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NEW TRENDS IN PETROCHEMICAL RESEARCH AND DEVELOPMENT

<u>Sectoral Working Paper Series</u>

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SECTORAL WORKING PAPERS

In the course of the work on major sectoral studies carried out by the UNIDO Division for Industrial Studies, several working papers are produced by the secretariat and by outside experts. Selected papers that are believed to be of interest to a wider audience are presented in the Sectoral Working Papers series. These papers are more exploratory and tentative than the sectoral studies. They are therefore subject to revision and modification before being incorporated into the sectoral studies.

Preface

This study was prepared by the Sectoral Studies Branch, Division for Industrial Studies, to be used as background material for the Third Consultation on the Petrochemical Industry to be held in Vienna, Austria, from 2 to 6 December 1985. In view of the central role of research and development in the past, present and future of the petrochemical industry it has been felt necessary to present an overview of the main trends and fields in the petrochemical R and D activity.

This overview intends to give information to the developing countries on the possible effects the results of ongoing R and D can have on their future investment projects. At the same time it tries to present, in conclusion of the research situation investigated and the situation in the different developing countries ideas on the general strategies to adopt in the R and D work.

This document is based on a paper prepared by Prof. Dr. H. Schindlbauer, University of Vienna.

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1. INTRODUCTION

1.1 Background

The petrochemical industry, representing today around half of the total gross output of the chemical industry, approaches a production of half a billion US$ in 1985. This industry was practically nonexistent fifty years ago. Our everyday life, our high technology industries would be inconceivable without the products of the petrochemistry: plastics, synthetic fibres, synthetic rubbers, etc. Its spectacular growth rates of the 1950s and 1960s, amazed the world. Even the six-fold escalation in prices of feedstock and energy attacking this industry at its most vital point could only slow down its development temporarily. In spite of the supposed maturing of the production processes this industry was among the first and the quickest to respond to the early signs of economic recovery: a 9 per cent growth rate in 1984 and 4.5 per cent for 1985 will again place the petrochemistry among the most dynamic sectors of the industry.

Research and development activity has been the key factor enabling the petrochemical industry to overcome the difficulties, to exploit fully all the opportunities offered by the favourable economic climate of the 1950s and 1960s and to adapt itself to the impact of the oil crisis and economic recession. Research and development has always been a high priority area in corporate strategy: expenditure averaged around 5 per cent of the gross sales, well above the industrial average. The research and development activity is the only means through which the maturity symptoms observed in some end products and classic production processes can be overcome and a continuation of the remarkable results of the last two years ensured in the long run.

The very intensive research and development work undertaken in corporate laboratories and other facilities as well as in governmental and scientific institutions will certainly bring many new processes and products to industrial scale implementation and will give new competitiveness to many existing processes and products by a great number of important improvements. The very nature of all research work makes forecasts of the actual processes and products, impossible. Nobody would have guessed the possibilities of linear polyolefin technologies before the work of Professor Natta. It is nevertheless possible to define the areas, where intensive research and development activity is concentrated and new goals endeavoured. This can give a general picture of the fields where new results can be expected and show the broad outlines of possible future achievements. These new achievements will to a great extent shape the technical and economic future of the petrochemical industry. For the developing countries, both those which intend to proceed with the development of their petrochemical industry already well underway and those which only now are engaged in the creation of this sector, it is of paramount importance to know, what to expect from ongoing research, what impact the results will have on industrial projects and on their technical and economic viability. This study aims at giving an answer to this question.

Research activity and therefore process technology and product know-how in the petrochemical field is still concentrated in the hands of big companies in a few industrialized countries, although some developing countries have been able to surprise the world with new processes of great interest.

Developing countries are mostly dependent on foreign technology for the establishment of their petrochemical industry. The transfer of technology faces severe obstacles in most cases. Technologies conceived under different conditions are difficult to adapt. Technical assimilation is difficult where the necessary educational, scientific and technical background is missing. Technical back-up from process owners is sometimes inadequate. A major factor in overcoming such difficulties could be support given by the appropiate domestic research and development organizations and activities for the development of industrial projects in the country.

All the above considerations make it necessary to investigate the actual trends and activities in petrochemical research, what impact they can have on the future development of this industry in the developing countries, and how they can influence the projects and production structures to be implemented in these countries.

1.2 Problems

The questions to be discussed in this study are: how can research and development

(a) improve the competitiveness of primary and intermediate petrochemical producers in developing countries;

(b) assist to reduce imports of petrochemicals through local production for use in industries as plastics, synthetic fibres and synthetic rubbers and

(c) contribute to the development of technologies more suited to conditions in developing countries, e.g. with respect to market size, infrastructural requirements, complexity of operation etc.

1.3 Objective

This study will demonstrate, through a few illustrative examples, the importance of considering new scientific discoveries in medium-term production planning in the petrochemical field.

1.4 Research and development trends

The scientific and technical background of the petrochemical industry is vast and diversified. Applied research is not confined to process and product research and development work but includes many similar activities in the chemical operations field (catalyst, operation techniques, etc.) as well as in the technical sciences (instrumentation and control, heat recovery, machinery, etc.) all playing a concerted and important role in the development of the petrochemical industry.

Therefore the scope of research and development will be presented in three chapters: the process and product development, the operations and the technical research.

2. PROCESS AND PRODUCT RESEARCH AND DEVELOPMENT

From this vast domain, three main fields have been selected: alternative raw materials, primary products and end products. The question of the intermediates is so complex and large, that it is only possible to cover a few of the most important items.

2.1 Feedstocks

The two steep oil price rises and tight supply situation of the 1970s put everywhere a heavy accent on the research for alternative feedstocks. Today, this endeavour has lost most of its momentum, but important research and development work is still underway in many countries, mainly in those dependent on hydrocarbon imports. Most of this work is directed towards fuel, first of all motor fuel substitution but research for alternative feedstocks for the classic and also for new primary petrochemicals is also actively pursued.

This study will only briefly treat the research oriented towards new energy supply routes in order to give a complete picture, but will try to give a more detailed view of the petrochemical problems.

In the petrochemical field this kind of research is going on in two main directions, viz:

- Alternative hydrocarbon feedstocks
- Alternative non-hydrocarbon feedstocks.

2.1.1 Alternative hydrocarbon feedstocks

Today naphtha is the overwhelmingly most important petrochemical feedstock. This oil fraction is becoming more and more demanded every day and all over the world, while the heavier fractions are more easily replaced by alternative fuels (coal, nuclear), for power generation and by natural gas for household energy supply. New sources of light hydrocarbons (LPG, NGL) as well as the gradual shift of the oil production towards heavier crudes also favour the tendencies towards the use of both heavier and lighter hydrocarbons for the production of the primary petrochemical groups: olefins and aromatics.

Well known commercialized processes exist in these fields. The research and development activity endeavours to raise the efficiency and yield of the existing processes and to provide the maximum of flexibility in the choice of the feedstock following established trends. Further improvements in both directions will be continuously achieved during the years but no brand new or fundamentally modified process can be expected, neither in the olefin production by steam cracking nor in the catalytic reforming for aromatics and high octane motor fuels.

Methane is available in big quantities in many countries where the domestic supply of liquid hydrocarbons is relatively scarce or even nonexistent. Natural gas often contains enough NGL to provide the necessary feedstock for olefin production. Methane itself serves mainly the fuel market, but also feeds most of the ammonia and methanol plants. Other chemicals are also manufactured directly from methane.

The methane chemistry will be treated in section 2.2.1. The bulk of the methane used in the petrochemical field is used for the production of synthesis gas (syngas).

Syngas however, can be manufactured from most of the fuels, from hydrocarbons and others (figure 1). Syngas production from methane is one of the most well developed processes (steam reforming under medium pressure). Improvements are still being researched, but the main effort is devoted to the extension of the feed range. Naphtha has performed successfully in the 1960s already.

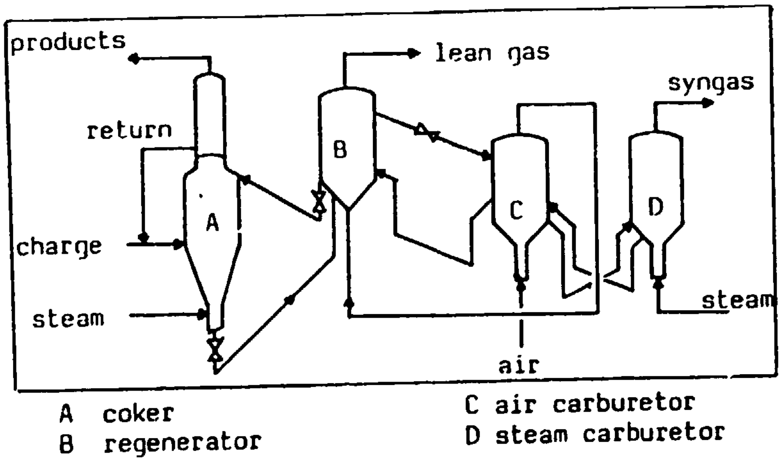
Figure 1. Raw materials for syngas production

$$\left.\begin{array}{l}\text{Brown coal}\\ \text{Mineral coal}\\ \text{Natural gas}\\ \text{Petroleum fractions}\\ \text{Biogas}\\ \text{Organic waste}\end{array}\right\} \longrightarrow CO + xH_2$$

The scientific work aims to extend the range to the residual oils and thus substitute the partial oxidation of residual oils by the energetically more efficient steam reforming. The basis of this new process, called "total hydrocarbon reforming" (THR) are two new catalysts with high reforming activity for heavy oils, from crude oil to vacuum residues. In an externally heated primary reformer the raw material reacts with superheated steam (higher than 800°C) to give a gas mixture, which still contains higher hydrocarbons. In a secondary reformer where oxygen or air is introduced these hydrocarbons are completely reformed with steam giving a syngas mixture ($CO + H_2 +$ impurities).

Another development combines the production of light hydrocarbons by thermal cracking of residual oils with synthesis gas production - a modernization of the flexicoking processes. The procedure is shown in figure 2.

Figure 2. Production of synthesis gas by modified flexicoking



The first reactor is in reality the thermal cracker, where the light hydrocarbons are produced. The coke produced in this first reactor which would be a byproduct otherwise, is gasified with air and steam in the following reactors. This modified flexicoking process is called "dual gasification" because the gasification of the coke is split in two reactors, the air and the steam gasifier.[1]

The production of syngas from other non-hydrocarbons sources is treated in the next subsection.

2.1.2 Alternative non-hydrocarbon feedstocks

Among the numerous possibilities, only two are relevant for the petrochemical industry, namely coal and biomass. Both are actively researched for chemical feedstock as well as for fuel uses.

Coal chemistry

Research and development up to the semi-commercial scale was heavily financed in the last decade in the gasification field. Synthesis gas production for motor fuel (by Fischer-Tropsch and coal liquefaction processes) and methanol manufacturing also mainly for fuel uses were the main goals. As useful byproducts, the coal based ammonia processes and both methanol and syngas as feedstocks for the production of primary petrochemicals were also objectives of this research work. Today this activity has been considerably reduced and less funds are allocated to this sector. However research is still going on, first of all in the gasification field.

Several industrial scale processes for syngas production are not only proven, but in operation today. For synthetic natural gas (SNG) proven processes are also available but not applied on a large scale. Research and development work is aimed at efficiency improvement and at higher operating pressure. No major breakthroughs are probable, which could substantially improve the competitiveness of syngas or methane from coal against those

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[1] P.E. Allan a.o., Oil and Gas Journal 80 (20), 93 (1982).

manufactured from hydrocarbons, where evidently the same kind of activity is deployed in the process improvement research. It can accordingly be concluded that the competitiveness of coal as alternative raw material against hydrocarbons, first of all methane, for the production of syngas and its derivatives will depend on the relative price/heating value evolution and not on the competition between the research results in the two respective fields.

Syngas, methanol and methane on the other hand, independently of their source, are very attractive starting points for different petrochemical purposes and extensive research is going on for their utilization in the production of different primary petrochemicals and intermediates (see C_1 chemistry, section 2.2.1).

Biomass utilization

The different biomasses are either wastes, byproducts of agricultural or agro-industrial activity or crops specifically cultivated for this purpose (sugar, corn etc). They can be processed to petrochemicals (and/or for fuels) in several ways:

- Gasification
- Pyrolysis
- Hydroprocessing
- Fermentation processes (anaerobic and aerobic)
- Others.

