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Chemical Feedstocks from Coal: Towards A.D. 2000 [and Discussion]

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Chemical feedstocks from coal: towards A.D. 2000

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In the leading industrial nations, the demand for chemical feedstocks is mainly covered by oil and thus by a feedstock that will no longer be sufficiently available in a few decades. Coal is an alternative source for chemical feedstocks, the reserves being sufficient for several centuries. Coal gasification will play a key role as numerous heavy chemicals and chemical feedstocks can be produced from synthesis gas (e.g. Oxo, Fischer–Tropsch, methanol, olefin and ammonia synthesis). Moreover, aromatic hydrocarbons can be obtained via coking processes, carbonization of lignitic coal or via the hydrogenation of coal. Acetylene production from coal will also regain significance.

Coal was the basis of the organic chemical industry as recently as the 1950s when petrochemistry experienced an unparalleled surge in its industrial development. Thereafter, coal continually lost ground to the cheaper, apparently unlimited, oil reserves. In addition, oil can be more readily processed.

More oil has been consumed during the last 13 years than in the whole period before, due to the change-over from coal to oil-fired power stations, expansion of the chemical industry and world-wide car ownership. If this development continues unhindered, assuming an annual increase of around 8 %, then the proven oil reserves will be exhausted by the beginning of the new millennium.

The chemical industry's contribution to this growth in oil consumption is shown in figure 1. About 95 % of heavy chemical production in 1979 is estimated to have been based on oil or gas. This extreme situation shows that feedstocks other than oil must be found for the chemical industry. What paths are open to the chemical industry to solve this feedstock problem?

Obviously, we must use our oil reserves as economically as possible, but the chemical industry alone can only play a minor role as far as oil conservation is concerned: figure 2 presents a breakdown of the total primary energy consumption in Western Germany. Only 4 % of the total primary energy is used by the chemical industry as feedstock for the manufacture of chemicals, as well as a further 4.5 % as energy source. Primary chemicals use only about 7 % of the oil supply.

The largest consumers are electricity generating plants, domestic heating and transport. In the short term, oil should be replaced in power stations by nuclear energy and coal. This would enable us to extend our oil reserves, benefiting the chemical industry and the transport sector.

The present marked discrepancy between reserves and consumption of fossil fuels, shown in figure 3, could be best mitigated in this manner. As you can appreciate from the above, coal currently accounts for around 80 % of the total world fossil fuel reserves, while its share of present fuel consumption is around one-third. For various reasons, however, it is unrealistic to believe that all heavy oil-fired power stations can be converted within a short space of time or that light heating oil used in domestic heating can be replaced. Even if, in the ideal case,

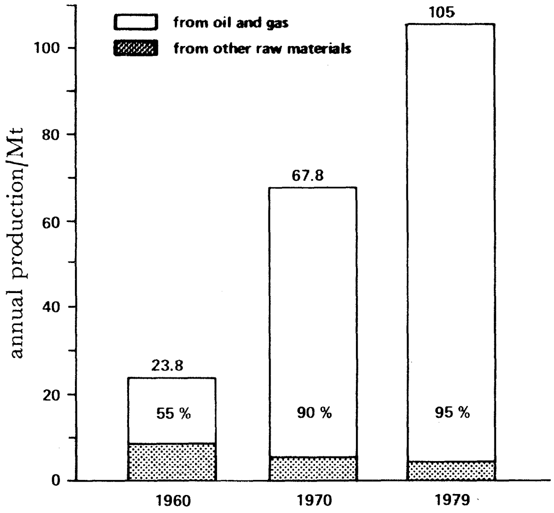


FIGURE 1. World production of organic chemicals (excluding the U.S.S.R., China and eastern Europe). The source of data for 1960 and 1970 was *Chemy Ind.*, 1 Dec. 1979, p. 806. The figure for 1979 is an estimate.

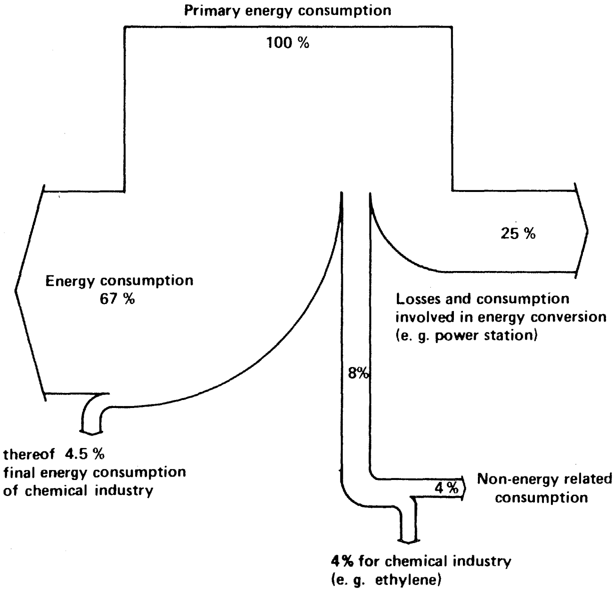


FIGURE 2. The chemical industry's share of total energy consumption in the Federal Republic of Germany.

maximum efforts were made in every area to find a substitute for oil this could not prevent depletion of oil reserves long before our coal deposits are exhausted (figure 4).

