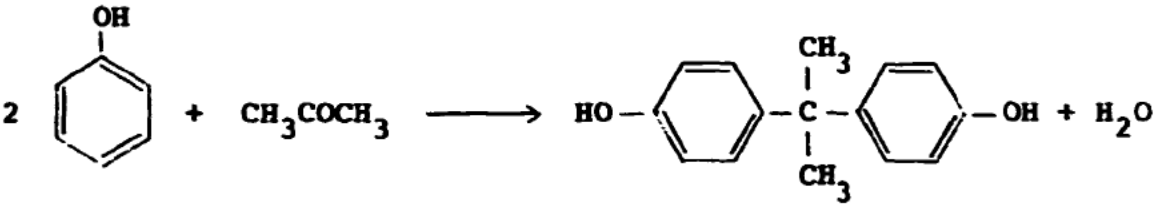
B. Ion exchanger-catalyzed condensations

Another example of a low-waste technology is the condensation of phenol with acetone. The product of this reaction is 2,2-bis(p-hydroxy-phenyl) propane, called Dian or bisphenol A.



The reaction is acid-catalyzed, and strong mineral acids such as sulphuric or hydrochloric have conventionally been used. However, not only did these give substantial corrosion problems and undesirable side reactions, such as polymerization, but the acids became, after extraction or neutralization, troublesome waste. When the mineral acids were replaced by a strong acidic katex, the reaction gained in selectivity and less waste was generated:

	Waste generated (kg/tonne product)	
	Sulphuric acid	Katex
Organic substances	155	27
Inorganic substances	2,200	0

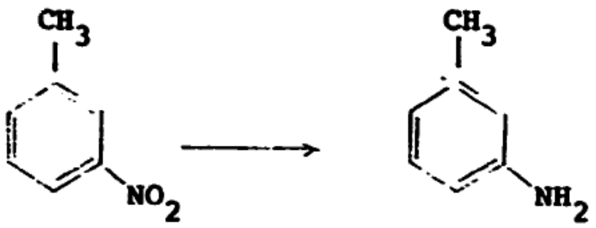
It may be noted that ion-exchangers can also catalyse the esterification of organic acids by alcohols and other reactions.

At present the preparation of important dye intermediates by catalysed hydrogenation processes is being demonstrated under laboratory and model conditions. In comparison with the conventional Béchamp reduction method, hydrogenation not only generates much less waste but also improves quality and plant working conditions. The following are specific examples of the reactions that are being developed.

p-Toluidine via the catalytic hydrogenation of p-nitrotoluene

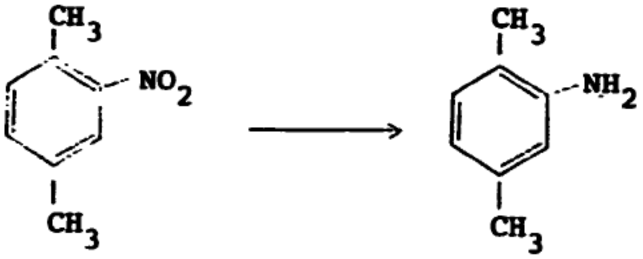
This hydrogenation takes place in a melt at 130 °C and 4.1 MPa pressure, using as catalyst palladium on activated charcoal (0.455 kg of catalyst for 1 tonne of product).

m-Toluidine



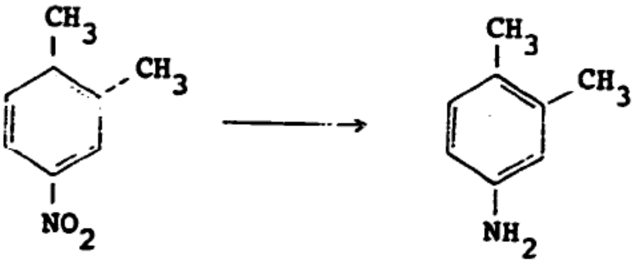
The production is analogous to that of p-toluidine. The temperature is brought to 135 °C, the pressure is 0.6-2.1 MPa, and the catalyst is palladium on activated charcoal.

p-Xylidine via the catalytic hydrogenation of 2-nitro-p-xylene



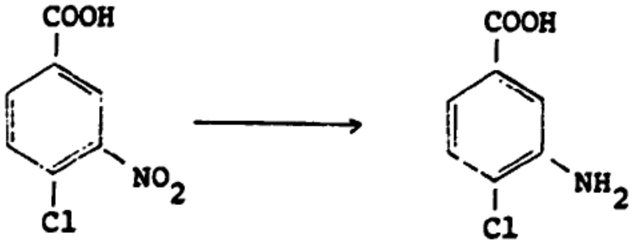
The hydrogenation takes place at nearly 130 °C and 1.1-2.1 MPa pressure, using a palladium on activated charcoal catalyst (0.43-0.61 kg/t).

4-o-Xylidine



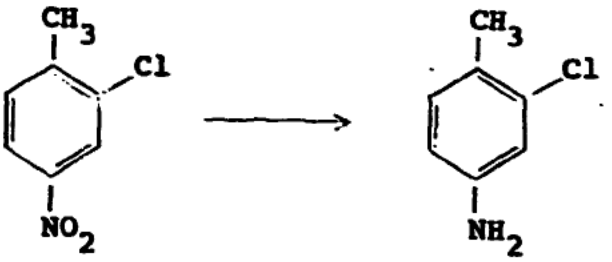
The catalytic hydrogenation of 4-nitro-o-xylene takes place at 110-130 °C and 1.6-2.1 MPa, using palladium on activated charcoal as catalyst.

3-Amino-4-chlorobenzoic acid



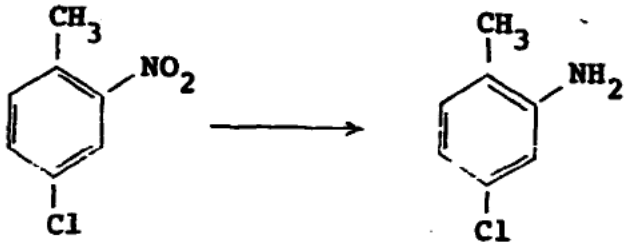
The catalytic hydrogenation takes place in an aqueous solution of 3-nitro-4-chlorobenzoic acid (sodium salt) at nearly 90 °C and 1-2 MPa, using a platinum on activated charcoal catalyst.

2-Chloro-4-aminotoluene



Hydrogenation takes place in a melt at about 100 °C and 4.1 MPa, using platinum on activated charcoal.