Gasification can use any kind of organic matter: wood, all solid wastes etc. In view of the low calorific value and relatively high water and oxygen content of the fuel, yields and efficiencies are inherently low and the gas produced contains high proportions of CO_2 and nitrogen. Industrial plants of comparable size to the actual hydrocarbon based syngas units would consume 500-1,000 t/hour of feedstock, quantities measurable only in millions of tons per year. In view of the collection, transport and storage problems, gasification can be suitable for local use only. For this purpose processes are available. No substantial research work is directed in this direction.

Pyrolysis

This process is not the most economic for the production of liquid fuel as it reduces rather than increases the H/C-ratio. The reaction products are gas, lighter distillates and charcoal.

Hydroprocessing

This is one of the most promising developments, because it increases the H/C ratio. The raw material may include wood wastes, corn cobs, cotton gin waste, pecan shell, peanut shell, rice hull and sugar cane bagasse. From all of these, the same process gives chemically similar products, despite the dissimilarity of the biomass feedstock. The product is a liquid hydrocarbon mixture which can be burned in conventional engines without needing the sort of modification which are required for the burning of ethanol or seed oil.

Fermentation

The two very old and widely used process routes are the anaerobic and the aerobic fermentation.

Anaerobic fermentation. Organic wastes of different origin but also digester sludge can be further decomposed anaerobically by microorganisms to carbon dioxide, methane, and other volatile components by a mixed culture of different, but determined microorganism strains. Solid wastes have to be dispersed in water. Under usual conditions about 350 $l/m^3.d$ sewage gas may be produced, during this 60-85 per cent of the organic matter is degraded. This degradation proceeds in three steps: the first one is strictly anaerobic, here microorganisms degrade polymeric compounds to short chain acids and alcohols. In the second step C_2 and C_1 compounds are built. In the third step methane is synthesized by methanobacteria. The biogas contains 50-70 per cent methane, the rest is carbon dioxide with small amounts of ammonia, hydrogen and hydrogensulphide. Process improvement is possible by better process control, especially temperature, pH-value, etc. by the use of optimized bioreactors and strain. The produced gas may be introduced to local energy systems after a simple washing and removal of sulphur. It is however, due to its low yields, not applicable to industrial petrochemical production.

Aerobic fermentation. The production of ethylalcohol practiced for other purposes, was used several times in our century for serving the chemical industry as primary product. Ethylene was in reality first manufactured from ethanol and many other chemical compounds can be easily made from ethanol.

Ethanol

The raw material for this purpose is sugar, usually glucose. From the polysaccharids, starch can be relatively easily hydrolyzed to sugar, but cellulose hydrolysis is a more difficult task. Most natural and waste biomasses consist of wood like materials called lignocellulose, composed of cellulose, hemicellulose and lignin with different structures. The organic solid wastes generated annually in the United States are estimated at 10 billion tons dry material (without manure) while 145 million tons would be needed only to cover the feedstock needs of the whole chemical industry and replace 10 per cent of the gasoline used in the United States.[2/] The economics of the available processes, however, cannot justify any implementation of this theoretical route. Intensive research is going on in the following fields.

(a) Pre-treatment
(b) Hydrolysis
(c) Fermentation
(d) Product recovery.

The third and fourth steps are common fields of research with the fermentation processes for normal glucose fermentation.

(a) Pre-treatment. It alters the composition and structure of the lignocelluloses by removing lignine and disrupting the hydrogen bonding between cellulose molecules, thus permitting the access of the hydrolytic agents to the carbohydrates (polysaccharides). Both existing physical (mainly

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[2/] J.H. Phillips, It need not to be "feedstock or food", Chemtech., 1985 milling) and chemical treatments (acids, steam or solvent) are all expensive and the yield and efficiency not good enough. The research work is directed not only to the improvement of the existing process routes, but is aimed mainly at finding biological methods (microorganisms or enzymes) capable to solve this problem in a selective and efficient way.

(b) Hydrolysis. Acids or enzymes are used for hydrolyzing the solids coming from the pre-treatment to soluble sugars. With the acid route, degradation of the sugars (monosaccharides) presents the biggest problem, limiting the yields. This problem is eliminated by the enzymatic reaction, which is specific, but significantly slower. Research is oriented mainly towards finding new and better microorganisms (in the first place fungi like the Trichoderma reesei or Thermomonospora sp. etc.) but as of today the activity and mechanism of cellulose enzymes is not yet fully understood. Basic research is looking into the mechanism problems while extensive mutation work is undertaken to find better species for eventual industrial use.

(c) Fermentation of glucose presents no problems,[3/] but the other hexoses and pentoses produced by hydrolysis of pre-treated lingnocellulose are not so easy to process. The classic yeasts used in alcohol production from sugar (Saccharomices) cannot ferment aldopentoses such as xylose. Use of isomerase enzymes converting xylose to xylulose and development of xylulose fermenting yeasts is one of the research routes, but many other ways are investigated to improve the efficiency of the microbial processes leading to ethanol. Some efforts are directed towards the integration of the biomass hydrolysis and sugar fermentation in one step.

(d) Product recovery. The main economic problem lies here. Biologic processes cannot produce ethanol solutions with more than 10-14 per cent concentration today. In this range about 150 kg of fuel oil equivalent heat energy is required for the classic distillation process to yield one ton of alcohol with 98 per cent concentration, equivalent to 600 kg of fuel oil. Below 8 per cent ethanol concentration in the feed to the distillation, energy requirement rises steeply.

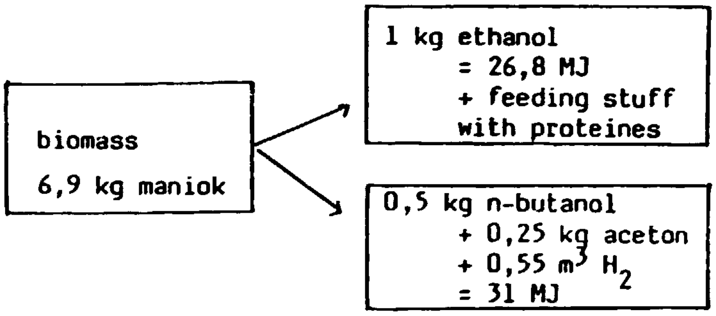
[3/] E. Rennefeld, E. Wagner and C. Wimmer, Zuckerindustrie 105, 25 (1980).

Research follows two distinct paths. The first looks for microbial methods yielding substantially higher concentration in the fermentation, the second is directed at alternate methods of concentration, replacing the classic distillation route. The heat pump effect, vacuum distillation and other similar methods are not very promising, the resulting thermal efficiency being lower than that of the original process. Two other methods are under investigation: vacuum fermentation coupled with vacuum distillation and extractive fermentation.

While the classic alcohol route has found industrial large-scale application in some developing countries (e.g. Brazil) the new possibilities under research discussed above will probably need a rather long time to arrive at commercializable processes.

Fermentation of biomass can in principle lead to other products than ethanol, using conveniently chosen or developed microorganisms. So e.g. the production of n-butanol seems energetically more promising. Figure 3 shows a comparison between the production of ethanol or butanol from maniok.

Figure 3. Comparison between the production of ethanol or butanol from maniok



From the view of the energy transformation the butanol way from biomass is 16 per cent more efficient than the production of ethanol. But the chemical engineering and the mode of application of using a butanol-aceton-mixture for fuel has to be studied further in detail.

Little is known about the production of gasoline from harvest wastes. But in Australia there are already two plants which use cereals straw and other harvest wastes as well as wood and sugarcane fibres for the production of gasoline. One such refinery is already working and will produce 4,5 million liters gasoline per day.[4]

2.2 Primary petrochemicals

Although today ethylene (C_2), propylene (C_3), butadiene (C_4) and aromatics are the main building blocks of the petrochemical industry, a great part of the research and development activity is devoted to the C_1 chemistry which could open the way for the use of methane and syngas from alternative sources for petrochemical purposes. Therefore the main emphasis was laid on the C_1 and the C_4 chemistry, where most of the research activity is concentrated and the most important results can be expected.

2.2.1 C_1 chemistry

Methane, syngas and methanol are the three starting points for the manufacturing of quite a number of important primary and intermediate products. Since syngas and methanol can be used for the same purpose, these two will form one subsection only.

Methane

Today methane is mostly used for energy purposes. Production of syngas by steam reforming, acetylene and ethylene by pyrolytic methods, chlorinated products, hydrocyanic acid and CS_2 are all well known processes, currently used commercially with the exception of the pyrolysis or partial oxydation methods, replaced by naphtha or ethane cracking because of the distinctly lower energy consumption. Direct conversion with good energy balance to C_2- and C_3-olefins, aromatics and oxygenated C_1-derivates like methanol or

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[4] Erdöldienst, 19 July 1983.

formaldehyde, an alternative to liquid hydrocarbon feedstock, has been the goal of intensive research and development activity in the field of methane chemistry in the last years.[5]

In the following short discussion only some illustrative results are reported on the way from methane to methanol, formaldehyde and C_{2+}-hydrocarbons.

Oxygenated compounds

The direct route without intermediate syngas production to methanol by homogeneous oxidation of methane by ferric sulphate in a sulphuric acid solution, after a previous heterogenic activation on a Pd/C-catalyst is described[6] as follows:

$$CH_4 \xrightarrow{Pd/C} CH_4,\ ads \xrightarrow[25^\circ C,\ 50\ bar]{Fe_2(SO_4)_3} CH_3OH$$

The reaction has 92 per cent selectivity to methanol.

In another reaction the methane is radically activated by chlorine, which functions also as an oxidant. Chlorine and methane react in an adiabatic flame at normal pressure and 700-1,700°C to ethane and ethylene, with the side products hydrogen and hydrogenchloride.[7]

$$2\ CH_4 + Cl_2 \longrightarrow 2\ HCl + (1-x)C_2H_6 + xC_2H_4 + xH_2$$

$$x = 0,1$$

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[5] Nachr. Chem. Techn. Lab. 33 (4), 292 (1985).

[6] G. König, DE-OS 31010224.

[7] S.P. Heneghan e.a., Int. J. Chem. Kinet. 13, 677 (1981).

With methyl chloride as intermediate at high temperatures (500°C) and normal pressure mostly ethane is built, at low temperatures (400°C) and higher pressure (6.7 bar) hydrocarbons in the naphtha region are isolated.

The reaction of methane in the presence of metal oxides (i.e. a heterogenous activation) is also an oxidation to methanol and formaldehyde as an oxidative coupled reaction to higher hydrocarbons. Especially the last reaction seems to be realizable on a technical scale. Methane reacts with N_2O on a molybdenum/silica catalyst at 550-600°C. The methane conversion is 3 to 6 per cent and the overall selectivity for methanol and formaldehyde 65-80 per cent (HCHO: CH_3OH = 4 : 1).[8]

Similar results are reported in the Russian patent literature: methane reacts with air on a catalyst to formaldehyde. In a laboratory fluid reactor at 650-700°C for example formaldehyde selectivities up to 65 per cent are described with the methane conversion at 30 per cent at a contact time of 1 second. On another catalyst ($Sn_3(PO_4)_4/SiO_2$) at 500-650°C selectivities up to 94 per cent formaldehyde are reported.

The production of ethylene and acetylene from methane with formation of hydrogen with acceptable yields is only possible at high temperatures (1,500-4,000°C) because of thermodynamic reasons. So direct routes (partial oxidation and pyrolysis) cannot be competitive in the near future.

Oxidative Alkylation

In the presence of oxidants methane can react more efficiently. Especially the oxidative methylation of toluene, propene and isobutene is economically hopeful with respect to ethylbenzene and styrene, respectively butadiene or methylbutadiene. In a similar reaction acetonitrile and methane gives acrylonitrile. For the reaction pathways see figures 4 to 7.

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[8] H.P. Liu e.a., J. Am. Chem. Soc. 106, 4117 (1984).