At this point, at the latest, the chemical industry must be in a position to cover its fossil carbon requirements from other sources, e.g. coal. The search for alternative feedstock sources must be instigated long before depletion of the oil reserves as the development of suitable processes takes much time. Furthermore, the political situation can experience dramatic upheavals in a short space of time. The events of 1973 and 1979 should serve as a warning for the future. Replacing oil by coal would weaken political pressures since coal deposits are more uniformly distributed over the surface of the globe (figure 5) than are oil reserves.

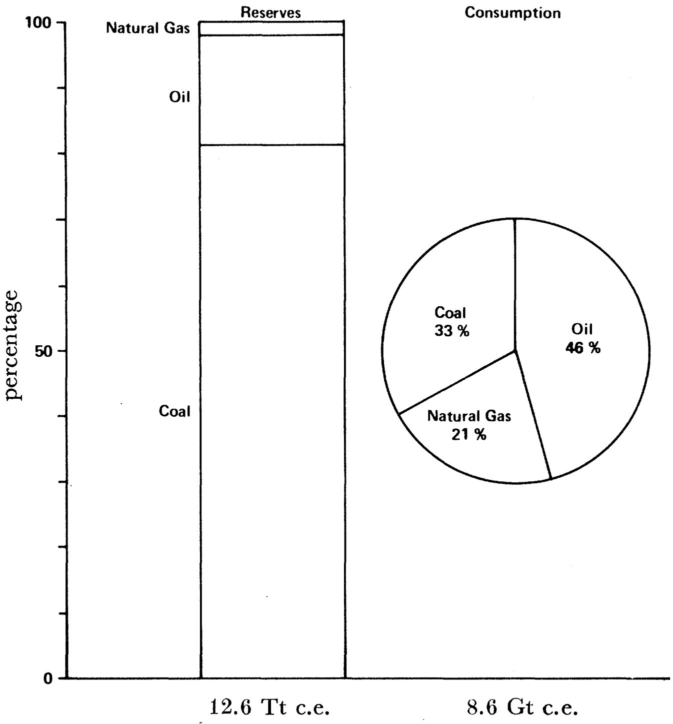


Figure 3. World reserves and consumption of fossil fuels, 1978. (1 t c.e. (tonne of coal equivalent) = 29.3 GJ.)

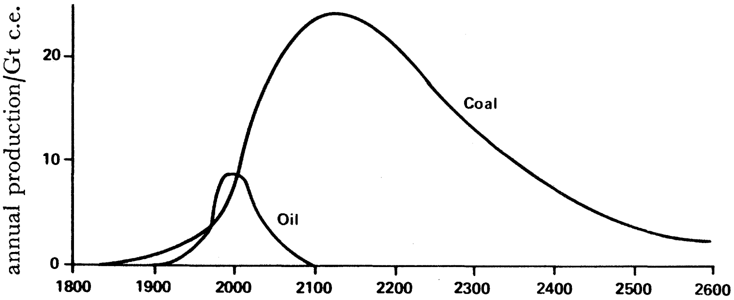


Figure 4. Expected world production of oil and coal.

Before I discuss coal's future role in the chemical industry, the current production of heavy chemicals from oil by various processes requires comment.

Aromatics can be produced by reforming and light olefins by cracking. Synthesis gas can be obtained by gasification, i.e. by partial oxidation. Synthesis gas is a suitable feedstock for methanol. Oil refining supplies higher olefins and paraffins. Oxidation processes present routes to various oxygen-containing compounds and acetylene can be produced by pyrolysis.

Basically, and I stress the word 'basically', all oil-based chemicals can be produced from coal: figure 6 shows existing industrial coal-based processes (solid lines) as well as those currently being developed (broken lines).