4-Chloro-2-aminotoluene



The hydrogenation takes place in a melt at 80 °C and at 4 MPa. The catalyst is platinum on activated charcoal.

THE LOW-WASTE TECHNOLOGY CONCEPT AS APPLIED IN BRAZIL

Sergio A.S. Almeida*

INTRODUCTION

The Federal Republic of Brazil is made up of 24 states, 3 territories and a federal district, where the capital city of Brasilia is located. The country's environmental control network consists of a central environmental protection agency, SEMA, located at Brasilia, and 24 state environmental protection agencies, one in each of the states.

At the highest level is the National Environmental Council, CONAMA, which is made up of representatives from the state agencies and a few other organizations. CONAMA meets regularly and sets the federal regulations on environmental matters.

Each state environmental agency may issue its own regulations and may approve, or disapprove, industrial and other projects as well as solicit and review monitoring programmes. These agencies also have the power to issue warnings and fines and to stop construction and/or operation of any project that is not in compliance with environmental regulations.

While all industrial projects must fulfil at least the local state requirements, the large chemical or petrochemical projects that span a number of industries must consult the central agency, SEMA, and also fulfil any additional requirements it lays down.

The whole bureaucratic process is complex and time-consuming: in many cases, it takes more than a year to obtain a construction licence.

A. LWT concepts in Brazil

Low-waste technology (LWT) is not yet practiced to any significant extent in Brazil, nor is it practised widely in any developing countries. At any rate, it will probably be the potential economic advantages of low-waste technology, rather than just its environmental advantages, that cause it to be investigated and eventually adopted.

Probably the only large-scale application of the LWT concept in Brazil is at PCA, the chlorochemical complex of Alagoas, in northeastern Brazil, near the city of Maceió. Until a decade ago, the economy of the state of Alagoas was based entirely on the cultivation of sugar cane, to produce sugar (for domestic use and export) and alcohol. Industrialization started when a large chlorine-soda plant, Salgema, was brought on stream. Located near Maceió, which had over 500,000 inhabitants, the plant used as its raw material the salt contained in the extensive reserves under the urban area.

At first, Salgema was able to market all of its soda production but had to dispose of the chlorine by discharging it, in the form of HCl, into the Atlantic Ocean. The area's inhabitants reacted very negatively to this practice. To solve the problem, Salgema started producing EDC (ethylene dichloride), using the surplus chlorine and ethylene made from alcohol, an abundant product in the region. This undertaking can be said to constitute the first application of LWT in Brazil.

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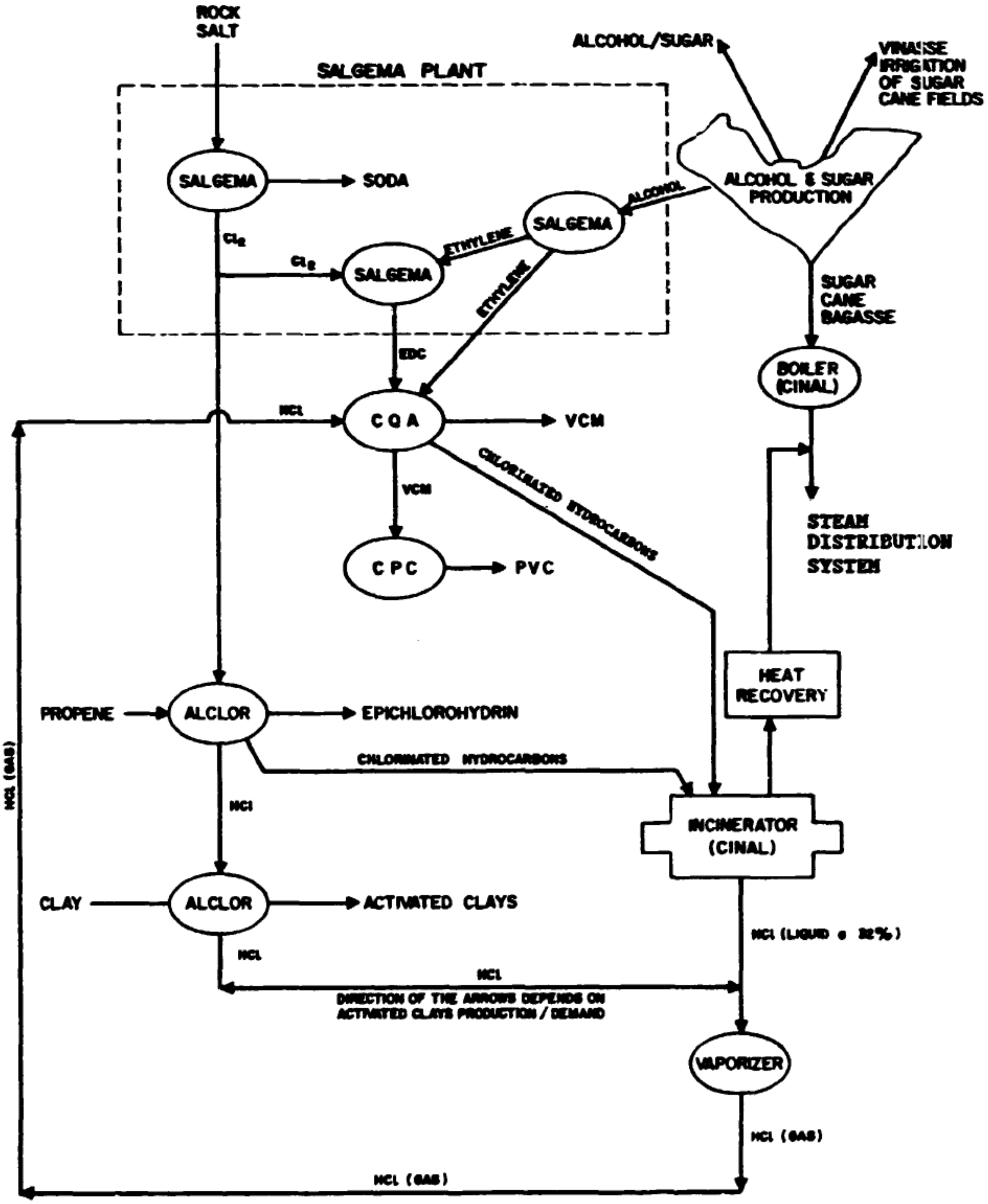
Figure I. Low waste technology as applied to Alagoas, Brazil



Subsequently, a federal decree allowed an industrial area to be set up about 8 kilometers from Salgema. This area was developed into the chlorochemical complex of Alagoas, known as PCA, a series of chemical and fine chemicals industries that use as their raw materials the products generated by Salgema, plus locally available natural gas, sugar-cane wastes, and other resources. The complex is a good example of LWT principles in action.