Figure 4. Principle of oxidative methylation

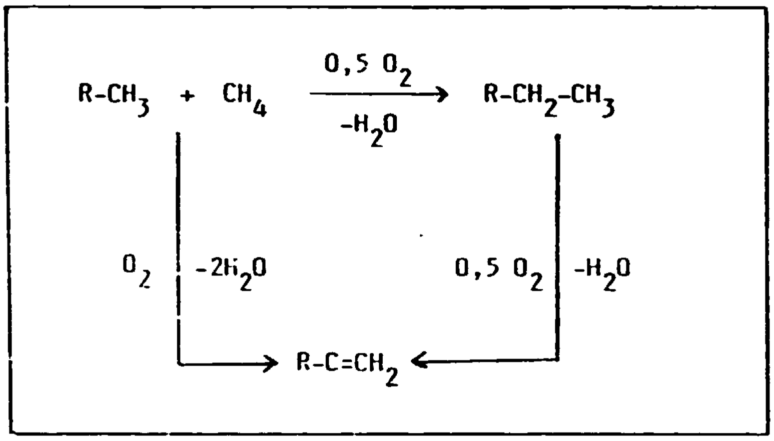


Figure 5. Oxidative methylation of toluene, propene and isobutene

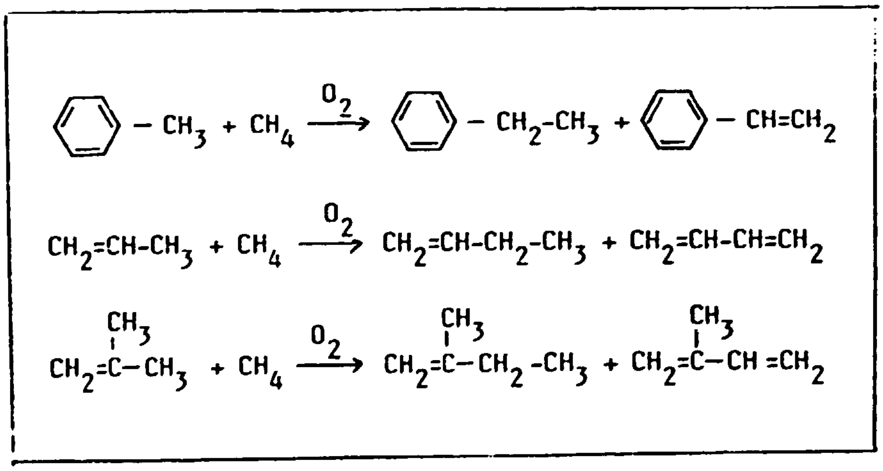


Figure 6. Oxidative methylation of acetonitrile to acrylonitrile

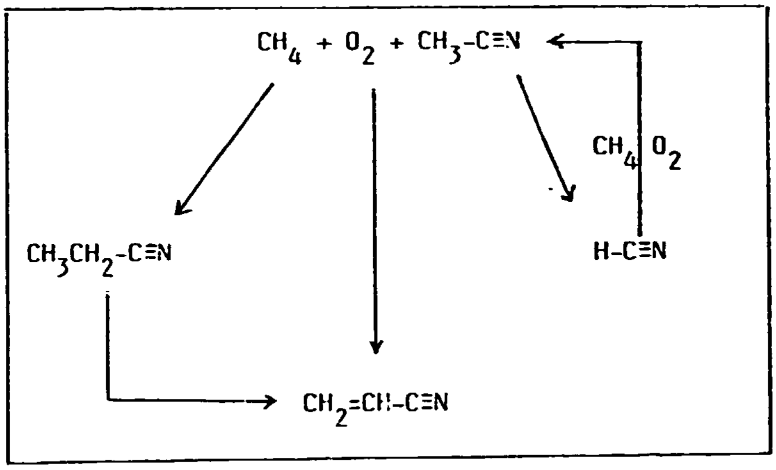
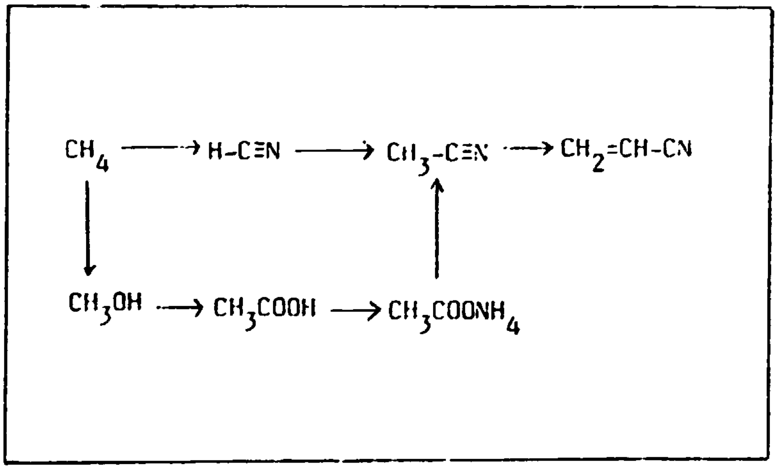


Figure 7. Potential ways from methane to acrylonitrile



The oxidative reaction was also observed on acidic zeolithes. In this reaction aromatics can be built. Another reported possibility for alkylating of olefinic hydrocarbons with methane uses Ni-catalysts in a gas phase process.[9/] This study shows, that methane reacts in the presence of oxygen with compounds possessing an activated methyl group; the result is an elongation of the chain by one carbon atom. In this way an ethyl group may be built or directly a vinyl group. The ethyl group may subsequently be oxydehydrated to a vinyl group. The overall reaction therefore is a conversion of a methyl group into a vinyl group. Thus toluene gives ethylbenzene and styrene, propylene gives 1-butene and butadiene, and the reaction of isobutene with methane gives isopentene and isoprene. The first of these reactions is an interesting alternative for styrene without using ethylene.

The oxidative methylation of acetonitrile gives a mixture of propionitrile, acrylonitrile and hydrogen cyanide. But since propionitrile is oxydehydrated to acrylonitrile and hydrogen cyanide is oxymethylated with methane to acrylonitrile, both these side products can be recycled. In this way a 90-93 per cent yield of acrylonitrile is possible. Combining the oxidative methylation with known reactions gives new ways to acrylonitrile only using methane, as shown in figure 7.

This methane chemistry seems to be of high scientific interest and promising from an economic viewpoint. Further scientific programmes are needed for the transfer of this idea to industrial applicability.

Syngas and methanol

One of the most interesting results of the last years was the development of processes to produce a series of chemicals from methanol respectively syngas.

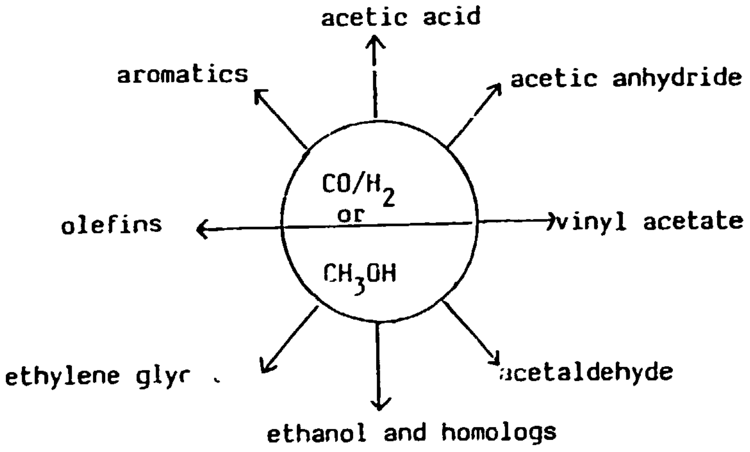
9/ J.D. Löffler e.a., J. Chem. Soc. Chem. Commun., 1984, 1177.

Two ways are open in the production of primary petrochemicals from syngas, the direct route and the indirect going through methanol as an intermediate.

Direct synthesis from syngas

The most important chemical besides ammonia, made from syngas is methanol. Recent big scale industrial projects were realized mainly for fuel purposes, but methanol is also an important primary petrochemical product. Many other chemicals: hydrocarbons, olefins, aromatics, oxygenated compounds can or could be manufactured from syngas and the same group of chemicals can be derived from methanol too. Figure 8 gives an idea of the main possibilities.

Figure 8. Chemicals from syngas or methanol



All the reactions, including the synthesis of methanol are catalytic processes. The decisive feature being always the catalyst, most of the research is directed towards the theoretical understanding of the mechanisms involved and the development of more efficient, more active and more selective catalysts. Both heterogenous and homogenous catalysts are widely used in direct synthesis.

Heterogenous catalysts for direct syngas conversions readily dissociate CO to surface-bound carbon and oxygen. Surface oxygen converts to H_2O or CO_2 and surface carbon is readily hydrogenated to methylene and methyl groups.

Methylene-group insertions give growing alkyl chains. In Fischer-Tropsch syntheses these chains produce alkanes or alkenes. In modified Fischer-Tropsch systems, CO insertion terminates as oxygenated products. To date, however, heterogenous catalysts give broad product mixtures with respect to both carbon number (methyls to higher alkyls) and oxidation state (from alkanes to aldehydes).(2) Such mixtures can have fuel value but are not well suited for chemical production. Heterogenous catalysts do not control CO insertion well enough to give an oxygenated product in high selectivity.

Homogeneous Group VIII metal-carbonyl catalysts for direct syngas conversions do not dissociate the CO bond. Methanol and/or C_2 dioxygenates are the initial reaction products. Although dioxygenates such as ethylene glycol are attractive targets, prospects for a commercially viable reaction remain poor. This results from reactions proceeding via two different modes of CO activation. Although both carbon units of ethylene glycol are equivalent, in fact, glycolaldehyde is the primary reaction product, and ethylene glycol results from its hydrogenation.

Methanol-based routes offer technical advantages for the overall conversion of syngas to two-carbon oxygenated chemicals. The carbon units in these target chemicals are typically non-equivalent; they differ in their oxidation state. Methanol and formaldehyde each provide a prereduced carbon centre (relative to CO) for reaction with carbon monoxide or syngas to yield the two-carbon product.

The growing spectrum of the newly developed sp [illegible] c zeolit catalyst offer new possibilities every day for different chem [illegible] syntheses.

Oxygenated compounds

Figure 9 and figure 10 show the routes leading from methanol and from synthesis gas respectively to the different oxygenated compounds. The routes to the different oxygenated chemicals usually involve either catalyzed carbonylation, reductive carbonylation, oxydative carbonylation or oxydative dehydrogenation by different transition metal complexes or basic catalysts.

Figure 9. Scope of chemistry for chemicals from synthesis gas via methanol-based routes