Coking, acetylene production from calcium carbide, first-generation gasification processes and the Fischer–Tropsch synthesis are all mature processes. It will be necessary to further

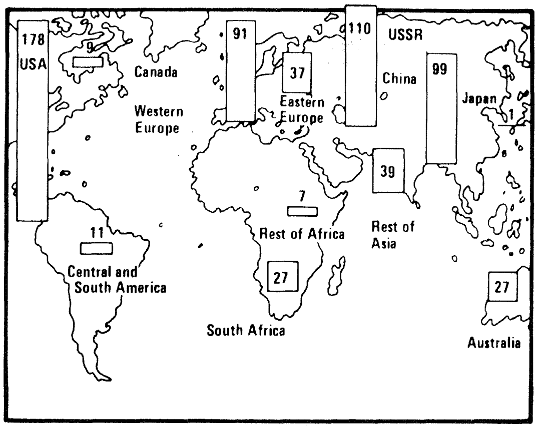


FIGURE 5. World coal reserves (gigatonnes of coal equivalent).

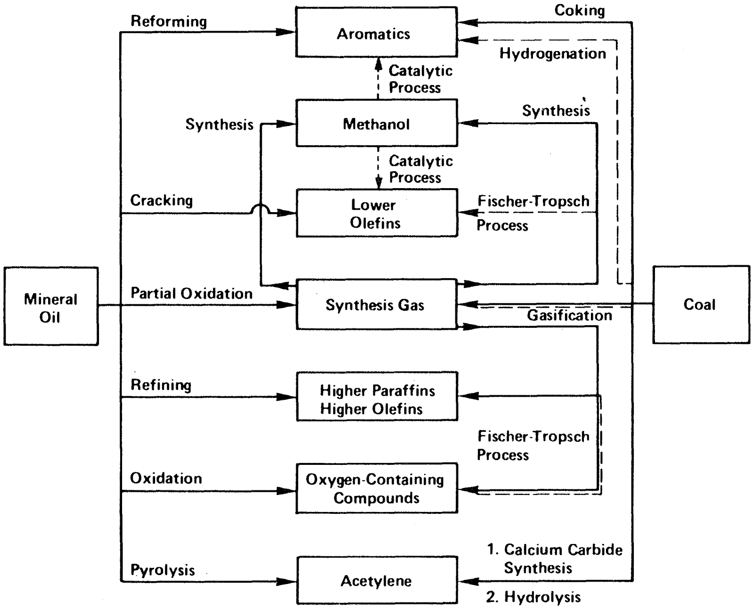


FIGURE 6. Production of oil-based chemicals from coal.

TABLE 1. FOCAL POINTS OF THE FUTURE DEVELOPMENT OF COAL CHEMISTRY

1. synthesis gas via coal gasification for chemical syntheses
2. aliphatic heavy chemicals (olefins, paraffins, methanol, substitute naphtha) from synthesis gas
3. aromatic heavy chemicals via hydrogenation or hydrogenative extraction of hard coal

develop or modify the coal gasification or liquefaction processes to help achieve the breakthrough of coal. These processes are the first steps in its chemical upgrading.

Future work will be focused on the areas shown in table 1. The gasification of coal to synthesis gas has a high priority as this useful gas can be converted to a multitude of higher aliphatic compounds. Finally, hydrogenation processes must be developed for production of aromatics. However, the significance of established processes will of course increase with the growing shortage of oil.

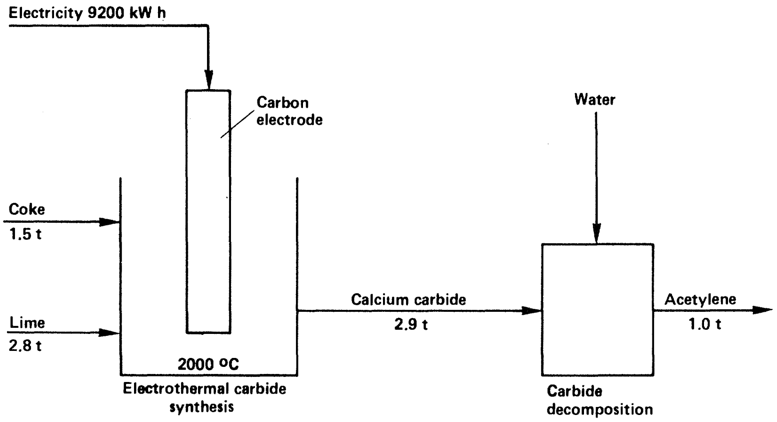
The coking process should perhaps be mentioned first. In this instance, coal is degassed by dry distillation in the absence of air. Table 2 summarizes the products obtained from the coking of hard coal. A series of valuable aromatic hydrocarbons results along with coke and coke-oven gas.

