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2. Draft

PROJECTION OF R & D TRENDS IN THE PETROCHEMICAL INDUSTRY: POSSIBLE IMPACT ON PRODUCTION STRUCTURE IN DEVELOPING COUNTRIES BY THE YEAR 1990

H. Schindlbauer

1. INTRODUCTION

1.1. Background

The raw material for the petrochemical industry is crude oil and natural gas. But oil and gas supplies are finite and non-renewable. Therefore the part of the oil, which is used in the petrochemistry generally should be enlarged and the part for energy production should be diminished At this time this relation is about 11 : 89 %. The general importance of research and development activities in the petrochemical industry is to work out methods for a better use of the available oil and gas. But we also need new possibilities for enhanced oil recovery. Worldwide there is at this time only a recovery rate of approx. 35 % of the oil in the deposit. For longer periods research also has to concentrate to petrochemical uses of oil sands, coal and other organic material.

The needed financing funds for R & D in the petrochemistry are large. Often they cross over the possibilities of the companies, therefore in industrial countries the government gives subventions to individual research projects. In industrial countries the spendings for R & D are between 1 and 2,5 % of the cross national produkt, 25 - 50 % of the R & D costs financed by the government and 50 - 75 % by the economy.1)

At this time the feedstock and the processes have to be adapted to the changes of the costs and their availability. Often also the environmental protection requires

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1) OECD Secretary

changes in the raw materials or processes, esp. in industrial countries. Examples are the repeated diminishing of the allowed sulfur content in petroleum products, which needs different manufacturing processes; or the prohibition of using polychlorinated biphenyls as transformer oils, the use of gasolines without a lead content a. s. o. All this requires adaptable and flexible production facilities.

Some important categories of R & D activities are:

- better use of side products from the refineries (e. g. C_4^+ fraction)
- better use of high or non boiling fractions of crude oil
- introduction of new catalyst systems, which allow the use of new feedstocks for the production of petrochemicals
- more flexibility in feedstock for different processes, e. g. syngas may be produced from naphtha, methane, coal or biomass
- process automation etc.

A very illustrating example for changes in the feedstock for vinyl chloride since the beginning of its production is shown in the following lines:

In the first time vinyl chloride was produced by addition of hydrochloric acid to acetylene. Later on the production was changed to a two step process using ethylene because of the higher price of acetylene. But this preparation gives the byproduct hydrochloric acid and therefore a combined process using acetylene and ethylene was introduced, giving no excess of hydrochloric acid.

Further on an oxychlorination process was developed; this uses also ethylene, but the formed hydrochloric acid is oxidized within the process to chlorine, so giving lower production costs. Now a day it is tried to produce vinyl chloride by a multiple step process starting with ethane. It may be cheaper to use ethane instead of ethylene, even with one additional reaction step.

Process control and automatic operation using computers and microprocessors is a basic requirement for the flexibility of refineries and production plants and will be discussed later.

The situation of petrochemical R & D in DCs is as follows: In countries with large amounts of crude oil and universities with the needed equipment and scientific staff, there we will find already research work. It is very important to establish special research institutes for petrochemistry, if such an industry is planned in a country. For technological development pilot plants are needed to study different processes. This institutes in DCs not should try to discover new processes, but they should solve problems in existing equipments and further develope used processes. Research possibilities for the application of final products are very important for DCs, but only a few installations are known.

1.2. Problem

The questions to be discussed in this study are:

how can research and development

(i) improve the competitiveness of primary and intermediate petrochemical producers in DCs

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

(iii) contribute to the development of technologies more suited to conditions in DCs, e. g. 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.

2. METHODOLOGY

DCs have been classified by UNIDO as follows:

1. Countries with a big domestic market (over 100 mill. 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 mill. population) and adequate hydrocarbon resources.
4. Countries with a medium-size domestic market and no adequate 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.

ad 1.:
Countries with a big domestic market and adequate hydrocarbon resources are already on the way to reconstruct the development of countries with high technology. An example of such countries may be Nigeria. This country has 3 refineries and the development of its petrochemical industry is devided into three phases[2]. Phase I of the petrochemical project will be attached to two refineries. The aim is to use the byproducts of these refineries for the production of plastics, fibres, carbon black for tyres,

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[2] OPEC bulletin July/August 1985

detergents and solvents for paints. Based on the availability of the necessary feedstocks, benzene and solvents will be produced in the one refinery, carbon black, polypropylene and linear alkylbenzene in the other. Phase II consists of the building of an olefin complex, based on gas and other petroleum products, and will produce ethylene, low density polyethylene, monomer vinyl chloride, polyvinyl chloride, chlorine/soda and ethylene oxide/ethylene glycol. In phase III mainly aromatic petrochemicals such as benzene, toluene, xylenes, pure paraxylene and orthoxylene, phenol, polystyrene etc. will be produced. I mean, that the production of methyl tert. butylether (MTBE) would also be a possibility for future, to export this to industrial countries for gasoline addition.

ad 2.:
What can countries do with a big domestic market and no adequate hydrocarbon resources? This point is more difficult. An answer will be given within this group of countries looking at India. This large country has some oil, but its main energy source is coal. India needs large amounts of fertilizers, therefore a project is underway for the construction[3] of six large fertilizer factories, to be sited along a pipeline. Also hydrogen sulphide oxidation processing plants and LPG (liquified petroleum gas) plants will be placed along the route. Coal opens India the possibility to produce methanol via syngas. All petrochemicals producible from syngas as shown in the next chapter may be synthesized also in future in this country. But not only coal may be a raw material for syngas, also biomass may be used. Another possibility for such countries like India may be the alkylation of toluene with

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[3] OPEC bulletin September 1985

methanol to ethylbenzene/styrene for styrene production.

ad 3.:

Algeria may be an example for countries with medium-size domestic market and adequate hydrocarbon resources. The country with its oil and gas fields has five refineries, four liquefaction plants to produce LNG, LPG and condensate, but also four fertilizer plants for the production of ammoniac. ammonitrates and phosphate fertilizers. Petrochemical activities include plants for ethylene, low density polyethylene, PVC and methanol. In the course of its industrialization process, Algeria has installed a basic petrochemical industry, which is capable of valorizing the upstream extraction and refining of its hydrocarbon resources, as well as developing a downstream processing industry in order to fulfil its needs in the different sectors of the national economy. One plant includes a methanol unit, most of the product is intended for export. There are three resin units (phenolic, urea and melamine) in operation. The plastic products plant [4] produces petrochemical intermediates (ethylene, vinylchloride) and plastics (PVC and low density polyethylene). It includes an ethane cracking unit, producing ethylene, one vinyl monochloride production unit and its polymerisation equipment, units for the ethylene polymerisation to low density polyethylene, for chlorine production, and one soda producing unit by salt electrolysis. There are also plants for the production of all the needed sorts of fertilizers. Since 1980 also insecticides, fungicides and pesticides are produced in Algeria. The most important development projects, either under way or about to be started, are concentrated on programmes to increase capacities for the production of natural gas and to improve

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[4] OPEC bulletin July/August 1984

the recovery methods in the oil fields. Based on the methanol production the synthesis of all chemicals from syngas/methanol (the new methanol chemistry) would be possible, but also the production of MTBE and all the other C_3^+-chemistry from refinery gases.

ad 4.:

In countries with a medium-size domestic market and no adequate hydrocarbon resources there are less possibilities for new productions. If there is some natural gas in a country a C_1-chemistry would be possible (the way syngas - methanol - petrochemicals). For the same chemistry coal or biomass may also be the starting material. Another possibility is to develop an application technology. If it is possible to buy some intermediate petrochemicals from a neighbouring country the production of duromers (condensation products of formaldehyde with melamine, urea or phenol) would be possible, but also the preparation of pesticides, cleaning preparations (wap and detergent). Starting with syngas an important chemical is acetaldehyde, the procedure is already known and for some years in technical use.

ad 5.:

Examples for countries with small or no domestic market and large hydrocarbon resources may be Qatar, Kuwait and Saudi-Arabia. Qatar has built up a modern refinery. It is ultimately intendend to meet local demand and the completion of a petrochemical complex has enabled the country to enter the petrochemical sector by production of ethylene, low-density polyethylene, sulfur and fertilizers[5]. Kuwait as another example in this group of countries has decided

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[5] OPEC bulletin October 1984

that the greater part of its oil exports should take the form of refined products and manufactured materials[6]. Beside fertilizers, produced in several plants, a petrochemical complex produces aromatics and olefins. Now a polypropylene and a polystyrene plant are projected. This is the right way for such countries.

The petro-chemistry project in Saudi-Arabia: The Saudi Basic Industries Corporation, the Arabian Petroleum Investment Company and two European companies have signed a jointventure agreement for the construction of a large petrochemical plant to produce 500.000 t MTBE, 125.000 t butadiene and 80.000 t butene-1 p.a. Petromin will guarantee the raw material of the new plant in supplying 700.000 t butane. 170.000 t methanol needed for the MTBE production comes from the Saudi Basic Industries Corporation.

ad 6.:

Countries with small domestic market and hydrocarbon resources smaller than necessary for a competitive petrochemical production have only the following possibilites: to use energy from sun, wind and tides where possible and to use biomass for chemistry or energy.

Four ways for energy production in these countries are possible:[7]

a) Gasification

A small gasification unit has been developed, which could work with all sorts of organic matter, such as

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[6] OPEC bulletin May 1985

[7] Communication of Dr. G.A. Pogany to Unido

poor quality coal, wood, organic waste, etc. It uses air and produces tar-free, directly usable gas. It's special value is that it is small, works at a capacity of 20 kg/h and is still efficient to use. It could provide an instant source of energy for a small area.

b) Direct fermentation of Organic matter to methane

It is now possible to use fermentation of all kinds of organic wastes by micro-organism direct to methane. The process is working continuously on large scale and with high yield. The main advantage of this process is that it requires low capital cost to install. It needs no separation equipment for the recovery of the product. The methane gas is freely bubbling to the surface and can be collected, its purity is about 50 %.

c) 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.

d) Hydroprocessing

This is one of the most promising developments, because it increases the H/C ratio. The raw material may include wood wastes, corn coks, cotton gin wraste, pecan shell, peanut shell, rice bull und 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 modifications which are required for the burning of ethanol or seed oil.