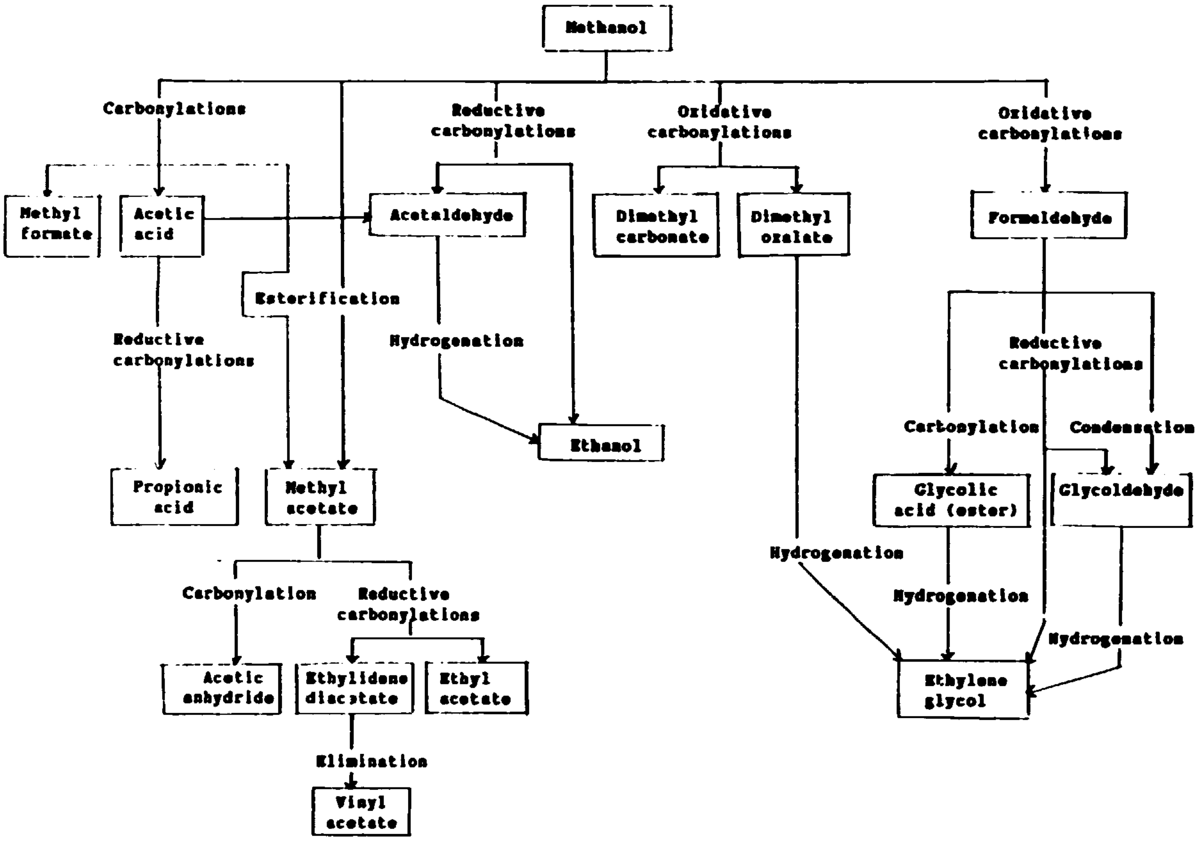
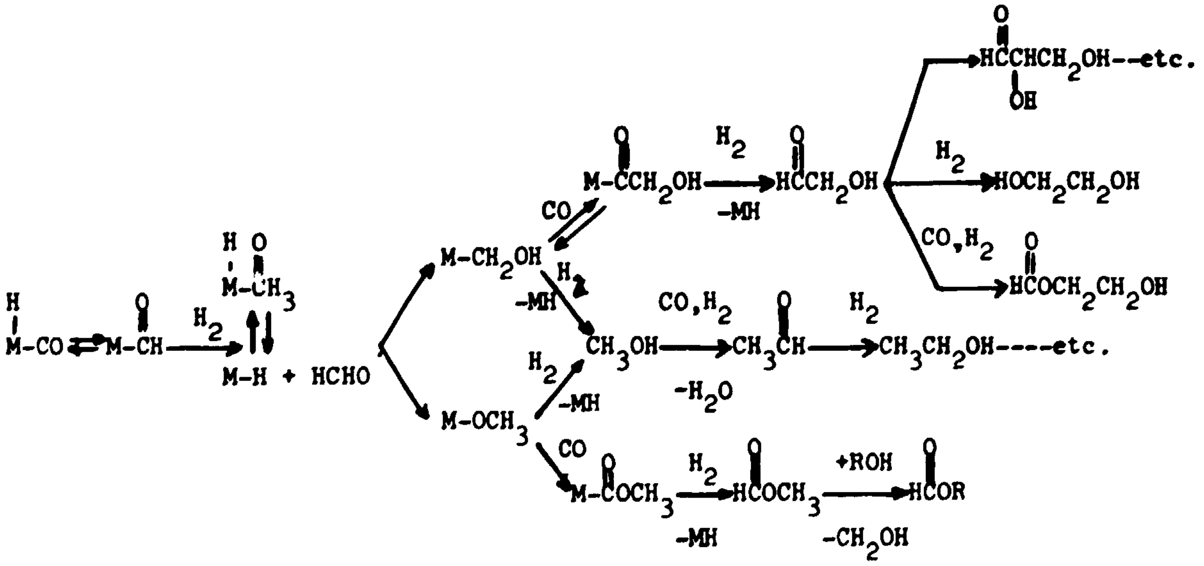


Figure 10. Reaction pathways for the direct conversion of synthesis gas to oxygenated chemicals. M represents a Group VIII metal carbonyl centre



Methanol. The most important is methanol. Until the 1970s the activity of the known catalyst made it necessary to use 340 bar pressure. With the new better catalysts working at much lower pressures even at 50 bar became possible. In industrial practice the pressure used is around 100 bar for economic reasons (better yield at lower energy costs).[10/]

The giant units realized in the last years, mainly for fuel purposes embody the latest results of research and development. Further improvements in catalyst activity, energy conservation etc. should emerge as results of the ongoing research, but the discovery of new processes or radical changes is unlikely.

A new process, called the Octamix-process could be interesting for the synthese of methanol as gasoline substitute or additive. Only 53.5 per cent of the product is methanol, the rest is higher alcohols. This mixture is an advantage when using methanol as gasoline additive. Pure methanol is sensitive to water and therefore usually a higher alcohol (mostly tert. butanol) is added. This process gives a convenient mixture directly.

Ethanol. Two ways are possible to ethanol: direct from syngas or with an intermediate stage. In the direct synthesis the compounds react in the gaseous phase at 250-300°C and 100 bar; but the selectivities for ethanol (70-80 per cent) are lower than with the two step synthesis via methanol. Sideproducts are methanol and propanol. The indirect preparation of ethanol from syngas is a homologization of methanol.[11/] From carbon monoxide/hydrogen even the synthesis of higher alcohols, up to C_6, is possible. The amount of C_{2+}-alcohols in the reaction mixture can be varied by the catalyst composition and reacion conditions between 20 to 50 per cent in an adiabatic multilayer quench reactor.[12/]

[10/] W. Seyfert, G. Luft, Chem. Ing. Tech. 57 (5), 482 (1985).

[11/] H. Bahrmann, V. Cornils, Chem. Ztg. 104 (2), 39 (1980).

[12/] P. Courty a.o. PD 9, 11. World Petroleum Congress, London (1983).

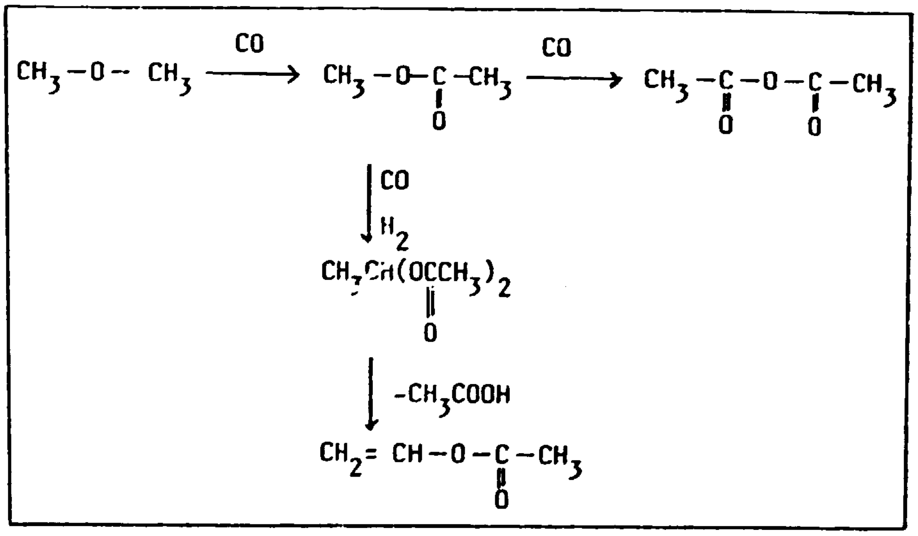
The process starts with high sulphur bituminous coal and makes methanol through syngas. This methanol is esterified with the acetic acid recycled.

Acetic acid. The reaction of methanol to acetic acid is already possible in a high and a low pressure reaction. Now the homologization of acetic acid with synthesis gas to longer carboxylic acids is described. The used reaction conditions are: liquid phase, 220°C, 270 bar, with homogenous catalysts on the basis of ruthenium, rhodium, palladium or nickel with methyl iodide as promotor.

Acetic anhydride. The first commercial large-scale plant has been working since 1983 in the United States, and produces acetic anhydride as another product of syngas chemistry. The methylacetate reacts with carbon monoxide at 175°C and 25-50 bar on special catalyst systems, containing an aromatic N-heterocyclic compound.

Other compounds. Syngas and methyl acetate can also react to ethylene diacetate which may be thermally cleaved to vinyl acetate. Another feedstock is dimethyl ether, its reaction may be directed to acetic anhydride or ethylene diacetate.

Figure 11. Preparation of acetic anhydride and vinyl acetate from syngas and dimethylether



Methyl formate, a syngas based intermediate, is already today produced on a large scale by base catalyzed methanol carbonylation. A new alternative synthesis, based on methanol dehydrogenation, seems to be ready for commercialization, whereas other routes including direct carbon monoxide hydrogenation, formaldehyde disproportionation or methanol oxydehydrogenation are less advanced. Besides being used as a solvent or an insect control agent, methyl formate serves as a feedstock for e.g. formic acid, formamide, N, N-dimethylformamide, and N-formyl morpholine. Newer formic acid processes are based on direct hydrolysis of methyl formate, and appear to replace the traditional indirect formamide base route. Future use of methyl formate could include the production of pure carbon monoxide, methanol, dimethyl carbonate, diphosgene, ethylene glycol via methyl glycolate, acetic acid and methyl propionate. All these processes either avoid the use of high purity carbon monoxide or proceed under milder conditions than conventional routes. They could gain interest if syngas and methanol become available at a large scale as competitive feedstocks for the chemical industry.[13/]

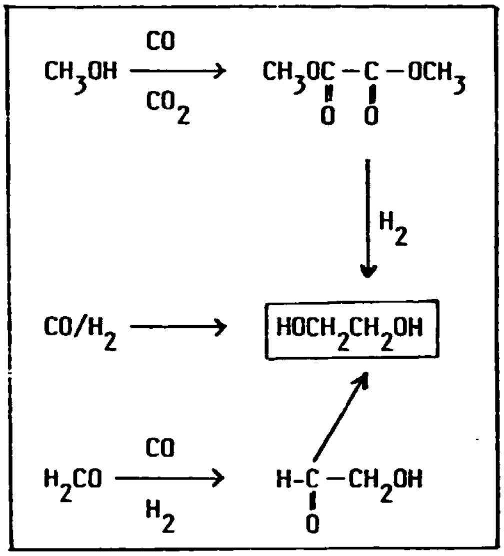
A new focal point of research is the direct way from syngas to acetaldehyde or ethanol. One possibility is the reaction of methanol and syngas to acetaldehyde in liquid phase. With some catalyst combinations acetaldehyde dimethylacetal is produced.

The direct synthesis of ethylene glycol from syngas is possible as well as the indirect way with methanol or formaldehyde. A glycol synthesis with a special ruthenium catalyst is reported, which needs 340 bar.[14/] In some cases acetic acid was used as solvent and here glycol diacetate was the end product. The optimal yield is 50-60 per cent glycol, with some methanol. Two ways are possbile for the synthesis of glycol via methanol (see also figure 12).

13/ M. Röper, Erdöl und Kohle, 37 (11), 506 (1984

14/ Erdöl und Kohle, 34. 97 (1981).

Figure 12. Glycol synthesis from syngas



The oxycarbonylation gives in the first step oxalic dimethylester, which is further hydrogenated to glycol.[15] The second way is an oxidative coupling of methanol to glycol by organic peroxides in the presence of formaldehyde but the yields are too low at this time for technical realization. The indirect way to glycol from syngas and formaldehyde gives the intermediate glycol aldehyde, which is also hydrogenated to glycol.

Olefins

For the selective production of C_2-C_4-olefins from methanol, zeolithes have been optimized as catalysts. The advantages of the narrow-pore zeolithes (e.g. eriomite, chabasite and offretite) lie in their high

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[15] A.M. Caffney a.o., J. of Catalysis 90, 261 (1984).

selectivities to olefine which is sometimes greater than 80 per cent, while zeolithes with middle-sized pore-openings, such as pentarils, have a lower selectivity but with a smaller tendency to coke-building.[16/]

A study of the reaction mechanism shows, that the olefins are a preliminary stage to aromatic compounds. The advantage of the zeolithic catalysts is their easy variability with different metals, which leads to different mechanism and products. So methanol conversion to hydrocarbons over an untreated ZSM-5 catalyst at 370° gives a mixture of compounds with 41 per cent aromatics and for example silanation of this catalyst diminishes the aromatics to only 19 per cent.