Table 2. Coal as raw material: products from 1 t coal after coking

substance	amount	applications
coke	775 kg	reducing agent in iron production; fuel
gas	180 kg ($365\ m^3$)	heating fuel; illuminant
tar	30 kg	road surfacing; impregnation agent; heating oil; dyes; plastics; explosives; pharmaceuticals
benzene	10 kg	chemical feedstocks; motor fuels; solvents
ammonia	2 kg	fertilizers

While tar and benzene are of interest to organic chemistry, they represent only around 4% of the coal feed. These substances serve as the basis of impregnation agents, heating oil, dyes, plastics, explosives, pharmaceuticals, motor fuels, solvents, etc.

Coke is the main product from the coking process and can be employed as a chemical feedstock, e.g. for the production of acetylene via calcium carbide (figure 7). Coke and lime are converted into calcium carbide at high temperatures with the use of electrical energy. On hydrolysis, calcium carbide yields acetylene and calcium hydroxide. However, the whole reaction demands a high input of coal as well as energy, i.e. 1.5 t coke and 9200 kW h are required per tonne of acetylene. Secondary reactions of acetylene produce numerous organic chemicals, as shown in figure 8. Acetylene's significance will probably increase again because of the oil shortage.



$$CaO + 3C \rightarrow CaC_2 + CO \qquad CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

$$\Delta H = 463\ \text{kJ} \qquad \Delta H = -129\ \text{kJ}$$

Figure 7. Calcium carbide and acetylene from coal.

The established processes will not be able to cover the demand for chemical feedstocks from coal. In the future, coal gasification and coal liquefaction will play an important role. Table 3 shows a summary of the mass balance of several coal upgrading steps and the resulting quantities of raw materials.

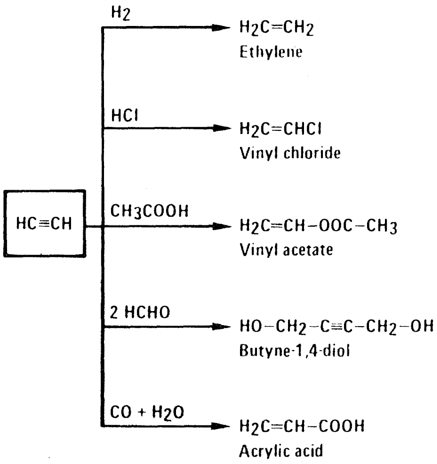


FIGURE 8. Acetylene-based products.

TABLE 3. COAL AS SOURCE OF FUEL: PRODUCTS FROM 5 Mt OF HARD COAL

by gasification
  2.5 km^3 gas
  or 4 Mt methanol (fuel additive)
  or 1 Mt motor fuel + 1 km^3 gas
by hydrogenation
  2.25 Mt motor fuel

TABLE 4. THREE PROCESSES FOR THE PRODUCTION OF SYNTHESIS GAS FROM COAL

	Winkler	Lurgi (pressure)	Koppers–Totzek
preferred coal feed	lignite	non-coking hard coals	coal dust
particle size/mm	0–8	3–30	90 % < 0.09 70 % < 0.074
process	fluidized bed	fixed bed counter-flow	entrained bed co-current
temperature/°C	850–1150	760–870	1500–1900
pressure	normal	< 3 MPa	normal

Coal gasification is particularly suited to provide the link between coal and chemistry as current oil gasification plants for synthesis gas production could be readily replaced by coal gasification plants. The basic processes and reactions have been known since the middle of the last century, when it became possible to commercially convert coal into synthesis gas by using steam and air at high temperatures. The two basic equations are

$$2C + O_2 \rightleftharpoons 2\,CO;$$

$$C + H_2O \rightleftharpoons CO + H_2.$$

Three processes of the 'first generation' are currently available for the production of synthesis gas from coal: the Winkler process, using a fixed bed; Lurgi pressure gasification, using a fixed bed; and the Koppers–Totzek process with an entrained bed (table 4). While both the Winkler and Koppers–Totzek processes employ finely divided coal, the reaction takes place at normal pressure. Moreover, both processes operate at relatively low temperatures. Although Lurgi gasification converts coal under pressure, it has constraints regarding grain size and quality of the coal.

Table 5. Typical features of second-generation coal gasification processes

gasification at high temperatures	lowers by-product yield and reduces gas purification costs increases carbon conversion
gasification at high pressures	raises space–time yields decreases syngas compression costs
gasification of coal dust	lessens demands made on coal quality compatible with modern mining technology which also produces finely divided coal

No process of the 'first generation' fulfills all the demands that must be made on a modern coal gasification process (table 5). A high gasification temperature is imperative as it increases carbon conversion, limits by-product formation and therefore reduces gas purification costs. Gasification at high pressures facilitates high space–time yields and reduces compression costs, assuming the gas is further processed under pressure. The possibility of gasifying coal dust is in accord with the trend of modern mechanized mining, which produces an increasing amount of fine coal. This development would therefore allow the gasification of all grades of coal.