For the production of chemical feedstock in countries without oil or gas there are also several possibilities:

a) Fermentation of cellulose to ethanol

Fermentation of sugar is well known, but microorganisms could also be developed to ferment cellulose to ethanol. If successful, this route would provide a much wider basis for the use of ethanol.

b) Production of synthesis gas

This is a well established process, but still subject to improvment.

c) Production of sugar from waste biomass

The hydrolysis of woodchippings using concentrated hydrochloric acid at moderate temperatures (20 - 50°C)

provides almost quantitative yields of glucose and related sugars. The alternative of less concentrated acids used at higher temperatures (200°C) is also effective. Engineering studies on various types of chemical reactors indicate that countercurrent reactors can produce high yields of sugars at economically viable costs. Further processing by conventional petrochemical technologies then yields a wide range of products.

d) Production of oxychemicals

Although only in the early stages of process research, biomass gasification routes to the production of acetate chemicals have many advantages for countries poor in fossil fuel resources. The process economics are already nearly competitive with oil derived routes. The process starts with hydrolysis of wood or crop residues to produce sugars and uses by-product combustion to generate carbon monoxide. From these two starting materials, a complex and interlinked series of reactions is used to produce vinyl acetate. Slight modifications of the scheme allow the production of ethyl acetate as an alternative.

e) Aromatic chemicals from lignin

Lignin is a byproduct, available in large quantities. Because of its high 0/C-ratio, it is less suitable for the production of liquid fuel than the cellulose component of biomass. Hydrocracking/hydrodealkylation process could be employed to recover phenols, benzene, and perhaps with improved isolation techniques, cresols and catechols. The process is not yet suitable for high purity products.

3. DISCUSSION

At the beginning of a detailed description of technical inventions and scientific discoveries in the field of petrochemistry we should discuss the question of availability of crude oil and natural gas in the years about 1990 and later on. The question is to be answered with yes. Therefore 1990 crude oil will be still the main source for energy and chemical products. We are ready to process oil sands and coal; corresponding research programs and pilot installations are running; their large scale production is not applied because of the price in reference to crude oil. The production of organic chemicals from this raw materials however should further be studied and developed.

3.1. Technical inventions:

In this chapter we deal with chemical or process-control developments which can replace or dramatically improve technologies currently in use for the manufacture of primary or intermediate petrochemicals and petrochemical products.

Process control and automatic operation:

The revolution of our work by the development of computers and microprocessors began in the field of analytical chemistry and these equipments are used now in oil refineries and for process control in petrochemical plants. Crude oil data bases are becoming more and more important as a planning tool and to make a refinery flexible for the processing of different crude oils.

Such a data base consists of

(1) a laboratory data base (including the experimental data)

(2) an estimated value data base and

(3) a revaluation program, which modifies partially the data found in laboratory product yields and properties, considering the differences found in comparison with refinery practice. This part also holds information on how to change yields and properties of cuts.

Computerized and automated on-line analysis equipment are the preconditions for process-control in production equipment. Computer controlled operations are described for

- crude destillation units
- application in existing refineries and for planing new refineries
- fuel gas processing
- reformer units
- olefin plants
- catalytic cracking units
- destillation of tar a. s. o.8)

Computers are especially used for planning and control of combined processes in refineries, e. g. electrodesalting-atmospheric and vacuum destillation-catalytic reforming or crude destillation-blending-reforming-hydrocracking-FCC.

We should not forget, that in the industrial countries more and more refineries are closed and new refineries are built up in developing countries with oil fields.

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8) H. Schindlbauer, "Application of Modern Analytical Techniques" RP 12, 11.World Petroleum Congress, London 1983

(i) New routes to primary chemicals

One of the most interesting things of the last years was the development of processes to produce a series of chemicals from methanol resp. syngas. Two ways are known to produce gasoline from syngas:

a) Fischer-Tropsch synthesis
b) reaction of methanol on zeolithes

The first process is the older one and is in use at this time only in South Africa. Raw material for this process is the coal of this country. The process is studied again in many industrial countries, but its disadvantage is the necessary of large factories to work off all side products. Therefore, we think, that the new catalyst systems of zeolithes will be the only used in future to produce a lot of chemicals. Fig. 1 shows the reactions, which were studied now for better yields and/or better reaction conditiones.

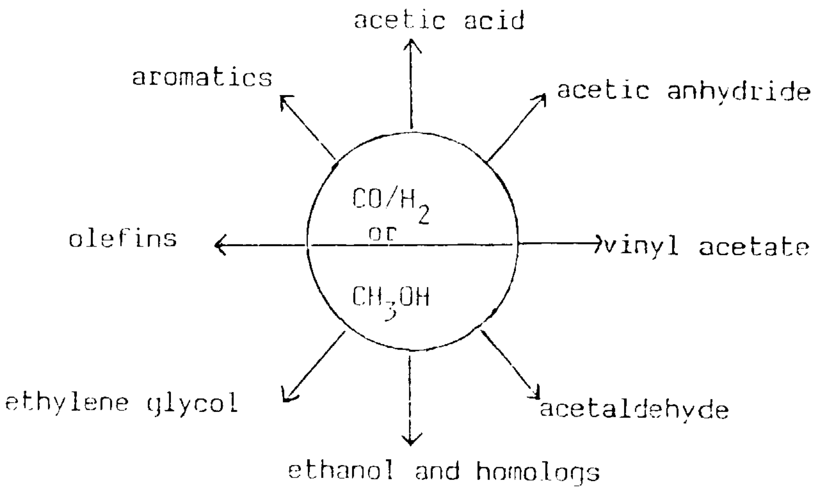

Fig. 1: Primary chemicals from syngas or methanol

It has to be mentioned here, that methanol can be synthesized from torch gas, and this will be a way for some countries to use this side product. Some scientists regard methanol as a transport vehicle for synthesis gas.

In connection with the use of methanol as gasoline substitute or additive, there is a new process, called the Octamix-process. Here only 53,5 % methanol are prepared, the rest are higher alcohols. This is an advantage in using methanol as gasoline additive, for pure methanol is sensitive to water and now the addition of another alcohol (mostly tert. butanol) is needed; but this alcohol is only limited available.

The reactions using methanol to produce organic chemicals are very promising for two reasons:

(i) different raw materials can be used for the production of syngas/methanol (see Fig. 2), which is very important for all countries without crude oil.

(ii)even if the individual processes are not technical matured and economical, this situation will change in some years.

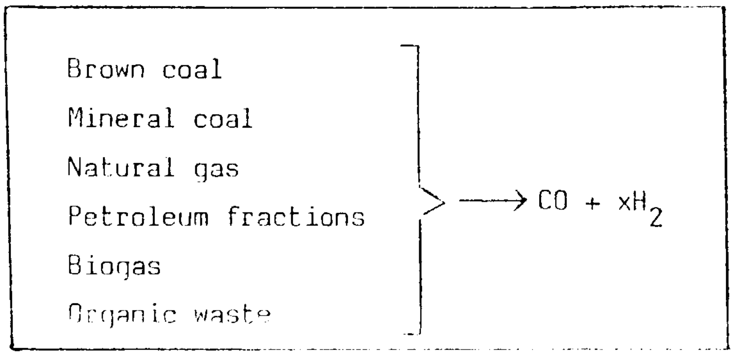

Fig. 2: Raw materials for syngas production

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}) 9). One of the direct ways uses methanol as an intermediate which is dehydratizated on zeolithes, as already described in many papers. The lower olefins are important basic products for industrial organic chemicals 10).

As already shown, syngas is on the top of primary chemicals. The used processes are known for a long period, but today scientific work is done to produce syngas cheaper. In more effective use of residual oils for syngas production, one way is to substitute the partial oxidation of residual oils by the energetic 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 vakuum residues. In a primary reformer the raw material reacts with superheated steam (higher than 800°C) to a gas mixture, which still contains higher hydrocarbons. In a secondary reformer this hydrocarbons are completly gassed with steam.

In a second development the production of light hydrocarbons by thermal cracking of residual oils is combined with synthesis gas production. This can be done by modernizing the flexicoking processes. The procedure is shown in Fig. 3.

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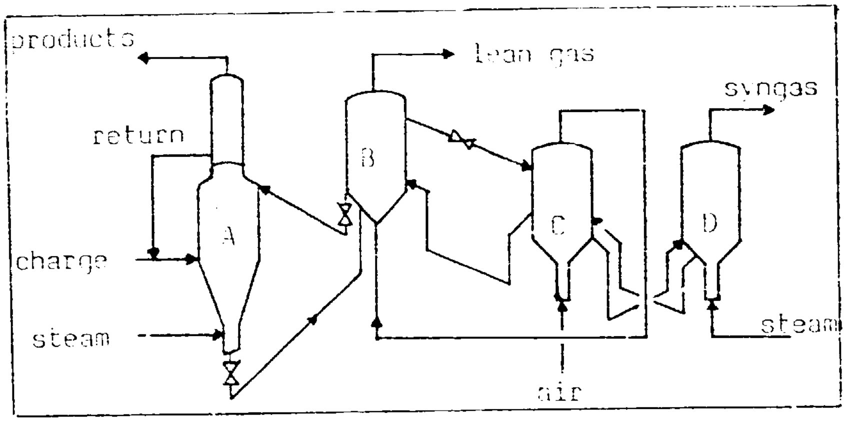
9) G. Hochstadt a.o., Erdöl und Kohle, Ergänzungsband 1980/81, p. 116

10) W.Dettmeier a.o., Erdöl und Kohle, 36 (8), 365 (1983)

Fig. 3: Production of synthesis gas by modified flexicoking



A coker
B regenerator
C air carburetor
D steam carburetor

The surplus of coke particles from the coke produced in the first reactor is vaporized with air and steam in the following reactors. This modified flexicoking process is called "dual gasification" for the gasification of the coke is split in two reactors, the air and the steam gasifier 11).

At the first time of the synthesis of methanol from syngas the reactivity of the catalyst was so low, that 340 bar pressure were needed for the synthesis. With better catalysts a production at 50 bar was possible and now the pressure is raised up to 100 bar for economic reasons (better yield at low energy costs) 12).