For the preparation of olefins from syngas also two ways are possible: in new variants of the Fischer-Tropsch synthesis it is possible by changing the catalysts to direct the reaction to C_2-C_4 olefins or to higher unbranched alkenes (C_6-C_{18}).[17/] One of the direct ways uses methanol as an intermediate which is dehydrated on zeolithes. The lower olefins are important basic products for industrial organic chemicals.[18/]

Hydrocarbons

The synthesis of hydrocarbons from synthesis gas (Fischer-Tropsch process) has been practiced for several decades to produce synthetic motor fuels on an industrial scale. For chemical purposes the process is less useful since the selectivity is low and a mixture of many different hydrocarbons is produced. The same applies to the coal hydrogenation (liquefaction) processes treating coal under high pressure and temperature with hydrogen in a series of catalytic reactors. Research work is directed mainly towards fuel production. Economic prospects are not encouraging,

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[16/] W. Dettmeier a.o., Erdöl und Kohle, 36 (8), 365 (1983).

[17/] G. Hochstadt, a.o., Erdöl und Kohle, Ergänzungsband 1980/81, p. 116.

[18/] W. Dettmeier a.o., Erdöl und Kohle, 36 (8), 365 (1983).

only a high price difference between coal and oil could make this route competitive. In the chemical intermediate field modified Fischer-Tropsch processes are investigated, as mentioned above.

Indirect routes to motor fuels by catalytical reactions of methanol on zeolites are more selective and the results are promising. This way, if economically viable, could more easily give chemical products than the direct route.

With bifunctional catalysts it is possible to combine synthesis and cleavage of methanol to produce hydrocarbons in one process, which allows the synthesis of aromatics direct from syngas. The products are mostly tri- and tetramethylbenzene.19/

2.2.2 C_4 hydrocarbons

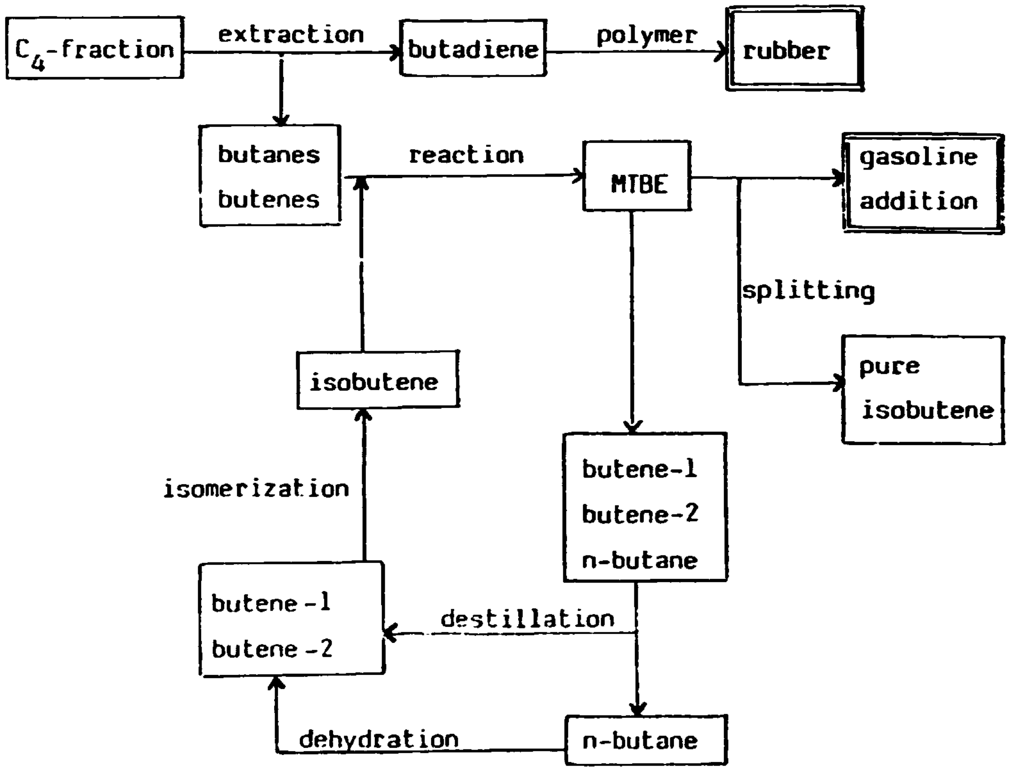
Isobutene is more and more used for the preparation of methyl tert. butyl ether (MTBE); this product is used in countries which use leadfree gasoline to rise the octane number. As the amount of isobutene in the C_4-fraction of the steam cracker is limited, the market prospects of isobutene and MTBE are favourable. In the MTBE process the whole remaining C_4 fraction is used after separation of butadiene by solvent extraction. From this mixture only the isobutene reacts with methanol on the catalyst. Acidic ion exchangers, perfluorinated sulphonic polymers or adducts of methanol to heteropolyacids are used as catalysts in the different processes. Figure 13 shows an integrated MTBE process combined with the separation of C_4-olefins.

A new process permits also the use of n-butane to produce MTBE and consists of three steps: the isomerization of n-butane to isobutane, secondly the dehydration of the isobutane to isobutene and last the reaction of isobutene with methanol to MTBE. This possibility enlarges the amount of MTBE

19/ US patent 4,180.560 (1977).

which can be made from a given quantity of C_4-fraction.[20/] It should also be noted, that the conversion of butanes to butenes is very important in the future, for the butanes are surplus products. As shown in figure 13 the formation of MTBE can also be used as a first step to separate pure products like the different butanes and butenes.

Figure 13. Separation of C_4-fraction and use of the different compounds



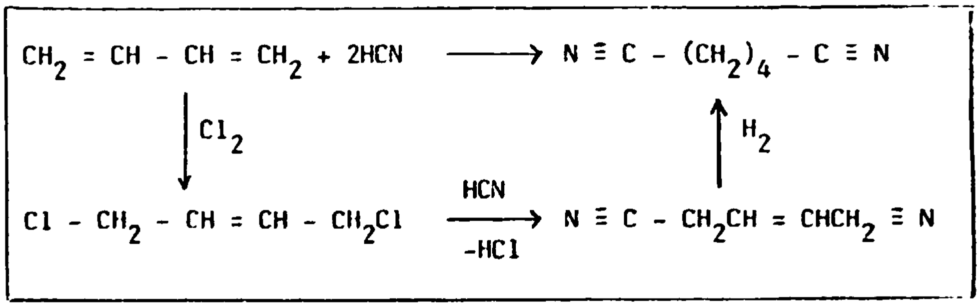
20/ G.R. Muddaris, M.J. Pettmann, Hydrocarbon Proz. 59 (10), 91 (1980).

The increased demand for isobutene for MTBE production led to new research work for the isomerization of n-butenes. In industrial laboratories a series of new catalyst systems are developed for this reason. The possibility of the reaction on fluroinated aluminium oxide or alumino silicates is reported, also the preparation of isobutene from n-butane by consecutive dehydration to n-butenes and subsequent isomerization.[21]

New scientific studies report the conversion of alkanes to aromatics. Two ways are known: the dehydrocyclization of alkanes with at least six carbon atoms, and the dehydrocyclooligomerization of shorter alkanes. For these reactions mostly noble metal and Pt/H-ZSM-5 catalysts are used.[22]

Butadiene as feedstock for chemical synthesis gives also new possibilities in the petrochemistry. In the United States one company has already changed the whole production of adiponitrile to a butadiene basis. Adiponitrile is a very important intermediate for the production of polyamides. In this process butadiene is hydrocyanized in the liquid phase in the presence of a catalyst, which contains phosphines or phosphites of Ni, Zn or Al-salts. This technology now substitutes the older hydrocyanation, with dichlorobutene as an intermediate (see figure 14).

Figure 14. Reaction of butadiene with hydrocyanic acid to adipodinitrile



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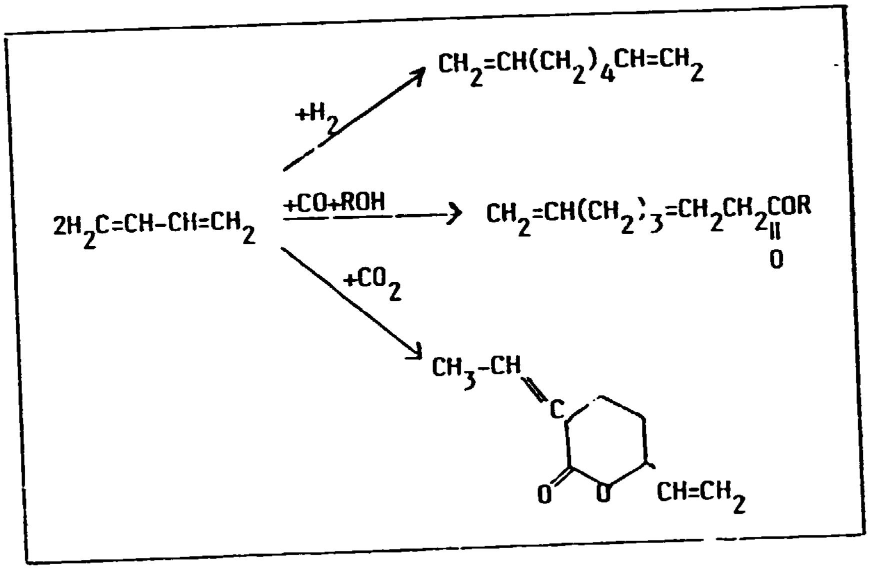
[21] Europ. patent 42 252 (1980).

[22] T. Inui, F. Okasumi, J. of Catalysis 90, 366 (1984).

With the new process 45 per cent energy saving can be achieved.[23/] Other dimerizations of butadiene give interesting bi- and polyfunctional C_8-molecules, as shown in figure 15.

Figure 15. Dimerization reactions of butadiene



From the available C_4- and C_5-alkanes, the n-butane is gradually replacing the more expensive benzene used before for the production of maleic anhydride. The new process uses gas phase oxidation of n-butane in a fluid bed.

C4- and C_5-isoalkanes serve increasingly for the production of isobutene and isopropene. The increased requirement of isobutene for the MTBE production was a motive to look for new processes for the selective

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23/ Chem. Eng. 87 (3), 49 (1980).

dehydration of isobutane. In a new process isobutane is dehydrated in the presence of steam on a fixed bed catalyst. Fifty per cent of the isobutane reacts per pass, the non reacted isobutane is recycled and so yields of 95 per cent can be achieved.[24]

2.2.3 Aromatics

Among the many important research projects several aim at finding new ways to produce aromatics. One of the possibilities is the catalytic reaction of ethylene (and ethane) to BTX-aromatics. With the following reaction conditions: noble metal catalysts on Al_2O_3-carriers and 450-500°C, 60-90 per cent of the liquid reaction products are BTX-aromatics and 10-30 per cent C_9-hydrocarbons. But the yield is only 10-22 per cent, therefore a commercial application is not considered at this moment.

The catalytic reaction of isobutene to p-xylene is an interesting variant of the dehydrocyclodimerization, but the yields and selectivities are not good enough for technical use.

Toluene

Toluene is a surplus product among the BTX aromatics. This was the reason to intensify research work in the direction of using toluene for primary chemicals to replace the benzene and the xylenes.

Good results are achieved with the selective alkylation of toluene. The gas phase reaction of this compound with methanol on a zeolithic catalyst at 400°C gave 50 per cent reaction products, with 70-80 per cent p-xylene.[25] Even better selectivities of $>$ 90-99 per cent for p-xylene were realized using crystallized SiO_2 with Ca-carbonate. In this case hydrogen has to be used to minimize coking on the catalyst.[26]

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[24] Chem. Eng. News 60 (4), 30 (1982).

[25] Europ. Patents 37.630 and 38.116 (1980).

[26] Chem. Systems: Process Evaluation and Research Planning, 3rd Quarterly report, p. 272-278 (1982).

It is also possible to alkylate toluene at the methyl group. Here with cesium oxide as a catalyst and 450°C ethylbenzene and styrene are obtained with 33 per cent and 11 per cent selectivity. If the yields could be increased, this reaction could be an alternative route to synthesize styrene without ethylene.