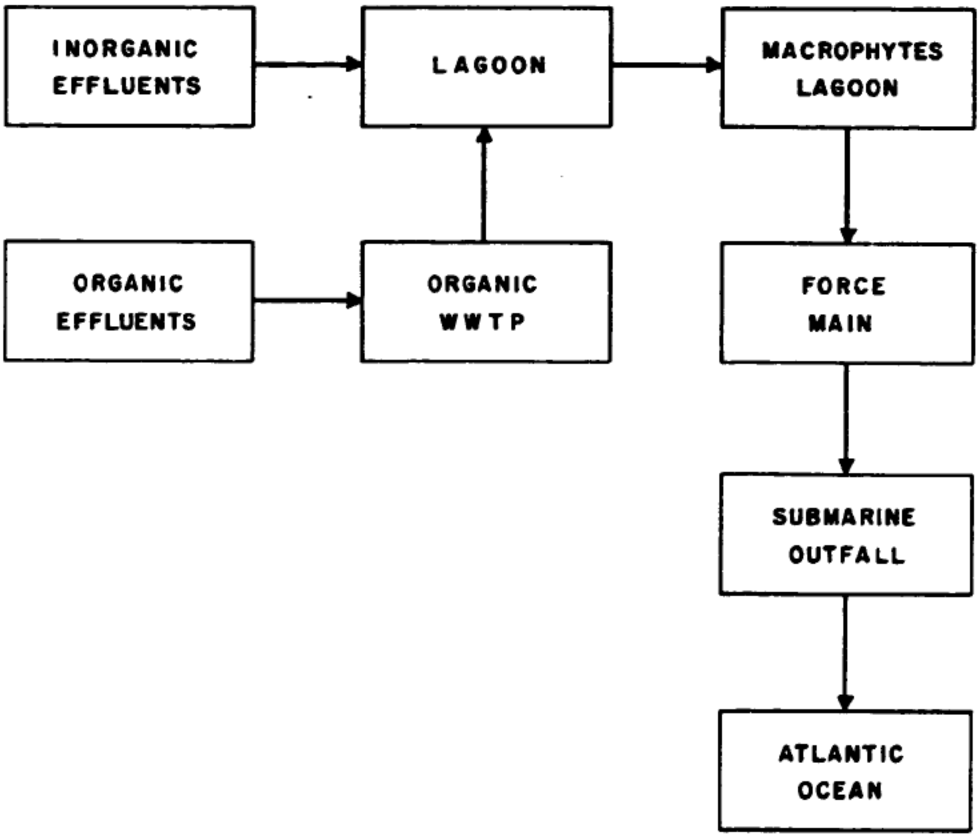
Figure I depicts the overall scheme at the Algoas complex. In the first stage, which has been completed, steam is generated in a boiler fueled by either sugar-cane bagasse or natural gas. VCM (vinyl chloride monomer) is produced from EDC and is used to make PVC. Epichlorohydrin is produced from chlorine and propylene. Activated clays are produced using the hydrochloric acid by-product from the production of epichlorohydrin.

In the next stage, chlorinated hydrocarbon wastes generated by the processes will be conveyed to a 99.99% efficient incinerator. There, the heat will be recovered, and the HCl generated by the incineration will either be vaporized to HCl gas and sent to the VCM plant or used, in the liquid phase, to make activated clays.

B. Waste water treatment and disposal

The effluents from PCA operations are of two kinds - organic and inorganic. They are treated and disposed of as shown in figure II.

Figure II. Effluent treatment and disposal system: macro-conception



The introduction of LWT sharply reduced the organic waste stream, and it is now practically the only sanitary waste from the complex. The initial flow is only 1,000 m^3/d and the ultimate flow 3,000 m^3/d. The organic effluents will be treated in a waste water treatment plant (WWTP) of the conventional carrousel/activated-sludge type and will then be transferred to the large inorganics lagoon (see below).

The inorganic waste stream consists essentially of run-off rain-water, which the state environmental agency does not allow to be directly disposed of, even when it comes from non-contaminated areas such as administration areas, internal and external roads, and parking lots. Thus, the complex is surrounded, at its perimeter, by a concrete ditch that collects the rain-water drained from the entire area. The inorganic stream also receives cooling water blow-down and other minor, non-organic effluents.

This inorganic stream is to be stored and processed in a lagoon having a capacity of about 600,000 m^3 equalization.

The contents of this lagoon will be conveyed to a second lagoon for conditioning with macrophytes. The final disposal of the effluents into the Atlantic Ocean will be by means of a submarine outfall, which will discharge some 5 kilometers offshore at a depth of about 20 m. The details of this outfall are presently under study.

Extensive environmental studies have already been conducted in the future discharge area. Under investigation are biological parameters (plankton, benthos and necton), several key water quality parameters and the sedimentation at the site.

Physical oceanographic studies will commence as soon as the final disposal point is determined and will include measurements of currents, tides, winds, salinity, temperature and other factors.

Until the PCA outfall is built, the effluents will be discharged through the existing Salgema outfall, which has capacity to handle all the effluent from the first phase of the PCA project.

C. Solid wastes

The solid wastes generated at PCA will be disposed of in a scheme that covers an area of 20 hectares and is divided into two systems: one for ordinary solid wastes and one for special solid wastes (the latter consists of specially designed and operated ditches). Although the water table at the site is at 50 m, the ditches are to be lined with impermeable materials.

The chlorinated hydrocarbons, which are hazardous materials, will be burned in the incinerator.

D. Investments

The first phase of PCA will require an investment of about $US 400 million, including $US 100 million for expansion of the Salgema plant. Included in the total investment is $US 55 million to form CINAL, a mixed Government-private enterprise company that will provide utilities and services, including water, steam, effluent handling and incineration. The investment for environmental protection, which will be managed by CINAL, is about $US 17 million.

DESIGNING AND IMPLEMENTING A WASTE REDUCTION POLICY

Will A. Irwin*

The first step in designing a waste reduction policy is to define the term "waste reduction". Strictly speaking, it means preventing or limiting the generation of waste, by in-plant modifications, i.e. changing the chemistry or chemical engineering operations or by in-plant reuse or recycling, i.e. returning potential waste for reuse within a process. Treatment, conversion, out-of-plant recycling, and storage, which deal with wastes after they have been generated, may reduce environmental and health risks, but since they do not reduce the amount of waste produced, they are more properly classified as "waste management alternatives".