The disadvantage in using a mixture of gasoline and methanol for motor fuel is the less stability of the mixture and therefore solution agents are used. In most cases these are higher alcohols. Their production is also possible from syngas:

Two ways are possible to ethanol: direct from syngas

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11) D.E.Allan a.o., Oil and Gas Journal 80 (20), 93 (1982)

12) W. Seyfert, G.Luft, Chem.Ing.Tech. 57 (5), 482 (1985)

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 with 70 - 80 % are lower than with the two step synthesis via methanol. Side products are methanol and propanol. The indirect preparation of ethanol from syngas is a homologisation of methanol 13). 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 reaction conditiones between 20 to 50 mass-% in an adiabatic working multilayer quench reactor 14).

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 (eg. Eriomite, Chabasite and Offretite) lies in their high selectivities to olefines which is sometimes greater than 80 %, while zeolithes with middle-sized pore-openings, such as Pentarils, have a lower selectivity with a smaller tendency to build coke 15).

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 lead 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 % aromatics and for example silanation of this catalyst diminishes the aromatics to only 19 %.

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13) H. Bahrmann, V. Cornils, Chem. Ztg. 104 (2), 59 (1980)

14) P. Courty a.o. PD 9, 11. World Petroleum Congress, London (1983)

15) W. Dettmeier a.o., Erdöl und Kohle, 36 (8), 365 (1983)

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[16].

The fermentation of organic matter to methane

(C_1-chemistry) is another route to primary chemicals. Organic wastes of different origin but also digester sludge can be further decomposed anaerobic by microorganism to carbon dioxide, methane, and some other volatile components. This biogas process is done by a mixed culture of different, but determined microorganism strain. This is one of the most important fermentation processes, for it is a potential source for methane. Solid wastes have to be dispersed in water. Under usual conditiones about 350 $l/m^3 \cdot d$ sewage gas may be produced, during this 60 - 85 % of the organic matter is degraded. This degradation procedes in three steps: the first one is strictly anaerobe, here micgroorganism degrade polymeric compounds to shortchain 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 % methane, the rest is carbon dioxide with small amounts of ammonia, hydrogen and hydrogensulfide. The last one and humidity have to be removed when using the biogas as fuel. The used bacterial strains are not optimized till now. Also it should be possible to improve the process control, esp. temperature, pH-value etc. by the use of optimized bioreactors. The produced gas may be introduced to local energy systems after a simple washing and removal of sulfur.

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[16] US Patent 4,180.560 (1977)

Fermentation of cellulose to ethanol. The mostly used raw material for the production of ethanol on a biotechnological way is glucose. Cellulose containing material, e.g. wood, straw and bagasse have a biological tough structure and need the highest expenditure for hydrolysing to glucose. Also the nonfermentable accompanying materials (lignin and pentoses) have to be separated. For this the yields are poor in relation to the raw material.

Hydrolysis of wood is done by thermochemical processes or by microbiological-encymatic degradation. The requirement on chemicals and energy for the chemical decomposition and the long reaction times with the biological processes are at this time adverse to an economical use. It is tried to reduce this costs for both methods 17). At the end of the hydrolytic cleavage of cellulose we have a solution of glucose, which may be fermented in the usual way.

In countries having extensive vegetation and a rather agricultural-oriented economy, ethanol will be the fuel of the future. But it is also discussed if it is possible to produce another fuel, e.g. n-butanol in a more economic way 18). Fig. 4 shows a comparison between the production of ethanol or butanol from maniok.

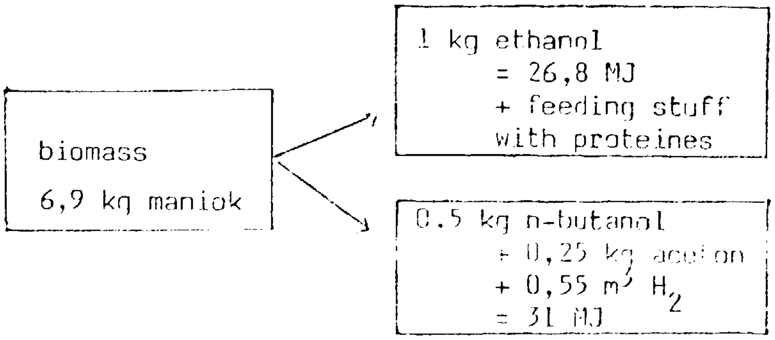

Fig. 4: comparison between the production of ethanol or butanol from maniok

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17) F. Reinefeld, E. Wagner and C. Wimmer, Zuckerindustrie 105, 25 (1980)

18) W.Bernhardt, ATZ 81, 151 (1979)

From the view of the energy transformation the butanol way from biomass is 16 % more economical 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 shall produce 4,5 mill. liters gasoline per day 19).

(ii) New routes to petrochemical intermediates

a) New methanol-syngas based synthesis routes:

Beside of the methanol conversion to gasoline, light olefins and aromatics, a lot of chemicals may also be produced on suitable catalysts. At this time nearly all syngas is produced from methane. Methanol, of course, is much more reactive. Therefore the synthesis of several methane-derived chemicals are synthesized via syngas and methanol. In the last 30 years a great deal of new chemistry has been developed, particularly in the field of homogeneous catalysis, starting with methanol 20). So methanol is used for the manufacture of formaldehyde (mostly used for resins), methylamines (for insecticides, surfactants, dimethylformamide, dimethylacetamide, alkyldimethylamine oxides, rubber chemicals, cholin chloride, biocides etc.), chloromethanes, acetic acid and methylesters of different acids (phthalates, methacrylates etc.).

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19) --, Erdöldienst 19. Juli 1983

20) W.H.Calkins, Chemicals from methanol, Catal.Rev.-Sci.Eng.26 (3 a. 4), 347 (1984)

In connection with new catalyst systems methanol has special chemical properties and promises to be the raw material that may displace ethylene and other petrochemical feedstocks from chemical synthesis. This is true especially for oxygenated chemicals: The only oxygenated chemicals now made commercially from methanol are formaldehyde, acetic acid, methyl acetate and methyl formate. Since 1984 a plant for the production of 500 million pounds per day of acetic anhydride from 900 tons/d of high sulfur bituminous coal is in operation. Methanol may be the source of emerging, hopefully improved synthesis of acetic anhydride, acetaldehyde, ethanol, ethyl acetate, vinyl acetate and ethylene glycol. The routes to these chemicals usually involve either the catalyzed carbonylation, reductive carbonylation or oxidative carbonylation of methanol or formaldehyde by transition metal complexes or catalysis by bases 21).

The reaction of methanol to acetic acid is already possible in a high and a low pressure reaction. Now the homologisation of acetic acid with synthesis gas to longer carboxylic acids is published. The used reaction conditions are: liquid phase, 220 ^{0}C, 270 bar, with homogenous catalysts on the basis of ruthenium, rhodium, palladium or nickel with methyl iodide as promotor.

Since 1983 in USA the first plant is working, which produces acetic anhydride as another product of syngas chemistry. The used feedstock is methylacetate which reacts with carbon monoxide at 175 ^{0}C and 25 - 50 bar on special catalyst systems, containing an aromatic N-heterocyclus. Syngas and methyl acetate

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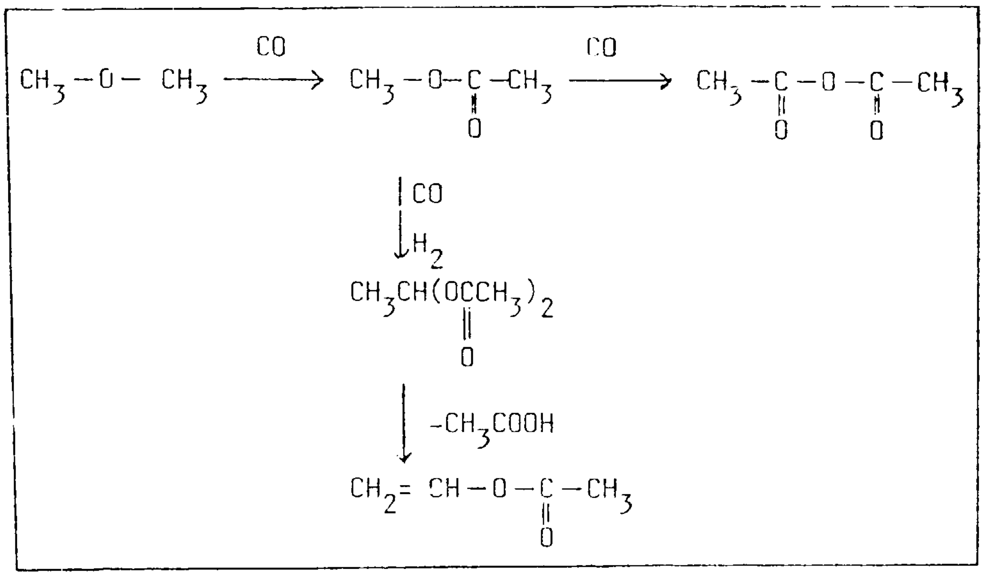
21) Irving Wender, Chemicals from methanol, Catal.Rev.-Sci.Eng. 26 (3 a. 4), 303 (1984)

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:

Fig. 5: Preparation of acetic anhydride and vinyl acetate from syngas and dimethylether



Methyl formate, a syngas based intermediate, is already today produced on 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. Beside 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 22).

A new focal point of research is the 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 only 340 bar 23). In some cases acetic acid was used as solvent and here glycol diacetate was the end product. The optimal yield is 50 - 60 % glycol, with some methanol. Two ways are possible for the synthesis of glycol via methanol (see also Fig. 6).