The reaction of toluene with ethylene on a zeolithic catalyst gives ethyltoluene with 90-99 per cent p-substitution. Its catalytic dehydration gives p-methylstyrene, which may be polymerized to poly-p-methylstyrene in the usual manner. This polymer has some advantages against polystyrene, e.g. better heat stability, the possibility of radiation crosslinking and higher sensitivity for flame stability additives. Styrene might be partly replaced by this monomer.

Toluene is already in competition to benzene in the preparation of phenol. Toluene is oxidized to benzoic acid, which is decarboxylized to phenol in a second step. The disadvantage of this method is that one carbon atom is lost in the form of CO_2 (figure 16).

In a new variant of this reaction toluene is oxidized in such a way, that phenol is built from the aromatic ring and the methyl group gives formaldehyde. The reaction path is somewhat difficult; in a first step toluene reacts with oxygen in the presence of Caro's acid and acetic anhydride to a mixture of acetoxy benzene and methylenediacetate. This mixture is pyrolyzed in a second step and acetoxybenzene gives now phenol and ketene; formaldhyde and acetic anhydride are formed from methylenediacetate. At the end the ketene reacts with acetic acid to the anhydride, which is recycled into the process.[27]

Progress is reported in the extractive distillation of the BTX fraction using pentenenitrile, e.g. for the separation of cyclohexane-benzene mixtures. The isolation of aromatics by molecular sieves is gaining ground: the separation of aromatics from mixtures with aliphatic compounds is possible with ZSM-5 zeolithes. The isolation of m-xylene from a mixture of

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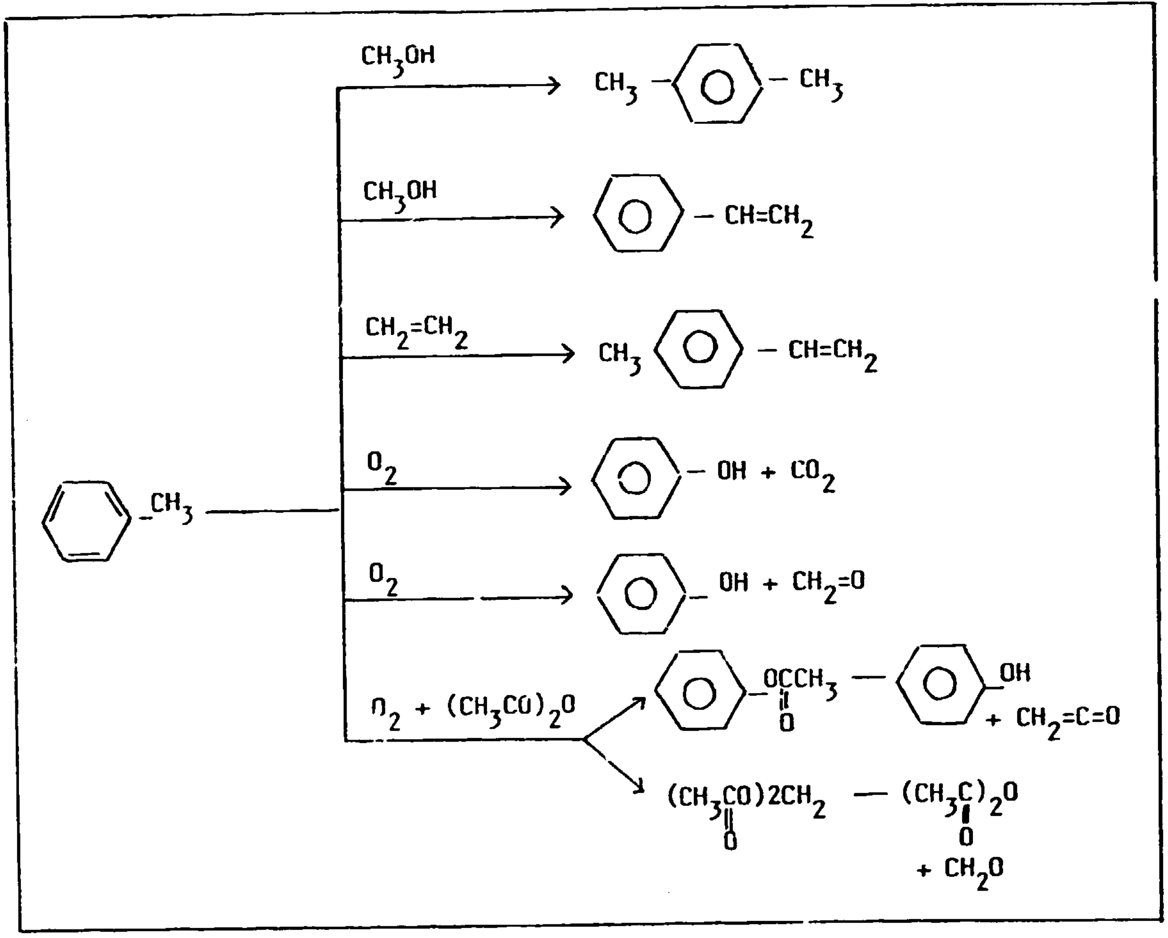
[27] US patent 4,156.783 (1979).

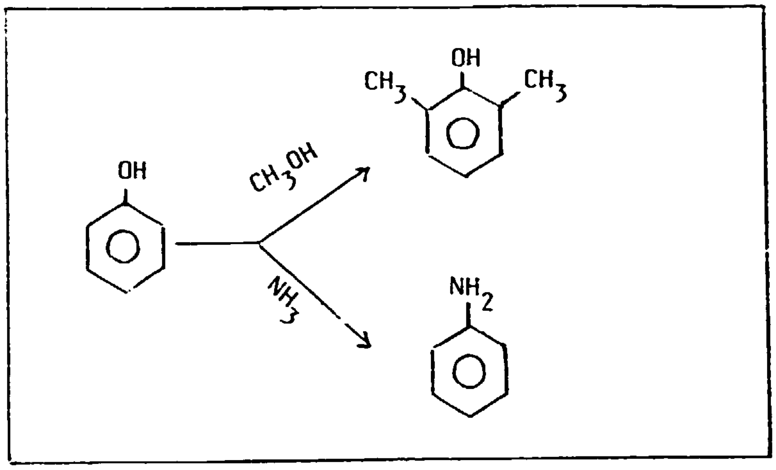
C_8-aromatics, o-, m-, p-xylene and ethylbenzene is successful with Na-Y-zeolithes with a yield of more than 98 per cent and 99.5 per cent purity. The process runs at 150°C and 7 bar. Zeolithic catalysts are also used to isomerize C_8-aromatics to p-xylene.

Figure 16. New reactions of toluene



Another point of research is the better use of phenol in chemical synthesis. The reaction of phenol with methanol on special catalysts (Fe-In-Cr-oxides on Si-oxide) yields, with high selectivity, 2,6-xylenol, an important additive for polymers. If it was possible to commercialize a new process, a new outlet for phenol would open. In this process phenol reacts with an excess of ammonia on a Lewis acid catalyst to aniline with a small quantity of diphenylamine as by product. No nitrobenzene production is needed and thus the use of the corrosive nitration acid is avoided (figure 17).

Figure 17. New uses of phenol



2.2.4 End products

Although intensive research activity is oriented towards the fields discussed above, the main effort is directed towards the end products. New products with better characteristics open new markets, improved old commodities find new applications, raising the demand for plastics, elastomers and fibres and with it for the whole petrochemistry. Therefore, R and D work is concentrated mainly on the product development with nearly equal emphasis on new products and product improvement. Plastics are in the forefront of this research activity with somewhat less accent on elastomers and fibres.

Plastics

In the commodity plastics field new improved products enter the market every day. Especially the copolymerization and polymer blending, like the polyamides combined with polyethylene or elastomers, have produced good results. The main activity and the most important achievements are and will be concentrated in the specialties, mainly the engineering plastics, electronic chemicals (polymers) and composite materials.

Engineering plastics have been introduced in the construction, aviation and space industry but have gradually become available for the more common machinery industry too.

High strength and elasticity, heat resistance and stability are the most researched characteristics.

Polycarbonates are one of the most important families used in different blends. Research activity is signalled in polycarbonate-ABS, polycarbonate-PBT (polybutylene-terephtalate) and polyester carbonate (co-condensate of aromatic polyesters and polycarbonate) and many similar fields. Products exhibit exceptionally good dimensional temperature stability, heat resistance and modulus. From car bumpers to very sophisticated parts for delicate machinery, different kind of uses are waiting for these new products.

Another group is formed by the different polyethers. Polyetherimides have not only the good properties cited above but are at the same time transparent. Many application in the lighting, aircraft and construction industry are expected if ongoing research produces results beyond those already in commercialization. Polyethersulphones and polysulphures are high temperature resistants and are researched mainly for delicate applications, e.g. miniaturization.

A new elastomer modified polyester with high impact strength, good low temperature stability and high load capacity at high temperatures allows on-line baking varnishes of large flatspread parts of car bodies, e.g. shock absorber elements.

New commercialized polyacetal-elastomer blends increasingly gain new fields of application. Another new product is a polyphenyleneoxide-polyamide blend. This polymer has better stability against fuels and lubricants than the known modified polyphenylene oxides and could be used in the car industry.

In the heat resistant field isocyanurate resins withstand temperatures up to 260°C, but other types of plastics, like the copolymer of tetramethyl-bisphenol A and of therephtalic acid gives a solder resistant flexible film well suited for printed circuits. Polypenylene sulphides form another heat resistant polymer group.

A range of polyethersulphone and polyether etherketone products have a promising future. Being heat resistants, they can be processed in standard equipment into films, pipes or sheets or be injection moulded. Wheel bearings, piston rings and skirts for engines as well as video tapes could be manufactured using such materials.

A new polysulphon-ABS blend with a heat stability of more than 150°C is recommended for moulded articles. This engineering plastic has a growth rate of 30 per cent and is used in the electro and electronics industry, but also for heat resistant elements in the car industry.[28/]

Polyphosphonates are not inflammable - a characteristic particularly well suited to hazardeous applications.

Polyurethanes are also intensively investigated both as materials as well as coating, where in many cases they can provide stress cracking protection to the underlying polymers.

In the field of polyurethanes monomeric methylene diisocyanate will become more important than toluene diisocyanate. For light-resisting polyurethanes new diisocyanates, like 1,3-bis (isocyanatomethyl) cyclohexane and tetramethylxylilene diisocyanate were developed. For better fire resistance of expanded plastics copolyoles and crafted polyoles were used. Special polyurethanes have technical and economical advantages as sealing material for insulating glass against polysulphides, silicones and polyisobutene.

[28/] Chemical Daily, 23 May 1984.

Electrically conductive polymers are much researched. The polyacetylene films developed thus far show high conductivity but this is not stable enough in air over time. Polypyrrole is better but still not the final answer for the development e.g. of an all-polymer battery.

Liquid crystal polymers have strength values normally only achieved by reinforcing plastics with glass fibre. These properties are due to stiff, rod like polymer segments which, even in the molten state, tend to form crystallites. These crystalline domains then retain their high degree of orientation after solidification. Elasticity moduls of over 8,000 N/mm^2 can be achieved.

Polypropylene reinforced with glass fibres or other fillers has higher impact strength, stiffness and heat stability than unfilled polyamide-6,6. The basis of the development is a special polypropylene quality and gives compounds moderate in price. Earlier, maleic anhydride or acrylic acid was needed for the modification of PP in order to make it suitable for the composite structure.

Combined with high performance graphite fibre, composites can be developed which can be 30 per cent ligher than aluminium, have high impact strength, fatigue resistance, combined with excellent water and solvent resistance and a very high temperature performance, making them particularly well suited to the aerospace industries.

Interpenetrating Polymer Network (IPN) blends are combinations of uncompatible polymers, in which each polymer forms a separate and continuous phase. The basis for first trading products are hydrated SBS-three block polymers. The physical two phase network is penetrated with a polymer melt and gives an IPN network which is stable at cooling. Such IPN blends are known with nylon-11, polypopylene and polyethersulphone. Magnetic data discs for laser scanning information systems may become a large market for some of these polymers. These have to possess high transparency, low birefringency, optical homogeneity, low hygroscopicity and good thermal form stability. At this time polymethylmethacrylate is used for video discs and polycarbonates for audio discs. Both polymers are in development for magnetic data discs.