It is next important to specify the kinds of wastes to be reduced. The term "wastes" can be understood to include all materials or energy not worth the cost of collecting, processing, or transporting for use, or it can include only hazardous wastes. Hazardous wastes, in turn, need further definition, a process that requires careful attention to what should be excluded from the definition. Waste reduction can also be applied to wastes containing specific substances or having certain characteristics or to wastes from particular manufacturing sectors.

Setting an *objective* for waste reduction policy is also crucial. It is possible, for example, simply to call for the maximum reduction technically possible, or to specify quantitative goals, although this could lead to economic inefficiencies. It would, however, be more circumspect to determine, for each kind of waste, the combination of reduction, treatment and storage techniques that would most cost-effectively reduce the burdens and risks (both short-run and long-run) to society. In any event, the objective must take into account the impact of the wastes on all environmental media - air, water, and land - in order to avoid simply transferring the wastes from one medium to another.

Once the definitions and policy objectives are clear, selecting the means of implementing a waste reduction policy is largely a matter of deciding which means are most suitable and what level of financial support can be provided. Some of the possible approaches include:

(a) Grants or loans for research and development in waste reduction technologies, with an emphasis on generic and transferrable approaches, and for technical assistance to waste generators;

(b) Education programmes for engineers and supervisors at all stages of production, with improved dissemination of information by means of publications, conferences etc.;

(c) Awards for developing and demonstrating innovative waste reduction approaches;

(d) A requirement that waste generators report regularly on their waste reduction efforts and plans and that these reports be organized according to analytical possibilities for reduction, i.e., inputs, internal re-use, intermediates, and final products;

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(e) Creation of a Government office or agency for waste reduction with the same status as the pollution control agency, to facilitate complementary work between the two;

(f) Tax reductions, exemptions or credits for waste reduction technologies;

(g) Consistent enforcement of pollution control requirements to ensure that all generators have the same indirect incentive to reduce wastes;

(h) Trading off pollution control requirements for waste reduction achievements;

(i) Encouraging Governments to purchase products manufactured by technologies that minimize waste;

(j) Imposing charges or taxes on wastes generated;

(k) Requiring that proposed Government regulations be analysed to determine their likely impact on waste reduction.

Some of these approaches have already been tried for waste reduction, while others would have to be adapted to it. In principle, they should be applicable in any economic system. Waste reduction will become more attractive as the real costs of safe treatment or storage are recognized and as the opportunity costs of using resources for these purposes are realized.

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NON-POLLUTING FERTILIZER TECHNIQUES

Jac Eimers*

INTRODUCTION

The main nutrient components of fertilizers are nitrogen, phosphorus, potassium and sulphur. The raw materials for these nutrients are, respectively, air, phosphate rock, potassium salts and elemental sulphur (formerly, sulphur oxides were used).

The nutrient elements occur in fertilizers as ammoniacal nitrogen and/or nitrates, calcium and/or ammonium phosphates, potassium chloride or sulphate, and ammonium or calcium sulphate. Fertilizer production can thus be said to entail the conversion of insoluble compounds into compounds that can be easily absorbed by plants.

The first steps in fertilizer production involve the manufacture of ammonia from nitrogen and hydrogen; sulphuric acid from sulphur; nitric acid from ammonia; and phosphoric acid from phosphate rock. The main effluents from these steps are (in sulphuric acid production) SO_2- and SO_3-containing waste gases (in nitric acid production) NO- and NO_2-containing waste gases (generally referred to as NO_x) and (in phosphoric acid production) waste gases containing HF, SiO_2 and SiF_4 as well as by-product gypsum.

The waste products of fertilizer manufacture are in solid, liquid and gaseous form, depending on the particular process: in mixed fertilizer production, the important effluents are in particulate form, whereas in complex fertilizer production the effluents contain not only particulates but also gases and aerosols.

A special case of air pollution can occur if fire destroys stored complex fertilizers that contain ammonium nitrate. The ammonium nitrate decomposes, giving huge poisonous clouds of NO and NO_2.

Table 1. Sources of air pollution in the Federal Republic of Germany
(Thousands of tonnes of effluent per year)

Source	SO_2	CO	NO_x	Hydrocarbons	Dust
Power plants, households	3 600	-	900	100	3 200
Industrial production, including chemical plants	300	50	200	900	800
Vehicular traffic	100	8 000	900	1 000	-
Total	400	8 050	2 000	2 000	4 000

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Nevertheless the fertilizer industry is not the only or even the main source of air pollution in our industrialized world. Indeed, overall industrial production, of which the fertilizer sector of the chemical industry forms only a small part, is itself only one of many sources of air pollution, as shown by an investigation in the Federal Republic of Germany (table 1).

A. Pollution problems in chemical plants (fertilizer plants)

In the chemical industry generally, as well as the fertilizer industry in particular, pollution may arise in a number of ways:

(a) Plant-specific process inefficiencies can lead to the discharge of unreacted materials (example: unreacted phosphate rock may be present in calcium sulphate crystals);

(b) Unwanted by-products can form as a result of impurities in the raw materials or undesirable side-reactions (example: impurities in the phosphate rock may react with the sulphuric acid);

(c) Raw materials and/or products may be subject to loss during handling and processing (examples: fertilizer dust from granulation, drying and cooling; ammonium nitrate aerosols from prilling plants).

The many ways in which pollutants can be generated show that non-polluting fertilizer techniques are unpractical (the title of this paper notwithstanding). Indeed the best that can be expected is for waste levels to be kept as low as possible - hence the expression "low-waste technology".

In fertilizer production, the sulphur and ammonia raw materials are quite pure, normally over 99 per cent, but the phosphate rock raw material contains a high proportion of impurities (table 2).

Table 2. Quantitative analyses of typical phosphate rock raw material
(Percentage)

Component	Range	Average
P_2O_5	29-38	33
CaO	46-54	51
SiO_2	0.2-8.7	2
R_2O_3	0.4-3.4	1.4
MgO	0.1-0.8	0.2
Na_2O	0.1-0.8	0.5
CO_2	0.2-7.5	4.5
F	2.2-4.0	3.7
Cl	0.0-0.5	0.1
SO_3	0.0-2.9	1.0
$CaO:P_2O_5$	1.35-1.70	1.5

B. Sulphuric and nitric acid plants

In sulphuric acid plants and nitric acid plants, both of which operate with pure raw materials, the main determinant of the amount of pollution is the yield of the particular process, which is governed by the laws of thermodynamics.