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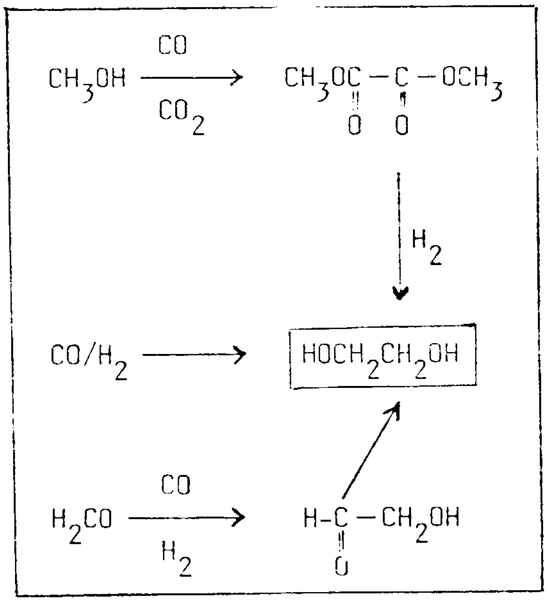
22) M. Röper, Erdöl und Kohle, 37 (11), 506 (1984)

23) –, Erdöl und Kohle, 34, 97 (1981)

Fig. 6: Glycol synthesis from syngas



The oxycarbonylation gives in the first step oxalic dimethylester, which is further hydrogenated to glycol $^{24)}$. The second way is an oxidative coppling of methanol to glycol by organic peroxides in presence of formaldehyde but the yields are too small at this time for a technical realization. The indirect way to glycol from syngas and formaldehyde gives the intermediate glycolaldehyde, which is also hydrogenated to glycol.

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24) A.M.Gaffney a.o., J. of Catalysis 90, 261 (1984)

b) New routes for the production of MTBE, isobutene and butadiene (C_4-chemistry):

The development of petrochemistry was distinct from one geographic region to the other. For a long time in Western Europe naphtha was the universal used raw material for the production of all olefins and aromatics and also for a large part of syngas and acetylene. This central position of naphtha had its reason in the surplus production; therefore it had a reliable and cheap availability.

This situation has changed in the early 1970's. The reason was an increasing demand of gasoline at diminished crude oil throuput. Now the petrochemistry has tried to diversify the used raw materials: From small hydrocarbons up to larger molecules till crude oil can be used on principle to produce syngas, olefins and aromatics.

In an analogous way the raw materials for the production of acetylene were fully substituted by gaseous hydrocarbons, mostly by natural gas or some liquified petroleum gas (LPG) [25]. For the olefin production naphtha was substituted much more slowly. Now a day steam crackers are constructed for the possible use of various raw materials, which may be changed easily. But also the alterations of existing installations are possible. This flexibility in the choice of imput material gives the ethylene manufacturer the possibility to respond to global, local or seasonal changes in the dispositions of the raw material.

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[25] W.Bickel, Chem.Ing.Techn. 55, A 308 (1983)

In most cases gas oil and LPG or components of LPG can be used as substitution products for naphtha in the production of ethylene. This is the reason for the slowly reduction of the relative portion of naphtha as raw material for the ethylene production in Western Europe since 1979. It is further expected that this trend goes on 26) (see Fig. 7).

Fig. 7: Changes in the raw material basis for ethylene production in Western Europe in the period 1979 to 1990 26).

year		1979	1980	1985	1990
production of ethylene	mio t	12,4	11,1	11,2	12,0
naphtha	%	87	85	71	65
gas oil	%	7	6	10	10
butane	%	3	4	6	6
propane	%	2	3	10	12
ethane	%	1	1	2	6
others	%	-	1	1	1

Also gas oil is a proper substitution product for naphtha. As a surplus production is predicted to it 27), it is proposed that it will reach a strong importance for the production of ethylene. In USA ethane is the most important raw material for the ethylene production.

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26) K. Griesbaum, W.Swodenk, Erdöl und Kohle 37, 103 (1984)

27) H. Kuper, Erdöl und Kohle 36, 119 (1982)

But the above told substitution process for naphtha in Europe will run slowly. Therefore naphtha will remain the outstanding raw material in this century as feed to the olefin installations. To this an intensified import of naphtha by Western Europe can contribute from surplus productions in countries which produce petroleum and are low motorized. Another or further possibility can be the release of naphtha from the gasoline pool for chemical uses by an additional application of conversion installations[26].

Ethylene is produced by a cracking process in a tube oven. The increase in price of the hydrocarbons led to the position for the raw materials being the paramount cost element. This portion increased from 35 % in 1971 to 78 % in 1981. Therefore countries with crude oil should try to develop a petrochemical industry. In this field some new methods were developed: To broaden the basis of raw material to lower and higher hydrocarbons the combined cracking of mixed introduction material was studied. For example it was reported, that cocracking of ethane-naphtha mixtures in a millisecond-oven improves slightly the yield of ethylene[28].

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, in the near future in industrialized nations there will be a shortage in this product. Here again is a possibility for countries with crude oil and own refineries to produce MTBE for sell. This will be a possibility for example

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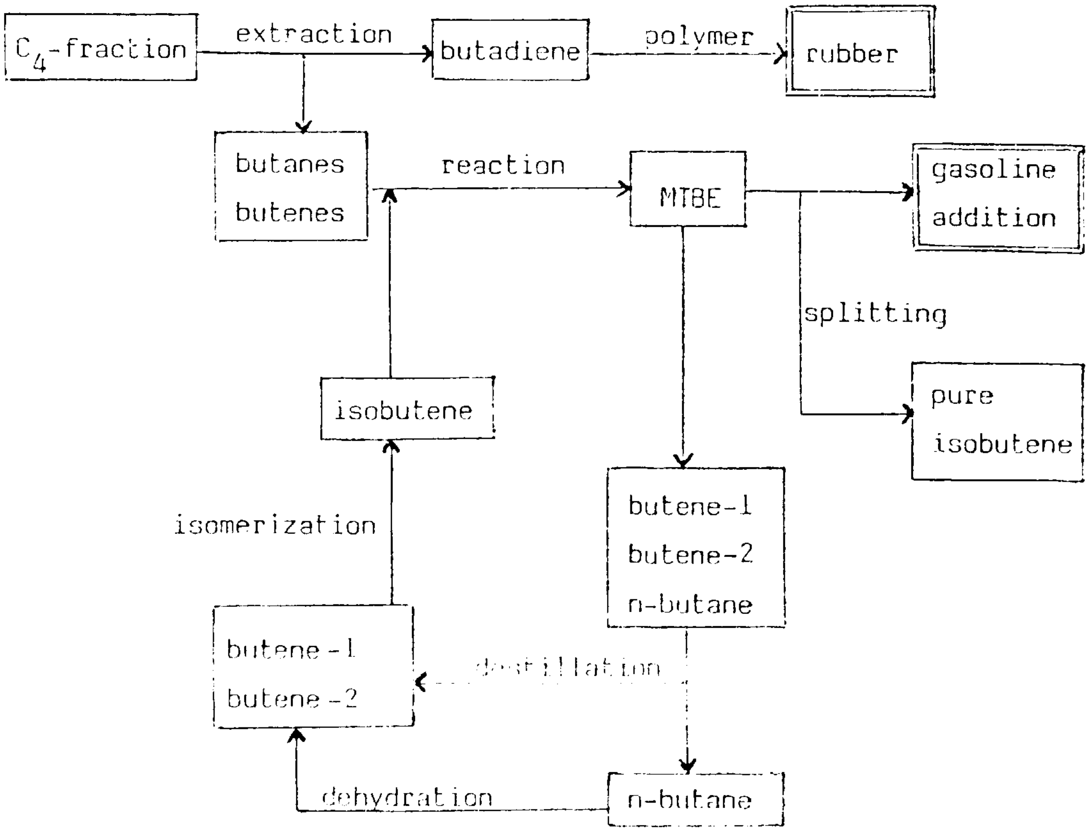
[28] G.B. Nowiljski e.a., Chem.Eng.Progr. 78,(5), 49 (1982)

to countries with big propylene capacity. The open question is to buy the needed methanol for this process or to synthesize it. In the MTBE process the C_4 fraction is used after separation of butadiene by solvent extraction. From the remaining mixture only the isobutene reacts with methanol on the catalyst. Acidic ion exchangers, perfluorinated sulfonic polymers or adducts of methanol to heteropolyacids are used as catalysts in the different processes. Fig. 8 shows an integrated MTBE process combined with the separation of C_4-olefins.

Fig. 8: Separation of C_4-fraction and use of the different compounds



A new combined 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 at last the reaction of isobutene with methanol to MTBE. This possibility enlarges the preparable amount of MTBE (29). 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 Fig. 3 the formation of MTBE can also be used as a first step to receive pure products like the different butanes and butenes.

The increased demand for isobutene to MTBE production caused new 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 fluorinated aluminium oxide or alumino silicates is reported, also the preparation of isobutene from n-butane by consecutive dehydration to n-butenes and subsequent isomerization (30).

c) Swimming petrochemical plants:

Of special interest may become the idea (31), to build up swimming petrochemical plants for the direct processing of natural gas and petroleum gas, esp. in the two cases

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29) G.R.Muddaris, M.J.Pettman, Hydrocarbon Proz. 59 (10), 91 (1980)

30) Europ.Patent 42 252 (1980)

31) W.Bickel, Chem.Ing.Techn. 55, A 308 (1983)

(i) in countries or regions without enough infra structure and
(ii) when the raw-material deposits are marginal.

This reduces the costs for obtaining and processing and may be a good possibility for some DCs.

For a complete use of the gas which accompanies the oil during production it should be utilized as near at the bore-hole as possible. Four examples shall explain the idea.

- swimming urea plants in the gulf of Iran.

  Because of the missing infra structure the accompanying petroleum gas shall be used in a swimming urea plant with a capacity of 1000 t/d. This fertilizer plant has the advantage that it can be built in an European shipyard and dragged to its berth. The produced fertilizer can be shiped without intermediate storage. The petroleum gas is transported to the plant from the nearly situated drilling region. If the gas is depleted the plant can be dragged to the next place. The omitted costs for installations on land, for roads, intermediate storages and post facilities compensate the costs of the swimming equipment. Also such natural gas recurences may be used by this mobility, which are not useable by common technology.

- swimming natural gas power station.

  This is a project, called EPOS (Electric Power On Sea) to erect the first swimming power station over a gas bore hole at the North German coast shelf. With an installed power of 350 MW the costs of the

- 33 -

power station including the energy transport on land will be 650 - 750 mill DM. With the expected gas quantity it would not be economic to construct a pipeline to the land.

- swimming methanol plant.