Electronic chemicals

A very specific low volume but high value product group consists of the polymers entering the electronic microcomponent field, mainly in the printed circuit and semiconductor chip manufacturing. Photoresists are the photosensitive materials which polymerise in ultra violet light giving a protective layer on the surface of the silicon wafers. Postive photoresists become more soluble in the developing solvent when exposed to light, while negative ones become less soluble. The positive resists are mostly based on the photodecomposition of substituted naphtalene quinone diazides while cross-linking of cyclized polyisoprene is used in most cases for negative photoresists.

The recent trends towards submicron conductor line thicknesses resort to the use of X-rays or electron beams. For this purpose new photoresists are under development, mainly from the copolymer field (containing e.g. glycidyl methanxoylate or allyle methacrylate in the negative resists and sulphur dioxide with alkenes and alpha substituted acrylate esters in the positive photoresists).

Elastomers

New developments in this field are oriented towards new tyre materials like the extruded or moulded polyurethanes and towards special rubbers. Hydrated nitrile rubbers among the synthetics and a special rubber, derived from the natural product which resists high temperatures, oxygen, ozone, peroxide containing fuels, oils with additives and hydrogen sulphide, could be produced by selective hydration of the olefin double bonds in natural rubber. This material can be used for sealing materials subjected to high strain, in crude oil production and in automobiles.

Synthetic fibres

Research is aiming to improve the polymerization processes, using higher active catalysts and to develop new technologies in fibre polymerization. For all steps in the production of polyamide-6 new processes are available giving higher polymerization output, postcondensation of granular material, continuous wash and drying processes and waste reconversion processes. It is now possible to realize a one step spinning-extending process, especially for tyre cord and technical yarns. It is also now possible to regulate the caprolactame polymerization process in such a way, that the monomer and oligomer content in the end product is so low, that an extraction before the spinning process is not necessary anymore.

A new solvent for cellulose, the N-methylmorpholine oxide shortens the production time for cellulosic fibres, lowers the energy costs and improves the quality.[29/]

Possibilities of fibre recycling are more and more interesting, for example the processing of cellulosic waste to fillers by fermentes; the use of fibre waste of polyamide, polyester or polypropylene to prepare needle fleece, and the production of dimethylterephthalate from polyester waste.

A new special material for technical yarns is polyamide-4,6. Its preparation from 1,4-diaminobutane and adipic acid gives a product with a melting point of 300°C, high strength and dimension stability. A new polyamide fibre with higher water absorptivity is also in development, which consists of 80 per cent polyamide-6 and 20 per cent polyadipat-4,7-dioxydecamethylene diamine.

Polyacrylic fibres, which contain cupric sulphide, have such a good electric conductivity, that the addition of less than 1 per cent to other man-made fibres is enough to avoid static electrical charge. The mixtures are used for floor covering, draping textiles, working and protective clothes.

Another development is the preparation of polyethylene fibres with high molecular weight ($M_n = 1,5 \times 10^6$), which are spun from decaline by a gel spinning process and are then extended to a high degree. They are used as reinforcing fibres.

[29/] Chem. Week, 25 April 1984.

The importance of polypropylene fibres is increasing. Their main fields are technical textiles and textile floor covering.

These comments about fibres are concluded with some notes on carbon fibres and high temperature fibres: in 1982 in Western Europe 300 t of carbon fibres were consumed and the yearly growth rate is 20-30 per cent. The production of carbon fibres from pitch is cheaper than from polyacrylic fibres. C-fibres which have a 5-10 times better absorptivity than activated charcoal are now prepared from polyacrylic or cellulosic fibres. For this the cellulosic or polyacrylic fibres are carbonized and treated with steam. In this way micro pores are developed within the fibres.

A new aramide fibre on the basis of poly(m-phenylene)-isophthalamide with very low heat shrinking is entering the market. It is used as electric isolation material, filter tissues and protective clothes. Ceramic fibres are used for the reinforcement of aluminium, lead, ceramic and organic resins.

3. OPERATIONS

The processes used in the petrochemical industry consist of several consecutive operations. These can be classified in three categories: preparation of the input materials, chemical reactions and treatment of the reaction products. The first and the third are usually physical or chemical separation operations, while the actual chemical transformation leads from the feedstock to the wanted product and takes place in different types of reactors. These operations are of a more general character and are used in many distinct processes and therefore outstanding research and development work is deployed in all these fields. The development work going on in the two main operations of interest, the reaction and separation techniques, will be discussed.

3.1 Reactions and reactors

Although several types of reactors are widely used and reactor construction is an important field of research full of new successes and promises, the catalytic reactors, i.e. in reality the catalysts are nevertheless in the focus of the development.

3.1.1 Catalysts

Today's chemistry is based mainly on catalysts. About 60 per cent of the organic compounds manufactured derive from catalytical reactions.[30/] Most of the recent advances in process and/or product development resulted from better catalysts. Therefore very intensive research and development activity is directed towards better understanding of the basic problems of catalyst science: mechanism and structure of catalysts and catalytic reactions. Equally big efforts try to improve the actual catalytic reactions and catalysts, and develop new ones.

30/ Catalysts: The shape of things to come. (Wittcoff, H.A., Luftglass, B.K.)

Catalysts are mainly used for polymerization and polycondensation, oxidation, hydrogenation, dehydrogenation and dehydration reactions in the petrochemical industry.

In the polymerization field a very interesting phenomenon can be observed: the catalytically made polymers show a consistently higher growth rate than the non-catalytically made compounds. This can be attributed to the constant improvements in process economics and product qualities due to the better catalysts.

In the oxidation reactions, therephtalic acid, adipic acid and formaldehyde constitute the main usages for catalysts, before ethylene oxyde and acrylonitrile. In all these reactions new and improved catalysts can be expected with higher activity and selectivity. The hardest problem in this field is always the selectivity and the newest results show that even this difficulty can be overcome with success.

Hydrogenation has produced interesting results, both in large tonnage manufacturing and fine chemicals. New ammonia, reforming and other catalysts reduced investment and operating costs as did the fatty acid hydrogenation. New achievements are expected mainly in catalyst.

Dehydrogenation and dehydration reactions are important, the most common being the production of styrene from ethylbenzene. Catalytic reforming is another example. Here many compounds appear in the product but the product composition is far from that corresponding to the demand. Platinum doped zeolite catalyst can achieve high selectivity giving mainly benzene and less or no toluene and xylene but the selectivity acts only in one sense. The formation of C_7 aromatics is prevented. On the other hand, some of the feed is degraded to ethane and propane which are low-value products. Development of catalysts with great selectivity in both senses could open new horizons.

The actual research and development work on catalysts are oriented mainly towards shape-selective catalysts (zeolites and enzymes), intermetallic compounds, homogeneous catalysts containing sophisticated selectivity-producing ligands, immobilized homogeneous catalysts and of course the old classic types are not neglected either.

So in all catalytical manufacturing processes serious improvement, in some of them revolutionary new results, can be expected in the next ten years.

The recent advances in recombinant DNA technology and cell fusion have led to glowing predictions of a new era in biotechnology. However, for biotechnology to take the giant step from the laboratory to full-scale commercial realization, a significant development effort is required in the area of process system design and, in particular, reaction system engineering.

The design and optimization of a reaction system for a biochemical process is the critical link in the successful exploitation of biotechnology.

An important step in the evolution of bioreactor design is the utilization of free or immobilized pure enzymes or non-growing whole cells as catalysts. Immobilization has eliminated the costly enzyme recovery process, product contamination and greatly increased the potential of enzymatic processes for industrial use. The simple batch reactor (fermenter) is being replaced with the fluid bed, fixed bed, membrane, hollow fibre, cell recycle, tubular, loop and other reaction systems for biochemical processing. The challenge awaiting the industry will be the translation of the existing knowledge in chemical catalytic reaction systems to biochemical reaction systems.

3.2 Separation techniques

It is less known in circles outside technical experts that in most petrochemical processes the actual reaction section represents a relatively small part of the investment and operation costs, in spite of its decisive role in the technical and economic success of the process. The operations (mostly separations) preceding and following the reactor need usually huge equipment and are usually relatively energy-inefficient. The modern research tendency is oriented in two directions. The first aims to reduce the need for separation techniques by improvements in the reaction. Better yields, less or no byproducts on the one hand and processes less demanding in the feedstock quality on the other hand are looked for. This is mainly the catalyst research task. The second investigates the possibilities of new separation techniques, with better thermodynamic efficiency and lower investment costs. The research work is actively pursued for all the separation operations: distillation, extraction, crystallization, filtration, reverse osmosis etc. but for the petrochemical industry the most important are the recent trends in the new directions: membrane separation and molecular sieves.

3.2.1 Membrane technologies

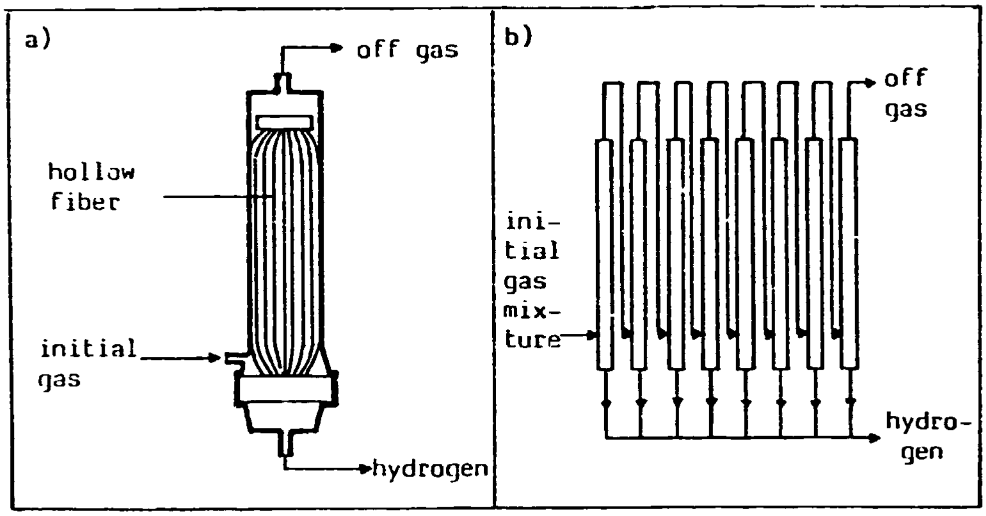
Modern membranes are themselves products of the petrochemical research and development work. The different polymers and copolymers developed are today widely used in many electrolytic processes but in the last decade they have conquered new fields in the gas and liquid separation techniques. Specially developed membranes have different diffusion resistence to different molecules permitting the separation of gas - gas, liquid - liquid or solvent - dissolved solid mixtures. In all these fields intensive research is going on, and as an illustrative example, a commercially proven process is presented below.

Hollow fibre gas separation

This process uses for hydrogen separation the principle of different permeation selectivities of different gases through polymer membranes, e.g. polysulphones. In the so-called Prisma Separator (Monsanto) (see figure 18) membranes are used as narrow tubular fibres.

The gas mixture enters the separation equipment under pressure from the bottom and streams up along the fibres. During this the hydrogen penetrates through the fibre walls and streams down within the fibres. Several such vessels are connected in parallel and in series. This technology is now used to regulate the CO/H_2 relationship for the oxosynthesis and also for the recovery of hydrogen from the blow-down gases of the ammonia synthesis and several other purposes.

Figure 18. New methods for the enrichment of hydrogen



a) prisma separator

b) arrangement of the separators

3.2.2 Molecular sieves

Used not only as catalysts and catalyst supports, these materials with high adsorption selectivity can be used for separation of gaseous or liquid mixtures. The most well known application of this principle commercially used for many petrochemical separation purposes is the Pressure Swing Adsorption (PSA) process. The gas mixture is led under pressure in vessels containing the appropriate molecular sieve. Only selected molecules are retained, the others pass through purified. The adsorbed gas is collected in a consecutive step from the sieve by pressure drop and the adsorbent regenerated by stripping or vacuum. This is a batch process needing a battery of adsorber vessels and an automated change-over system to become a continuous process.

Many other research and development fields and activities are promising too. It can be expected that the overall efficiency of the separations will steadily improve and in the selected domains as well as in others, new, more efficient processes will reach the commercialization scale.