In conventional sulphuric acid plants the yield is around 98%. The yield can be increased, however, by installing alkaline scrubbing or by using double catalyst. In this case the yield increases to 99.5%, and the quantity of effluent decreases correspondingly.

Conventional mono-pressure nitric acid processes have a yield between 92 and 95%, and the waste gases contain 1,000-2,000 ppm NO_x, which is an unacceptably high level. If the process includes a selective reduction, treating the waste gases with ammonia, the NO_x content can be reduced to 50-100 ppm. The use of high-quality stainless steels and advances in compressor design have led to a dual-pressure process (combustion at low pressure, absorption at high pressure). This process, which is economically justified at capacities of 500 tonnes per day (tpd) and over, gives NO_x emissions of between 75 and 125 ppm.

C. Phosphoric acid plants

Fertilizer phosphoric acid is produced according to the following simplified reaction:

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \longrightarrow 3\ H_3PO_4 + 5\ CaSO_4 2\ H_2O + HF$$

The pollution encountered in phosphoric acid production is due to impurities in the rock and to process inefficiencies.

Conventional plants are based on dihydrate processes, which means that the calcium sulphate is formed and separated as the dihydrate (gypsum). The yield of such processes is 92-95%. The P_2O_5 losses occur as water-soluble P_2O_5 (phosphoric acid in the gypsum cake) and as water-insoluble P_2O_5 (calcium phosphate included in the gypsum crystals). Research in phosphoric acid manufacture has led to the development of two-stage processes, or double-crystallizations. In such processes, the rock is attacked by sulphuric acid at high temperatures, resulting in the formation of calcium sulphate hemihydrate ($CaSO_4 1/2 \cdot H_2O$). When the reaction mixture is cooled, the hemihydrate dissolves, included particles are liberated and gypsum dihydrate forms. The yield of these processes is around 98.5%, which means considerably lower P_2O_5 losses.

Fluorine, an impurity in the rock, presents a pollution problem. Part of the fluorine disappears with the gypsum, part is liberated during reaction. Between 70 and 80% of the fluorine in the 30% product acid is liberated when the acid is concentrated to 54%. From the standpoint of pollution control, it is therefore very important to scrub the waste gases and recover the fluorine as soluble by-products such as fluosilicic acid, fluosilicates, cryolite or aluminium fluorides.

Addition of reactive silica promotes the volatilization of the fluorine, and the fluorine content of the acid is decreased accordingly.

Another problem in phosphoric acid production is the by-product gypsum. Considering that for every unit of P_2O_5 about five units of wet gypsum are produced and that modern phosphoric acid plants have capacities of 1,000 tpd P_2O_5 and more, the question arises of what to do with all the gypsum. Since markets for gypsum are limited, most of it must be disposed of, either on land or at sea. Moreover, in both of the existing gypsum markets - the building industry and the production of ammonium sulphate - the P_2O_5 content of the gypsum (both water-soluble and -insoluble) may cause problems.

To minimize these pollution problems, it is important when planning phosphoric acid plants to select processes with the highest possible reaction efficiencies, efficient scrubbing equipment for waste gases and filter equipment with excellent washing properties.

D. Production of fertilizers

Fertilizer production is based on the following reactions:

(a) Neutralization of mineral acids to obtain ammonium nitrate and mono- or diammonium phosphate:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

$$H_3PO_4 + NH_3 \rightarrow NH_4H_2PO_4$$

$$H_3PO_4 + 2\ NH_3 \rightarrow (NH_4)_2HPO_4$$

(b) Treatment of phosphate rock with mineral acids to obtain single superphosphate, triple superphosphate or complex fertilizers (with nitric acid or with nitric and phosphoric acids).

- Single superphosphate
  $2\ Ca_5(PO_4)_3F + 7\ H_2SO_4 + 3\ H_2O \rightarrow 3\ Ca(H_2PO_4)_2 \cdot H_2O + 7\ CaSO_4 + 2\ HF$

- Triple superphosphate
  $Ca_5(PO_4)_3F + 7\ H_3PO_4 \rightarrow 5\ Ca(H_2PO_4)_2 + HF$

- Nitric acid attack: ODDA process
  $2\ Ca_5(PO_4)_3F + 14\ HNO_3 \rightarrow 3\ Ca(H_2PO_4)_2 + 7\ Ca(NO_3)_2 + 2\ HF$

  Removal of part of the calcium nitrate
  $3\ Ca(H_2PO_4)_2 + Ca(NO_3)_2 + 5\ NH_3 \rightarrow 4\ CaHPO_4 + NH_4H_2PO_4 +$

  $(NH_4)_2HPO_4 + 2\ NH_4NO_3$

- Mixed attack:
  $Ca_5(PO_4)_3 \cdot F + 4\ HNO_3 + 4\ H_3PO_4 + 7\ NH_3 \rightarrow 5\ CaHPO_4 + 4\ NH_4NO_3 +$

  $NH_4H_2PO_4 + (NH_4)_2HPO_4 + HF$

In all these cases pollution is caused by impurities in the rock and the escape of both solid particles and gaseous effluents.

During handling of the rock and in several of the production steps, fine particles of rock or of product become entrained in the air. This happens especially during the granulation, drying, cooling and classifying steps.

In neutralization processes the heat of neutralization may drive off part of the ammonia.

When phosphate rock is treated with mineral acids, the impurities in the rock, such as F, SiF_4 and CO_2, are liberated and escape as gases into the atmosphere. A special case is the attack of phosphate rock with nitric acid. Here, a compromise must be achieved: if the temperature of the reaction mixture is too high, nitric acid is destroyed and NO_x vapours escape; if the temperature is too low, the reaction proceeds too slowly.

E. Minimizing pollution

To reduce pollution during fertilizer production, the following measures must be adopted:

(a) In neutralization processes, the vapours must be scrubbed with dilute phosphoric acid, with the neutralized acid recycled to the process;

(b) In cases where there are NO_x-containing vapours, a system of alkaline scrubbing must be applied;

(c) Handling equipment for rock must be designed so that practically no dust problems can arise; manual handling must be avoided entirely;

(d) Dust-laden process air from the "dry-part", granulation and subsequent process steps must be sucked off and treated in special high efficiency filtering equipment, with the collected dust recycled to the granulation section;

(e) Contaminated process water should be diverted to a neutralization pit. In tropical regions there is no need to dispose of waste water because the water from the neutralization pit may be evaporated by solar means. In other regions the salts must be recovered and returned to the plant, and the clean waste water may be discharged.