  One German and one American chemical engineering company offer swimming methanol plants for the same use of torch gas than above. Such a plant costs 300 mill US-$ with a capacity of 2800 t/d.

- swimming poly ethylene plant.

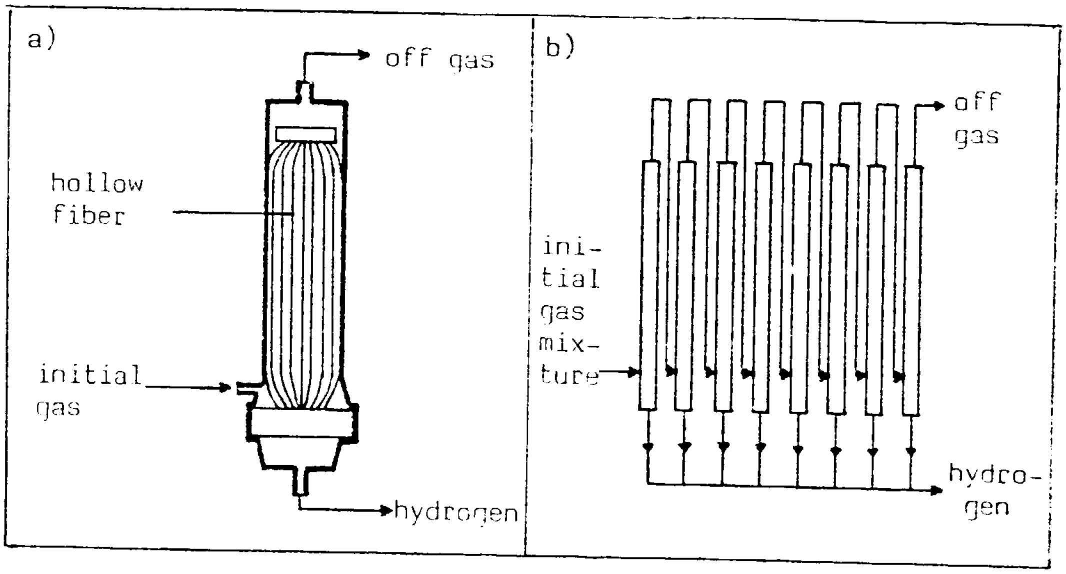
  All the above mentioned factories are only in the planning stage. But a swimming polyethylene plant was already built 1981 in Argentina and is situated in the Bahia Blanca Bay. The equiment was built in Japan and has a capacity of 120.000 t/a.

New separation techniques:

Two new noncryogenic procedures were developed for the production of enriched or high pure hydrogen from hydrogen containing gas mixtures. The first of them is an adsorption procedure which works with the pressure changing technique. Contrary to the known method with zeolithes here carbon molecular sieves are used for the separation. On this material the typical attendants of hydrogen in technical gases (e. g. nitrogen, carbon monoxide, carbon dioxide, or methane) are much stronger absorbed than hydrogen. Therefore a separation is reached in flowing through the adsorption material.

The second alternative process for hydrogen separation uses the princip of different permeation selectivities of different gases through polymer membranes, e. g. polysulfones. In the socalled "prisma separator" (see Fig. 9) membranes are used as narrow tubular fibers.

Fig. 9 : New methods for the enrichment of hydrogen



a) prisma separator

b) arrangement of the separators

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 equipments are connected 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 rest gases of the ammonia synthesis.

This new separation processes work much cheaper than the sooner used methods, like low temperature distillation and so on.

3.2. Scientific discoveries

In this chapter inventions will be discussed, which are in the laboratory stage today and might offer an economically feasible alternative in some years.

The use of crude oil and residual oils for the production of ethylene was the theme of further development because of the uncertain views of supply. A new process, called "thermal regenerative cracking" works with a solid heat transmitter (inactive Al_2O_3 or carborundum). The product is cracked at low pressure at 775 - 1010°C and a hold up time of 0,05 - 0,5 seconds in a fluid reactor similar to these for catalytic cracking 32). At this time the process is tested in a pilot plant and using residual oils it shall give the mean products ethylene and propylene as well as considerable amounts of aromatics.

Another realisation of an olefin process is reported from Japan 33). It works also on the basis of crude or residual oils and is called the COSMOS-process (Cracking Oil by Steam and Molten Salts). It is a variant of the conventional steam cracking process, which was not suitable so far using crude oil because of the higher tar and coke occurence. The additional used salt melt is sedimented in a thin film at the inner walls of the cracking tubes. So it prevents the sticking of coke and also catalyses the water gas reaction of the deposited tar and coke. The process was tested on a crude oil with low sulfur content and gave 26 % ethylene, 12 % propylene, 6 % C_4-compounds, 8 % crack naphtha and 26 % fuel oil.

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32) – Chem.Eng 86 (24), 55 (1979)

33) F.Ymaguchi e a. Hydrocarbon Process 58 (9), 167 (1979)

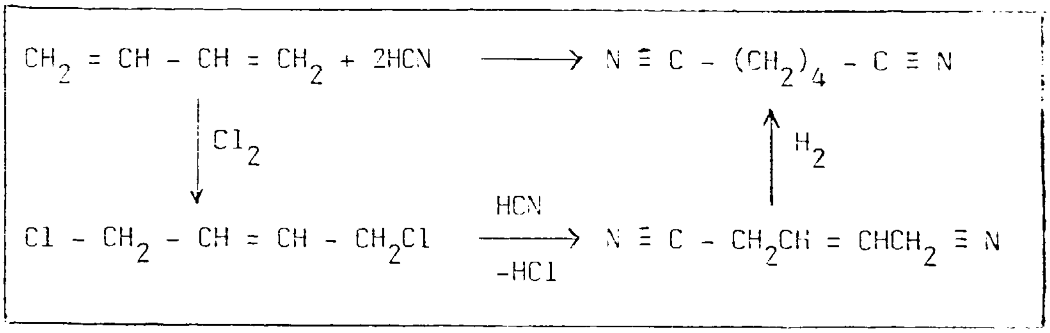
But generally experts say, that all the processes using crude or residual oils will not contribute to the production of ethylene in the near future for economic reasons.

The use of heavy feedstock in olefine producing plants gives an excess of ethylene, butylenes etc. Therefore new conversion processes are of importance for the optimal use of these side or coupling products. Several scientific groups persue this goal. 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 % of the liquid reaction products are BTX-aromatics and 10 - 30 % C_9-hydrocarbons. But the yield is only 10 - 22 %, therefore a commercial use is not considered at this moment.

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

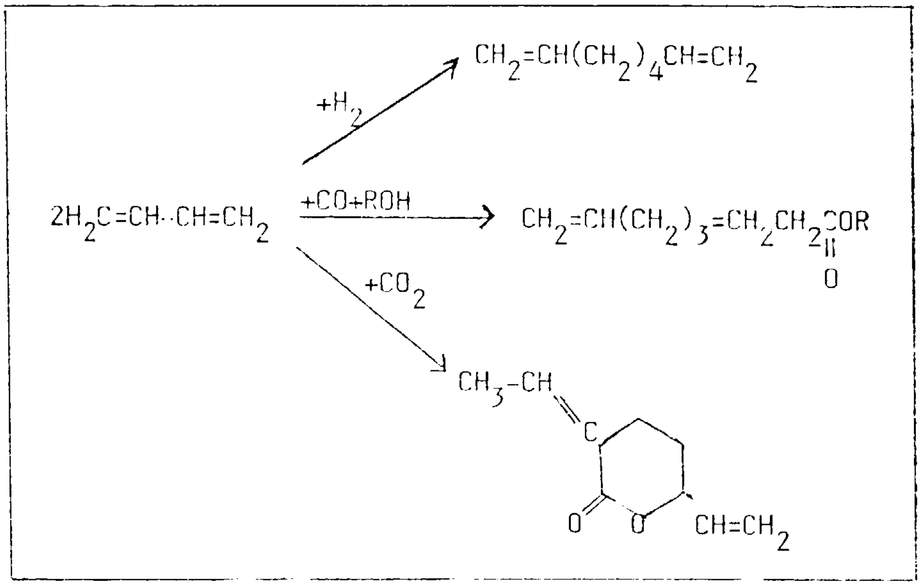
Butadiene as feedstock for chemical synthesis gives also new possibilities in the petrochemistry. In USA one company has already changed the whole production of adiponitrile to butadiene basis. Adiponitrile is a very important intermediate for the production of polyamides. In this process butadiene is hydrocyanized in the liquid phase in presence of catalyst, which contain phosphines or phosphites of Ni, Zn or Al-salts. This technology now substitutes the older hydrocyanation, with dichlorobutene as an intermediate (see Fig. 10).

Fig. 10 : Reaction of butadiene with hydrocyanic acid to adipodinitrile.



With the new process 45 % of the energy can be cut down 34). Other dimerizations of butadiene give interesting bi- and polyfunctional C_8-molecules, as shown in Fig. 11.

Fig. 11: Dimerization reactions of butadiene



For all these reactions Pd complexes with different ligands are used. In this way 1,7-octadiene, esters

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34) —, Chem. Eng. 87 (3), 49 (1980)

of 3.8-nonadienic acid or 1-ethylidene-6-heptene-5-olide are synthisized 35).

With the increased production of MTBE in future more butadiene is isolated from the C_4-gas fraction and therefore all the butadiene is not needed for polymerization. At this time such other uses of butadiene are an important alternative.

Methane

Today methane is essential used for the production of energy. Beside of its use for the production of syngas, acetylene and ethylene by pyrolytic methods, chlorinated products, hydrocyanic acid and CS_2, it would be very useful, to transfer methane into higher valuable and higher boiling products. If methane could be reacted directly to petrochemical raw materials, esp. C_2- and C_3-olefins, aromatics or oxygenated C_1-derivates like methanol or formaldehyde, it would be a substantial alternative to crude oil as chemical raw material. These perspectives are the reason for intensive research and development in the field of methane chemistry in the last years 36).

In the following short discussion only results are reported, which are ways from methane to methanol, formaldehyde and C_{2+}-hydrocarbons, and have a chance for technical realisation.