4. TECHNICAL BACKGROUND

The realization of modern petrochemical processes would have been inconceivable without the sophisticated technical tools made available by the research and development activity in fields outside of the petrochemistry. Modern machinery (compressors, pumps, furnaces etc.), high quality heat and corrosion resistant alloys, waste heat recovery boilers etc. play an important role in petrochemical processes. The development work is running at full speed and in all these fields new achievements are expected. It would be impossible to cover this topic too in this study, but a few selected issues, which are most relevant to the industry will be briefly reviewed.

4.1 Process control

Petrochemistry means in most cases highly instrumented processes with the maximum possible of automatic control. Automation is not a response to manpower saving requirements: it is an inherent feature of the process itself. These very demanding process conditions (high temperatures and pressures) with highly inflammable materials in huge quantities would be simply inacceptably hazardous without automatic control, not to mention environmental considerations. Therefore the achievements in the instrumentation and control field were of outmost importance for petrochemical processes. Many new on line analytic instruments were developed in this industry and the first attempts of computer control were realized here. However, it was only the microprocessor and with it the distributed hierarchical process control which proved to be the real answer to the needs of the petrochemical processes and plants. This needs a high level of analytic on-line instrumentation, good understanding of the process characteristics and plant machinery and a very sophisticated automatic control system. There is no way to circumvent this, neither from the economic nor from the safety standpoint. The systems available are improved every day and new systems become accessible every year. It is therefore of outmost importance, especially for developing countries to follow closely the latest achievements and take particular care to create the operational and maintenance background in their plants which will be necessary for the smooth operation of the highly automated systems.

4.2 Prefabrication

The high costs and problems experienced in the on-site works all over the world but especially in the developing countries urged contractors to push the prefabrication to the maximum extent possible. Vessels installed and fitted with all piping and fittings in the shipyards and shipped accordingly became customary. Skidmounted units were developed and successfully built. Further assembling in the shops was made possible by the developments in the offshore oil drilling and producing. The shipyards manufactured huge and sophisticated barges and platforms equipped with all the complex machinery needed for drilling and/or production and well-head treatment. This prepared the way to the idea of the barge mounted petrochemical plant, prefabricated and completely assembled in one or a few units which can be towed to the site and either operated offshore or placed on the shore and put into operation without local mounting work.

This idea received very different responses. Enthusiasts praised its cost advantages: the higher expenses in the yard would be more than compensated by the savings on the site, the time saved in the project implementation, the safety of the start-up, etc. Sceptics feared that subsequent maintenance would be hindered by the inherently tight layout and pointed out that the local mounting operations were the best school for the operation and maintenance workers to be acquainted with the equipment and machinery not only from the outside, and this would be the best guarantee for smooth operation.

Developing countries would have to follow closely the results of the realized plants, evaluate the practical results and take decisions in the light of this information and based on knowledge of the newest developments in order to find the degree of prefabrication best suited for their conditions.

5. RESEARCH AND DEVELOPMENT STRATEGIES FOR THE DEVELOPING COUNTRIES

From the point of view of the petrochemical industry the developing countries can be classified in the following groups.[31/]

1. Countries with a big domestic market (over 100 million population) and adequate hydrocarbon resources.

2. Countries with a big domestic market and no adequate hydrocarbon resources.

3. Countries with medium-size domestic market (over 50 million population) and adequate hydrocarbon resources.

4. Countries with a medium-size domestic market and no hydrocarbon resources.

5. Countries with small or no domestic market and large hydrocarbon resources.

6. Countries with small domestic market and hydrocarbon resources smaller than necessary for a competitive petrochemical production.

For each of the above groups a different approach can be recommended for the research and development activity to be deployed. An attempt at these recommendations is given in this chapter.

5.1 Group 1

These countries have universities, scientific and educational institutions as well as a petrochemical industry. They are big enough to strive towards a more or less comprehensive research structure covering the area from the fundamental to applied research. Their approach, however, would

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[31/] The petrochemical industry in developing countries - prospects and strategies, UNIDO/IS.572, Sectoral Studies Series No. 20.

necessarily be gradual in extent and also in depth. The main emphasis would be put on the development of ways and means for the best utilization of the local raw materials, for the development of products satisfying the given markets. Beginning with process and product improvement, customer service, training and education, preparation of the new investment projects, gradual extension towards new processes and new products could be envisaged.

5.2 Group 2

Having nearly the same scientific, educational and institutional background, the lacking or inadequate domestic hydrocarbon resources are not an obstacle to the research and development activity in these countries. Here also in the long run a more or less comprehensive research structure can be envisaged but the main goal will be to apply and later develop processes for alternative feedstocks available in the country and find the most appropriate choice for the alternatives and processes. Therefore links to research organizations and activity in the related fields (e.g. agriculture, biology) are obvious, but similar co-operation would be desirable with the domestic oil and gas processing even when working with imported raw materials.

5.3 Group 3

Countries in this group normally cannot afford to realize a complete research structure for the whole petrochemistry. Having nevertheless important scientific and educational background and - now or in the future - a fairly well developed but not all-embracing petrochemical industry, they have to make a judicious selection of the sectors where the investment in research and development could be most efficient. This selection will be different for each country and would have to take into consideration the shape of the petrochemical industry they intend to develop, the feedstock situation, the market and the co-operation possibilities among the developing countries both in production and in research and development.

5.4 Group 4

In size, potentials and market similar to Group 3, countries in this group would have to face the same selection problems. The emphasis in this case however would be laid on the utilization of alternative feedstocks whenever possible, as with Group 2 and in co-operation with them.

5.5 Group 5

The relatively small local market means also less scientific and educational background. Even with big and well developed petrochemical plants countries in Group 5 will have to limit their research and development activities to the extent allowed by their human research potential. This would in many cases be big enough to build up a fairly well developed research organization directed towards specifically selected projects, probably mostly in the primary petrochemical production processes but in several cases a relatively (to the extent of the petrochemical industry) lower extent of research would be possible only.

5.6 Group 6

These countries without sufficiently big feedstock resources and market possibilities will have to limit their research and development activity to a few selected areas where they can achieve good results, in co-operation with the industry to be implemented. These selected areas would be in most cases in the application field and not in the primary products or basic research.

6. CONCLUSIONS

Speculations about the end of the petroleum reserves have led to intensive research about the use of other resources (coal, oil sands, shale oil, biomasses), but have also brought about an intensive search for crude oil and for enhanced oil recovery.

The discovery of new catalysts has shown, that it is possible via the production of syngas, to synthetize a series of products like gasoline, olefins, aromatics, but also that special intermediates, which are again feedstock to classical organic chemicals, may be produced with known processes. Naturally, the indirect route via syngas raises the costs of the products. At the present time crude oil is becoming cheaper and available in larger amounts which explains why the alternative routes are less attractive at the moment. For many developing countries they can, however, represent a viable alternative even now.

A schematic overview of the products derived from crude oil and coal respectively is given in the next two figures.

Figure 19. Process of coal chemistry

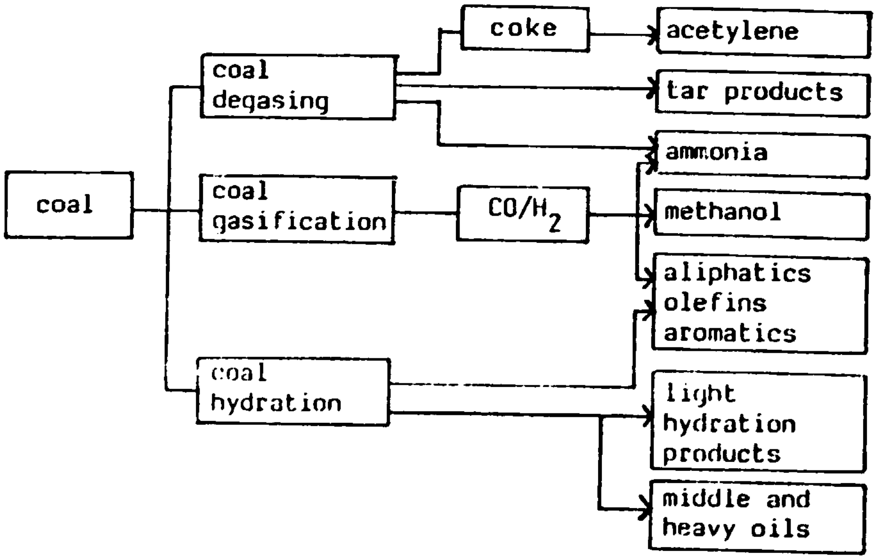
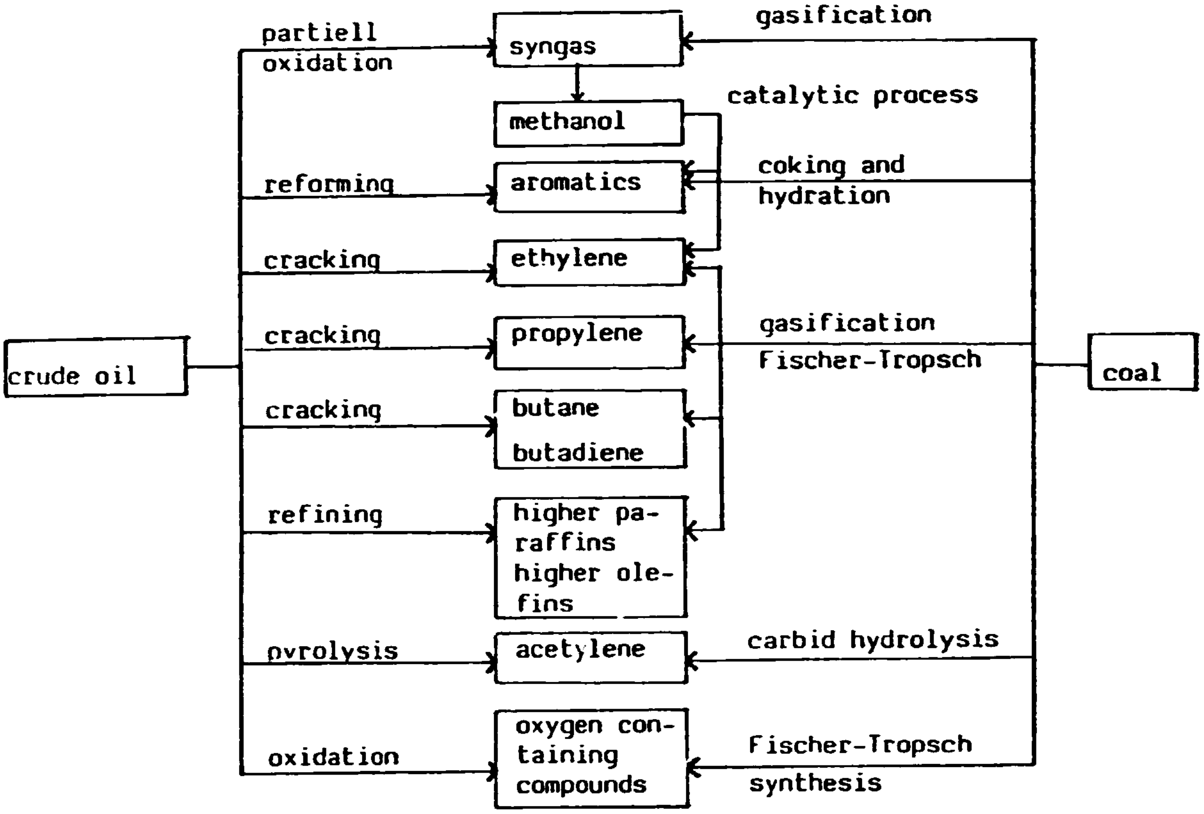


Figure 20. Production of chemical feedstock from crude oil or coal



Biomass can also produce primary petrochemicals and processes are intensively researched.

Although primary petrochemicals and intermediates are not neglected in the research efforts, the main activity is directed towards the end products first of all plastics, where the new speciality products and engineering plastics are the main issues.

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New trends in petrochemical research and development

(please check appropriate box)

	yes	no
(1) Were the data contained in the study useful?	☐	☐
(2) Was the analysis sound?	☐	☐
(3) Was the information provided new?	☐	☐
(4) Did you agree with the conclusion?	☐	☐
(5) Did you find the recommendations sound?	☐	☐
(6) Were the format and style easy to read?	☐	☐
(7) Do you wish to be put on our documents mailing list?	☐	☐
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