Only when measures (a)-(e) have been adopted will low waste be achieved.

THE ROLE OF CATALYSIS IN LOW-WASTE TECHNOLOGY IN THE CHEMICAL AND PETROCHEMICAL INDUSTRIES

Sieghard E. Wanke*

INTRODUCTION

The prime function of the chemical and petrochemical industries is the conversion of raw materials into consumer products or into industrial feedstocks for the production of consumer goods. The conversion of raw materials into useful products almost always requires chemical transformations, i.e. chemical reactions, and the majority of commercial chemical reactions are carried out in the presence of a catalyst.

Catalysts are employed in the chemical and petrochemical industries for a variety of reasons. This overview briefly discusses the reasons for using catalysts, presents some examples of catalystic processes and illustrates the vital role that catalysis plays in reducing the generation of waste.

A. Reasons for using catalysts

The extensive industrial use of catalysts is illustrated by the statement of Thomas and Thomas, 1/ who claim that nine out of ten chemical manufacturing processes involve catalytic processes. A general discussion of the main reasons for using catalysts and a few examples of catalytic processes are presented in this section.

Selectivity of catalysts

Catalysts suitable for industrial use increase the rates of desirable reactions without increasing the rates of reactions that yield undesirable products (sometimes they even decrease the rates of these undesirable reactions). This selectivity of catalysts results in better utilization of raw materials, i.e. a larger fraction of raw material is converted into useful product and a smaller amount of waste by-product is formed. The decreased by-product formation in catalytic processes often results in significantly lower product purification costs, that is, there is less energy consumption for product separation processes such as distillation.

Examples are plentiful of industrial processes in which increased selectivity has been obtained by the use of catalysts. The replacement of thermal cracking of crude oil by fluid catalytic cracking, initially using amorphous silica-alumina (in the 1940s) and later using zeolites (in the 1960s), greatly increased the utilization of crude oil for the production of valuable products. The discovery of naphtha-reforming catalysts (Platforming process) in the 1940s and subsequent advances in reforming catalysts, e.g. (Pt-Re)/Al_2O_3 and (Pt-Ir)/Al_2O_3, increased the utilization of crude oil for gasoline and aromatics production even further.

The chlorohydrin process for producing ethylene oxide has essentially been replaced by the catalytic (silver catalyst) process. The chlorohydrin process produces a number of by-products (ethylene dichloride, dichlorodiethyl

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1/ J. M. Thomas and W. J. Thomas, Introduction to the Principles of Heterogeneous Catalysis (London, Academic Press, 1967), p. 8.

ether and calcium chloride). The ethylene dichloride, and to a lesser degree the dichlorodiethyl ether, are useful by-products, but the calcium chloride, 1.2 kilograms of which are produced per kilogram of ethylene oxide, is essentially a waste by-product. The silver-catalyzed process for ethylene oxide production, because it enables direct oxidation of the ethylene with either air or oxygen, produces very few by-products, the main ones being CO_2 and H_2O. Improvements in the catalytic ethylene oxide process, such as changes in operating conditions and/or different catalyst formulations, should reduce the formation of CO_2 and H_2O.

The use of catalytic processes, instead of the older non-catalytic vapour-phase oxidation of propane and butane, for the production of oxygenated hydrocarbons such as alcohols, aldehydes, ketones and organic acids is another example of the substitution of catalytic for non-catalytic processes. The non-catalytic partial oxidation process produced a difficult-to-separate mixture of oxygenated hydrocarbons and converted a significant fraction of the feedstock into CO_2 and H_2O. The energy consumption for product purification was high and the carbon efficiency was low. The current heterogeneous and homogeneous catalytic processes for the production of oxygenated hydrocarbons are very selective. Examples of these selective oxidation processes include the Wacker processes for acetaldehyde (homogeneous $PdCl_2$ and $CuCl_2$ catalyst); vinyl acetate production from various feedstocks (the older catalytic processes have essentially been replaced by a vapour-phase catalytic process using a heterogeneous Pd-Au catalyst); formaldehyde production from methanol over either a silver or iron molybdate catalyst; the relatively new process for acetic acid production by methanol hydroformulation using a rhodium catalyst; and methanol production from synthesis gas (CO and H_2) over various metal oxide catalysts.

Many other examples could be cited, but the above list, though short, illustrates the importance of catalysts in the production of high-volume chemicals. However, for many of these catalytic processes to be feasible, catalyst poisons must be removed from the feedstocks.

Removal of impurities from feedstocks

Many feedstocks in chemical plants require extensive purification before they can be further processed. Impurities such as water, carbon monoxide, and organic compounds containing sulphur, nitrogen and metals have to be removed because they poison (deactivate) the catalysts used in subsequent processing. Often, impurity levels have to be reduced to the parts-per-million, or even the parts-per-billion, level. Catalytic or adsorption processes are commonly used to achieve the required purity. Adsorption processes are similar to catalytic processes since the impurities are chemisorbed on the adsorbent, and chemisorption is the first step in heterogeneously catalyzed reactions. The feedstock purification processes in themselves are not directly responsible for decreasing the production of wastes, but they are an integral part of low-waste chemical processes since highly selective (i.e. low-waste) catalytic processes would not be possible without feedstock purification.

The removal of heteroatoms, such as sulphur, nitrogen and oxygen, from hydrocarbon liquids is accomplished by hydrotreating the feed over supported catalysts containing Mo, Co, Ni and/or W. Fixed-bed adsorbers are used to remove traces of H_2O (zeolite) and H_2S (ZnO) from gases. Larger quantities of H_2S are removed from gases, such as natural gas, by absorption in amine solutions. The H_2S is recovered from the amine solution by heating and is then converted to elemental sulphur via the modified Claus process. The modified Claus process uses an alumina catalyst to convert H_2S and SO_2 into elemental sulphur and water, i.e. this catalytic process converts undesirable by-products and pollutants (H_2S and SO_2) into a valuable product. However, some H_2S and SO_2 are emitted from Claus plants, and the cold-bed Claus process has been developed to reduce these emissions.