For example a homogenous oxidation of methane by ferric sulfate in a sulfuric acid solution, after a previous heterogenic activation by adsorption on a Pd/C-catalyst is described 37).

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35) J.F.Knifton, J.Catal.60, 27 (1979)

36) --, Nachr.Chem.Techn.Lab. 33 (4), 292 (1985)

37) G.König, DE-OS 3101024

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

The reaction has 92 % selectivity to methanol.

In another important reaction the methane is radicalic activated by chlorine, which functions also as an oxidant. Chlorine and ethane react in an adiabatic flame at normal pressure and 700 - 1700°C to ethane and ethylene, with the side products hydrogen and hydrogenchloride [38].

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

$$x = 0{,}1$$

With methyl chloride as intermediate at high temperatures (>500°C) and normal pressure mostly ethane is built, at low temperature (<400°C) and higher pressure (6 - 7 bar) hydrocarbons in the naphtha region are isolated.

The reaction of methane in presence of metal oxides (that is a heterogenous activation) is as well an oxidation to methanol and formaldehyde as an oxidative coupled reaction to higher hydrocarbons. Esp. the last reaction seems to be realisable in a technical scale. So methane reacts with N_2O on a molybdenum/silica catalyst at 550 - 600°C. The methane conversion is 3 to 6 % and the overall selectivity for methanol and formaldehyde 65 - 80 % ($HCHO:CH_3OH$ = 4 : 1) [39].

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

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

Similar results are reported in the Russian patent literature: methane reacts with air on a catalyst to formaldehyde. In a laboratory fluid reactor at $650 - 700^{0}C$ for example formaldehyde selectivities up to 65 % are described, the methane reactivity was 30 % at a contact time of 1 second. On another catalyst $(Sn_3(PO_4)_4/SiO_2)$ at $500 - 650^{0}C$ selectivities up to 94 % formaldehyde are reported.

The production of ethylene and acetylene from methane and the formation of hydrogen at the same time with high yields is only possible at high temperatures ($1500 - 4000^{0}C$) because of thermodynamic reasons. Therefore a catalyst has no success, but in the presence of oxidants methane can react in a higher degree, because the evoluted hydrogen is bonded to water. Especially the oxidative methylation of toluene, propene and isobutene is economically hopeful to ethylbenzene and styrene, resp. butadiene or methylbutadiene. In a similar reaction acetonitrile and methane gives acrylonitrile. For the reaction pathways see Fig. 12 - 15.

Fig. 12: Principle of oxidative methylation

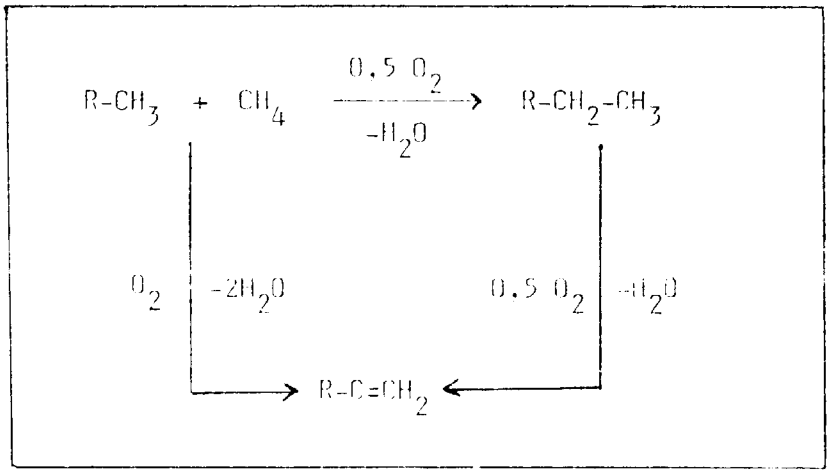


Fig. 13: Oxidative methylation of toluene, propene and isobutene

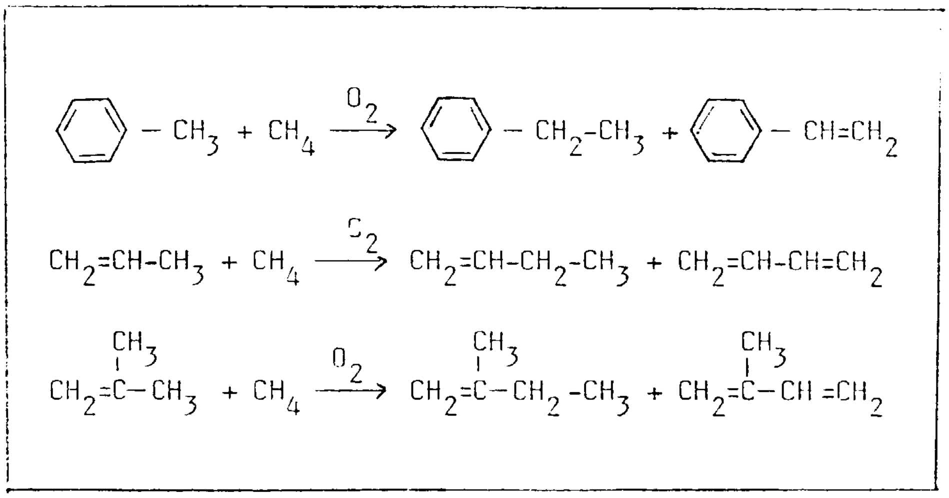


Fig. 14: Oxidative methylation of acetonitrile to acrylonitrile

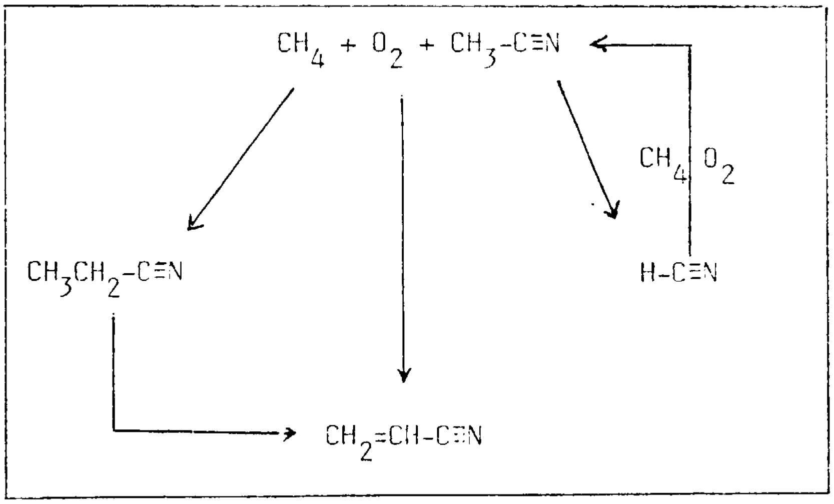
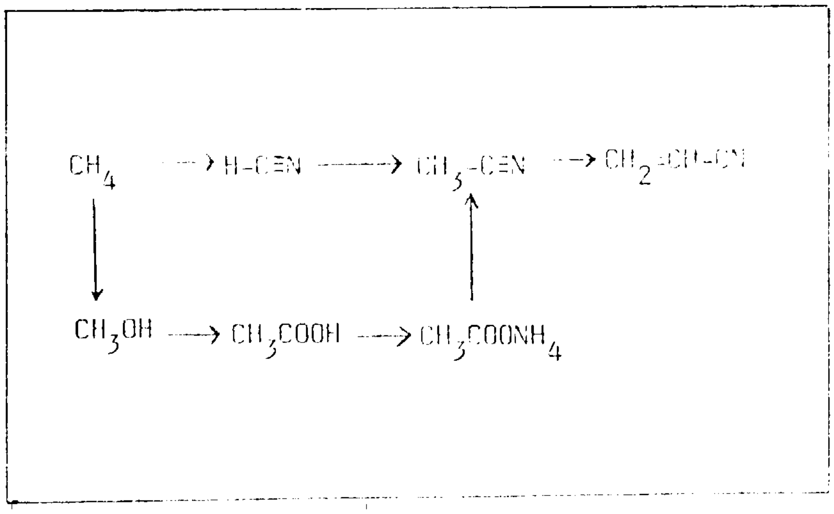


Fig. 15: Potential ways from methane to acrylonitrile



The oxidative reaction was also observed on acidic zeolithes. In this reaction aromatics shall be built. Another reported possibility for alkylating of olefinic hydrocarbons with methane uses Ni-catalysts in a gas phase process 40).

This principle studies show, 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 at first an ethyl group may be built or directly a vinyl group. Further on the ethylgroup subsequently may be oxydehydrated to a vinyl group. The overall reaction therefore is a conversion of a methyl group into a vinylgroup. 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 this reactions is an interesting alternative for styrene without using ethylene.

The oxydative 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, these both side products can be recycled. In this way a 90 - 93 % yield of acrylonitrile is possible. Combining the oxidative methylation with known reactions gives new ways to acrylonitrile only using methane, as shown in Fig. 15.

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40) J.D. Löffler c.a., J-Chem.Soc.Chem.Commun. 1984, 1177

This methane chemistry seems to be of high scientific interest and to be promising from an economic viewpoint. For countries with natural gas this chemistry in some years could be a possibility for industrial application, but further scientific programs are needed for the transfer of this ideas to industrial applicability.

Alkanes:

From the available C_4- and C_5-alkanes, the n-butane gaines importance for the synthesis of maleic anhydride. So it substitutes the now used raw material benzene, which is more expensive. This change in the raw material is possible by the new process of the gas phase oxidation of n-butane in a fluid bed, which is already commercially used.

C_4- and C_5-isoalkanes are increasingly used for the synthesis of isobutene and isopropene. The increased requirement of isobutene for the MTBE production was a motive to look for new processes for the selective dehydration of isobutane. In such a new process isobutane is dehydrated in presence of steam on a fixbed catalyst. 50 % of the isobutane reacts in one passage, after recycling the non reacted isobutane the yield is 95 % [41] (see also chapter 3.1).

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

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 [42].

Aromatics:

Toluene is a surplus product under the mostly used BTX aromatics and is also more available than benzene. This was the reason to intensify research work to the direction of using more toluene for primary chemicals. and monomers, esp. in competition to benzene and the xylenes.