Conversion of pollutants

Although many processes are very efficient and produce only small amounts of waste, it is not possible to eliminate undesirable by-products totally. Catalysts again play a key role in the conversion of polluting by-products into environmentally acceptable products. Catalytic reactors are used to remove pollutants such as hydrocarbons and vinyl chloride from the air in chemical plants. However, the largest single use of catalysts for pollution abatement is the automobile catalytic converter. Many automobiles manufactured since 1975 are equipped with catalytic converters that clean up the exhaust gases. These converters, which contain catalysts consisting of alumina-supported Pd, Pt and/or Rh, are very efficient at reducing carbon monoxide and hydrocarbon emissions from internal combustion engines, and their use has greatly reduced pollution from this source. The mass production of catalytic reactors that operate reliably for long periods without maintenance has been a significant achievement of catalytic and reactor research and development. Efforts to eliminate NO_x from automobile exhausts have not, however, been as successful, but with continued research, the right catalysts for this are expected to be developed.

Products only produced by catalytic processes

Many products can only be produced economically by catalytic processes, so waste reduction is not the prime reason for using catalytic processes in these cases. Examples of such processes are the catalytic process for ammonia, developed over 75 years ago, and the catalytic processes for the production of linear low-density polyethylene, developed during the last two decades.

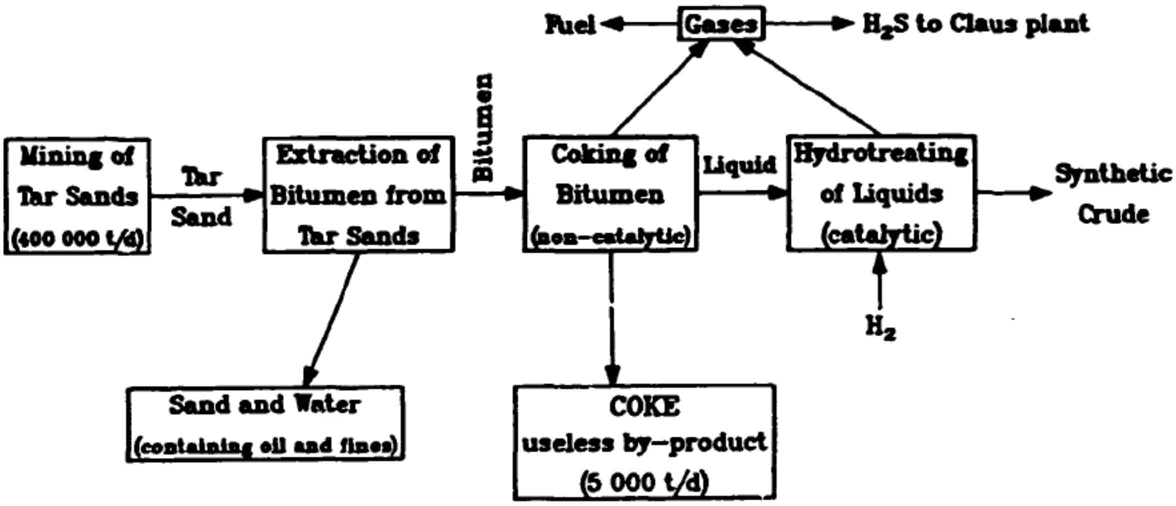
All the examples cited above have dealt with existing catalytic processes, and the examples cited cover only a very small fraction of the commercial catalytic processes. The next section contains a discussion of a catalytic process that will be of great importance to Western Canada.

B. Upgrading of oil-sands bitumen

Western Canada, specifically the province of Alberta, has very large deposits of oil sands. The oil sand deposits in Alberta contain over 140×10^9 m^3 of bitumen, and it has been estimated that 40×10^9 m^3 of synthetic crude oil can be produced from these deposits. This amount of synthetic crude oil is sufficient to meet Canada's total crude oil needs, at current rates of consumption, for several hundred years. However, the bitumen cannot be produced by the techniques usually used to produce crude oil because bitumen is a very viscous, tar-like material that does not flow out of the sand formations. Fortunately, a significant fraction (about 10%) of the bitumen-containing sands are located close to the surface and can be subjected to surface mining techniques. This has led to the development of processes for the recovery of bitumen from mineable oil sands Currently, two commercial plants, producing a total of about 30×10^3 m^3/day of synthetic crude oil, are in operation in the Fort McMurray area of northeastern Alberta.

The processes involved in the recovery of bitumen from the sands and upgrading of the bitumen to synthetic crude are shown schematically in figure I. The first step is the surface mining of the sand containing the bitumen; the mined oil sands contain about 10 wt% bitumen. The bitumen is extracted from the sand by the Clark hot water process. The extracted bitumen is very viscous, has a low hydrogen to carbon ratio (H/C atomic ratio about 1.5), and contains considerable amounts of heteroatoms and metals (~5 wt% S, 1.0 wt% O, 0.4 wt% N, 250 ppm Va and 100 ppm Ni). The heteroatoms and metals are present in organic compounds and complexes, and extensive processing is required to convert the bitumen into synthetic crude oil. The main objectives of the upgrading processes are to increase the H/C ratio, decrease the average molecular weight, and remove the heteroatoms and metals. In the two commercial plants in operation, these objectives are achieved by coking and hydrotreating. Coking increases the H/C ratio by rejection of carbon and decreases the average molecular weight by cracking; hydrotreating removes the heteroatoms and decreases the average molecular weight and boiling point by hydrogenation and hydrocracking.

Figure I. Schematic diagram of commercial process for conversion of surface-mined oil sands to synthetic crude oil



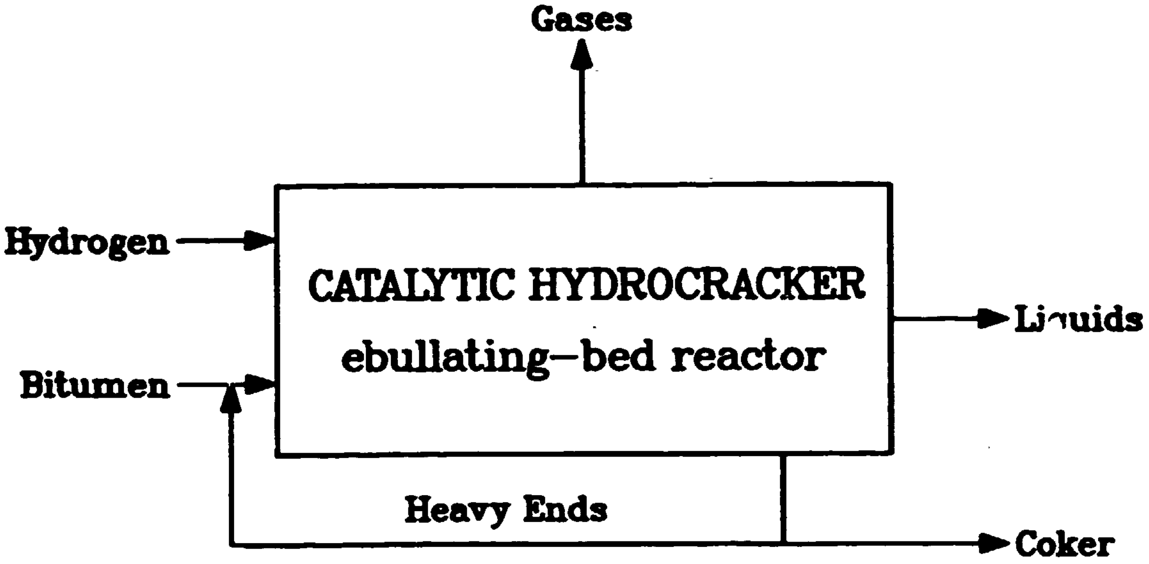
The coking processes (one plant uses delayed coking and the other fluid coking) produce a large amount of coke (in excess of 5,000 tonnes/day). Some of this coke is used for fuel, but most of it is stockpiled because no use has been found for coke with such a high sulphur content (over 5 wt% S). The coke produced in the primary upgrading of bitumen is therefore a waste by-product, and considerable effort has been expended to find uses for it. There are a number of possible solutions to the coke problem:

(a) Use coke as fuel in furnaces and boilers. Some of the coke is currently being utilized in this fashion, but its high sulphur and metals content seriously hinders its large-scale use;

(b) Gasify the coke to a low energy fuel gas. Flexicoking or coke gasification are methods to achieve this, but they are not economically viable;

(c) Decrease or eliminate the production of coke by increasing the H/C ratio of the bitumen by hydrogen addition rather than carbon rejection. Hydrogen addition can be accomplished by hydrocracking the bitumen. Several processes for the hydrocracking of heavy oils and residua have been developed, namely, fluid-bed or ebullating-bed reactors (H-Oil and LC-Fining) and fixed-bed hydrocracking similar to conventional hydrotreating, but none of them have been used commercially for the hydrocracking of bitumen. Nevertheless, a planned expansion to one of the commercial oil sands plants will use catalytic hydrocracking in an ebullating bed as the first step in the upgrading of bitumen. A schematic diagram of the process is shown in figure II.

Figure II. Schematic diagram for bitumen hydrotreating process



The expansion of the oil sands plant will increase synthetic crude oil production by about 3,000 m^3 per day without increasing the plant's total coke production. This is a good example of how a catalytic process can significantly reduce waste by-products. Additional expansions and new grass-roots oil sands plants will undoubtedly incorporate the catalytic hydrocracking of bitumen in their upgrading scheme; this will mean significantly lower quantities of coke per barrel of synthetic crude oil produced.

C. Concluding remarks

This brief overview has shown the importance of catalysis in reducing the generation of waste in the chemical and petrochemical industries. Catalytic processes will play an increasingly important role in the conversion of raw material to useful products as high quality raw materials become scarcer and as demand for new products increases. During the next few decades, numerous catalysts and catalytic processes will be developed, and many of these will make better use of raw materials, will be able to use lower quality feedstocks, and will reduce the generation of pollutants and waste by-products. Areas in which new developments are needed include processes for the reduction of SO_2 and NO_x from mobile and stationary combustion sources; the efficient (selective) conversion of $CO + H_2$ (synthesis gas) into liquid fuels; and economical processes for the octane enhancement of liquid fuels so that lead additives can be eliminated completely from gasoline. Another area that will require intensive research is the development of poison-resistant and readily regenerable catalysts so that deactivated catalysts are not one of the waste by-products of catalytic processes.

Research in catalysis has increased significantly during the last few decades, and it will continue to increase despite the current, and probably temporary, decline in research related to the energy scene, i.e. catalytic production of fuels from low quality raw materials. Intensive research in catalysis will be required to rectify the problems of air, water and soil pollution caused by industrialization. These problems were the result of technology and can only be solved by better technology. Catalysis will be an integral part of these new technologies.

WASTE REDUCTION IN THE UNITED STATES

John Yates*

This paper contains a brief discussion of waste reduction efforts in the United States over the last several years. Since about 1981 there has been a serious effort by manufacturing plants to reduce the waste generated by process operations. The primary reason for this was the passage by the U.S. Congress of the Resource Conservation and Recovery Act of 1976. The United States Environmental Protection Agency took four years to write the basic regulations authorized by this law. The law and the regulations essentially do two things. First, the regulations declare a large fraction of industrial process wastes to be hazardous wastes. Secondly, all industrial plants producing more than 1,000 kilograms per month of hazardous wastes are now responsible for the waste for ever.

Plants can no longer simply call in a waste disposal truck and forget about the waste. Now, the generator of the waste has to sign a shipping manifest, the truck driver has to sign the manifest, and someone at the final disposal point has to sign the manifest. A copy of the completed manifest is then sent to the state environmental agency.

In the ensuing years, the cost of disposing of waste increased dramatically and quickly. The new regulations forced industries to examine their waste production and disposal practices very carefully. They started putting waste reduction procedures in effect to reduce the cost of operation and to reduce legal liability. Every kilogram less of waste produced meant one kilogram less of waste to track and, perhaps, worry about for many years to come.

In November 1984 President Reagan signed into law an expansion and several amendments to the original Hazardous Waste Act. One section of the amendments authorized the United States Environmental Protection Agency to regulate waste production, not just waste disposal practices.

One section of this new law addresses "waste minimization" and requires companies to do the following:

(a) After 1 September 1985, manifests must contain a generator certification that the volume and/or quantity and toxicity of the waste have been reduced to the maximum degree economically practicable and that the method used to manage the waste minimizes risk to the extent practicable;

(b) Biennial generator reports must indicate efforts to reduce waste volume and the reduction actually achieved;

(c) After 1 September 1985, as a condition for an on-site permit, the generator must certify at least annually the efforts to reduce waste volume and the reduction achieved;

(d) By 1 October 1986, the United States Environmental Protection Agency had to report to Congress on the feasibility and desirability of establishing waste minimization regulations.

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Annex

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