Up to this time good results are received with the selective alkylation of toluene. The gasphase reaction of this compound with methanol on a zeolithic catalyst at 400°C gave 50 % reaction products, with 70 - 80 % p-xylene [43]. Even better selectivities of >90 - 99 % for p-xylene were received using cristallized SiO_2 with Ca-carbonat. In thiscase hydrogen has to be used to minimize coking of the catalyst [44].

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 received with 33 % and 11 % selectivity. If the yields can be increased, this reaction could be an alternative route to synthesize styrene without ethylene.

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

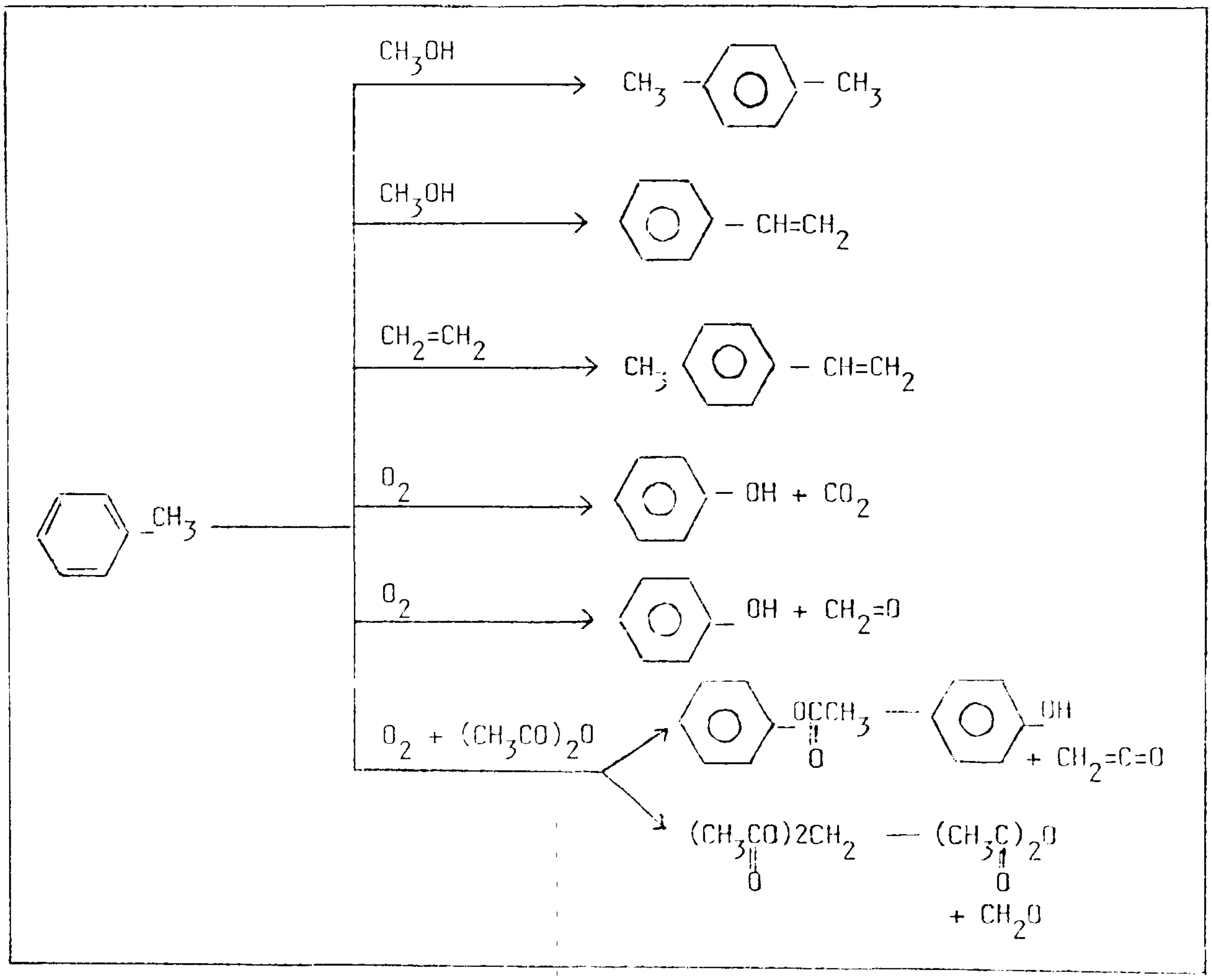
[43] Europ. Patents 37.630 and 38.116 (1980)

[44] Chem. Systems: Process Evaluation and Research Planning, 3rd Quaterly Report, p. 272-278 (1982)

The reaction of toluene with ethylene on a zeolithic catalyst gives ethyltoluene with 90 - 99 % 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. We therefore expect that styrene will be partly substituted by this monomer.

Toluene is already in competition to benzene in the preparation of phenol. To prepare this compound 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 by CO_2 (Fig. 16).

Fig. 16: New reactions of toluene



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 something difficult; in a first step toluene reacts with oxygen in presence of caro's acid and acetic anhydride to a mixture of acetoxy benzene and methylenediacetate. This mixture is pyrolized in a second step and acetoxy benzene gives now phenol and ketene; formaldehyde 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 45).

Aromatics:

The processes to isolate aromatic compounds from pyrolysis gasoline, reformate gasoline or crude benzene from coking plants are state of the technique. Progress is reported in the extractive distillation using pentenenitrile as a sluggish; e. g. for the separation of cyclohexane-benzene mixtures. Also the process for the isolation of aromatics with the molsieves is extended: the separation of aromatics from mixtures with aliphatic compounds is possible with ZSM-5 zeolithes. The isolation of m-xylene from a mixture of C_8-aromatics, o-, m-, p-xylene and ethylbenzene is successful with Na-Y-zeolithes with a yield of more than 98 % and 99,5 % purity. The process runs at 150°C and 7 bar. Zeolithic catalysts are also used to isomerize C_8-aromatics to p-xylene.

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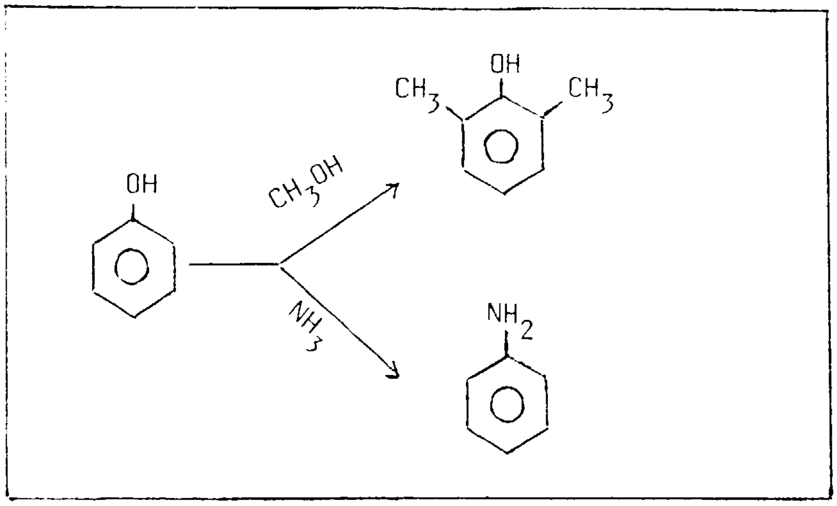
45) US patent 4,156.783 (1979)

Another point of research is the better use of phenol in chemical synthesis. So the reaction of phenol with methanol on spezial catalysts (Fe-In-Cr-oxides on Si-oxide) yields in high selectivity, 2,6-xylenol an important additive for polymers a.s.o. A new use of phenol should become important if it is possible to transfer the new process in which phenol and ammonia reacts to aniline to production scale. In this process phenol reacts with an excess of ammonia on a Lewis acid catalyst to aniline and little diphenylamine. This way of synthesis avoids the intermediate nitrobenzene and thus the use of the corrosive nitriding acid (see Fig. 17).

Fig. 17: New uses of phenol



Acetylene:

This primary product is now again in discussion as a potential substance in future [45 a]. The basis for this is a short time pyrolysis of coal in a hydrogen plasma; in this a successive degasing of the coal takes place as well as a subsequent reaction of the hydrocarbons to acetylene. Up to 35 % acetylene yield are reported.

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45 a) F. Pässler: Chem.Ing.Tech.55, 411 (1983)

Polymers:

The economic situation has been stabilized in 1984. The extent of preparation plant utilization was much better now for all standard plastics like polymethylene, -vinylchloride, and -styrene. The use of polypropylene always increased in the last years. In the field of polyolefins better catalysts and manufactoring processes give better economic efficiency 46). Engineering plastics and polymer blends show further high growth rates. Polymer blends are a new and difficult field of polymer chemistry, for polymers are only compatible if they have a negative blending enthalpy. This is the reason, that the possibility to prepare blends is very reduced.

An example for the development in the field of engineering plastics at this time is the capacity duplication for a new shock-prove butadiene-styrene copolymerisate 47).

A number of new engineering plastics had been developed in the last ten years, but now clear indications are to be seen to improve and modify wellknown polymers fulfilling in this way the requirements of the market.

Here are some examples of new developments: Polypropylene reinforced with glass fibres or other fillers has higher impact strength, stiffniss and heat stability than unfilled polyamide-6.6. The basis of the development is a special polypropylene quality and gives compounds moderate in price. The hither known possibili-

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46) --, European Chem. 31. 522 (1984)

47) -, European Chem. 33, 569 (1984)

ties for the preparation of reinforced PP needed maleic anhydride or acrylic acid for the modification of PP.

A new elastomer modified polyester with high impact strength, good lowtemperature 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 commerzialized polyacetal-elastomer blends increasingly gain new fields of application. Another new product is a polyphenyleneoxide-polyamide blend. This polymer has better stability for fuels and lubricants than the known modified polyphenylene oxides and shall be used in the car industry.

A new polysulfone-ABS blend with a heat stability of more than 150°C is recommended for molded articles with higher using temperatures. In Japan a production plant for polyphenylene sulfide is under construction. This engineering plastic has a growth rate of 30 % and is used in the electro and electronics industry, but also for thermal claimed elements in the car-industry 48).
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 down. Such IPN blends are known with nylon-11, polypropylene and polyethersulfone. Magnetic data discs for laserscanning information systems may

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48) --, Chemical Daily, 23. Mai 1984

become al large market for some polymers. These have to posess high transparency, low birefringence, 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, but also silica glass.

In the field of polyurethane 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 polysulfides, silicones and polyisobutene.

The world production of man-made elastomers which decreased 1980 - 1982 about 17 %, increased 1983 for 4 %. This trend continued in 1984, but new developments belong more to spezial rubbers than to tire elastomers. Germany began to produce hydrated nitrile rubber. Another special rubber, which resists high temperatures, oxygen, ozone, peroxide containing fuels, oils with additives and hydrogen sulfide, is produced by selective hydration of the olefin double bonds in natural rubber. This material is used for high strained sealing materials for crude oil production and automobiles.

In the field of man-made fibres only a small growth is expected. What is now to be done is to improve the polymerization processes using higher active catalysts and to develop new technologies like fibre polymerization. For all steps in the production of polyamide-6 new processes are available: higher polymerization output, pastcondensation of granular material, continuous wash and drying processes and waste reconversion processes. The filament manufactoring is now possible as a one step spinning-extending process, esp. for tire 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 endproduct is as low, that an extraction before the spinning process is not necessary.

A new solvent for cellulose, the N-methylmorpholine oxide, shortens the production time for cellulosic fibres, lowers the energy costs and increases the quality 49).

Possibilities of fibre recycling are more and more interesting, for example the work up 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 300°C melting point, high strength and dimension stability. In development is also a new polyamide fibre with high water absorptivity,

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49) --, Chem.Week, 25.April 1984

which consists of 80 % polyamide-6 and 20 % polyadipat -4,7-dioxydecamethylene diamine.

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

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

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

Let us conclude the comments about fibres with some notes to carbon fibres and high temperature fibres. In 1982 in Western Europe 300 t of carbon fibres are consumed and the yearly growth rate is 20 - 30 %. The production of carbon fibres from pitch is cheaper than from polyacrylic fibres. C-fibres which have a 5 - 10 fold better adsorptivity than activated charcoal are now prepared from polyacrylic or cellulosic fibres. For this the last called fibres are set on fire and treated with steam. In this way micro pores are developed within the fibres.

A new aramide fibre an 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 protecting clothes. Ceramic fibres are used for the reinforcement of aluminum, lead, ceramic and organic resins.

It is to hope that in the near future the study of the connection between the structure of a polymer and the electric conductivity will be successful. In this field other polymers in addition to the classical substance polyacetylene gain more importance.

3.3. Possible implications on current production structure

Already now and in the near future countries with large hydrocarbon resources should install

- more facilities for cracking, hydrocracking, visbreaking and other conversion possibilities, to be able to produce more fuel and less fuel oil.
- this gives more low molecular olefins and paraffins; esp. plants to isolate butadiene and isobutene, and to isomerize the n-butenes should be installed.
- more manufactoring plants should be erected for MTBE, which is needed in industrial countries for leadfree gasoline.

Countries with coal deposits should participate on research of coal chemistry, to be able to produce petrochemicals in the near future from coal as shown in the next two tables:

Fig. 18: Process of coal chemistry

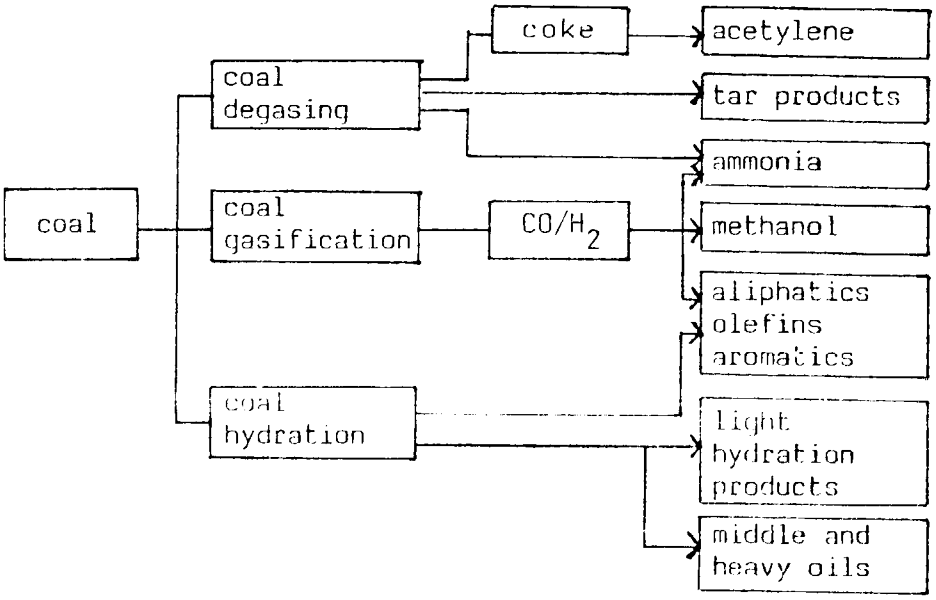
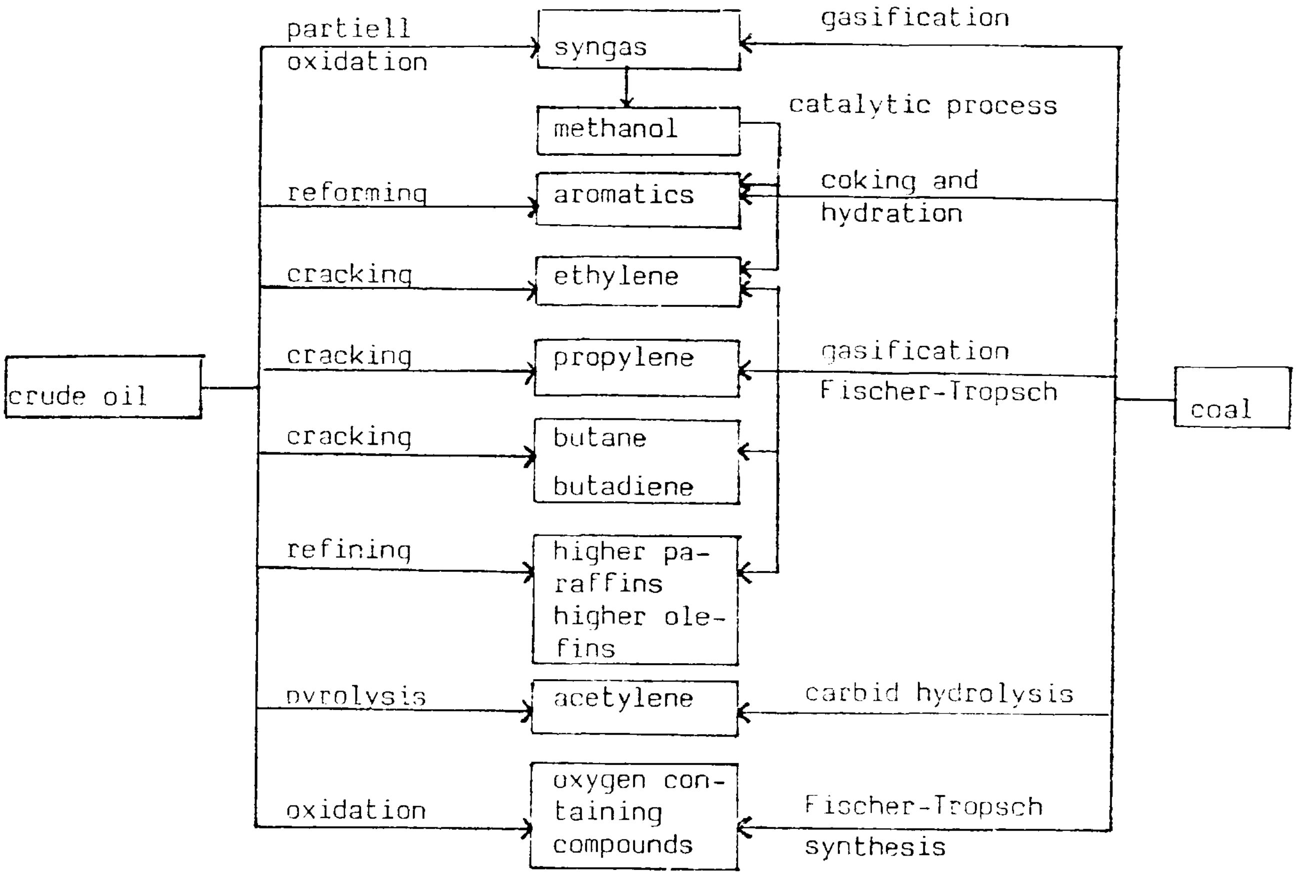


Fig. 19: Production of chemical feedstock from crude oil or coal



Countries with no hydrocarbon resources should intensify their efforts to produce chemical feedstock from different biomass and waste biomass:

- production of syngas/methanol
- production of sugar
- production of oxychemicals
- production of aromatic chemicals (from lignin)
- fermentation of cellulose to ethanol

4. CONCLUSIONS

News 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 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, th synthesize a pallet of products like gasoline, olefins, aromatic, but also of special intermediates, which are again feedstock to classical organic chemicals, may be produced with known processes. Naturally, the circuit route via syngas rises the costs of the products. At this time crude oil is something cheeper and therefore available in larger amounts; this is the reason why the alternative ways are repressed at the moment. But as the occurrence of crude oil is finite, in short or large periods the alternative resources will become significant again.

Trends in research and development indicate the wishful thinking to as high a flexibility of the production equipments and processes as possible. To give a chance to all countries, especially such processes should be treated intensive, which produce petrochemicals from biomass or waste biomass.

In future there will be less new monomers in the field of polymeric material, but more new processing technologies (polymer blends, high temperature resisting fibres, carbon fibres etc.) which give better plastic materials, synthetic rubbers and synthetic fibres. But till today the scientists did not succeed in the preparation of synthetic hollow fibres to imitate the absorptivity of natural fibres.

There is a need to found the corresponding university and research institutes parallel to the erection of an own organic industry and to supply with enough funds to enable these institutes to adapt foreign processes to the own conditions and to train native experts.