Professor Kölling has given, elsewhere in this volume, a detailed report on the various processes of the 'second generation' currently being developed. Table 6 summarizes the most important development projects in the United Kingdom, U.S.A. and the Federal Republic of Germany (F.R.G.). Six large-scale processes for the gasification of hard coal are currently being discussed in the F.R.G.: (1) Ruhrchemie/Ruhrkohle/Texaco; (2) Ruhrgas/Ruhrkohle/Lurgi; (3) Shell–Koppers; (4) P.C.V. (Flick); (5) Saarberg/Otto; (6) Thyssengas. Rheinbraun still plans to operate two gasification processes based on lignite, i.e. the high-temperature Winkler process, and hydrogasification.

Table 6. Second-generation coal gasification projects

F.R.G.	United Kingdom	U.S.A.
Ruhrchemie/Ruhrkohle/Texaco	slagging pressure gasifier (British Gas Corporation)	Cogas process (Cogas Development Co. (U.S.A.) B.C.U.R.A. (U.K.))
Ruhrgas/Ruhrkohle/Lurgi		
Shell–Koppers	low-energy gasification (National Coal Board)	Hygas process (Institute of Gas Technology)
P.C.V. (Flick)		
Saarberg/Otto		
Thyssengas		
Rheinbraun (Winkler process)		
Rheinbraun (hydrogasification)		

In the U.K., the British Gas Corporation is studying coal gasification by the slagging pressure gasifier, and the National Coal Board is working on the low energy gasification process.

Two main processes are being developed in the U.S.A.: the Cogas process, a joint venture of the Cogas Development Co. and the U.K.-based B.C.U.R.A., and the Hygas process, operated by the Institute of Gas Technology, Chicago.

Coal gasification will permit a rapid revival of coal chemistry via the existing synthesis gas route.

I now turn to the second focal point of future coal conversion technology: coal hydrogenation. The coal hydrogenation process (figure 9), originally pioneered by Bergius and coworkers, involves the addition of hydrogen to a slurry of pulverized coal and heavy oil. A hydrocarbon mixture with high aromatic content results from this pressurized process. As Professor Kölling has also reported on developments in the coal hydrogenation field, I shall restrict myself to summarizing current projects. Table 7 gives an impression of activities currently being carried out in the U.K., the U.S.A. and the F.R.G.

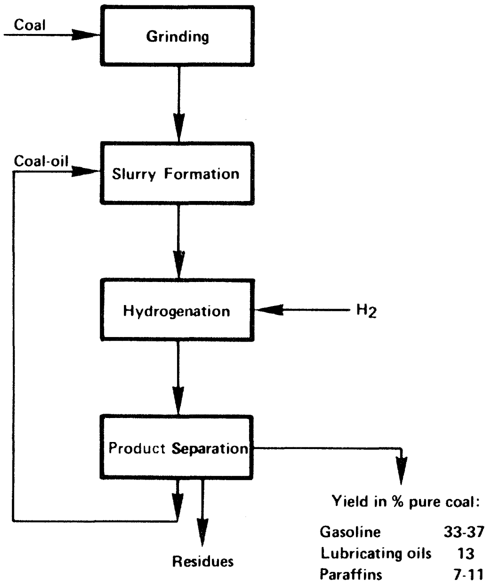


Figure 9. Hydrogenation of coal.

Table 7. Coal liquefaction projects

United Kingdom		
liquid solvent extraction	National Coal Board	
supercritical gas solvent extraction	National Coal Board	
U.S.A.		
Donor Solvent process	Exxon	
H-Coal process	Hydrocarbon Research Inc.	
Solvent Refined Coal process (SRC-I)	Pittsburg and Midway Coal Mining Co.	
Solvent Refined Coal process (SRC-II)	Gulf/Ruhrkohle/Steag	
F.R.G.		
hard coal	Ruhrkohle/Veba Öl	modified I.G. Farben process
	Saarbergwerke	
lignite	Rheinbraun	

In the U.K., the National Coal Board is working on the Liquid Solvent Extraction Process as well as on the Supercritical Gas Solvent Extraction Process, which has already been discussed in an earlier paper at this symposium.

The most important U.S. projects are: (1) the Exxon Donor Solvent process, already described by Dr Neavel; (2) the H-Coal process of Hydrocarbon Research Inc.; (3) the Solvent-Refined Coal process (SRC-I) of the Pittsburgh and Midway Coal Mining Co.; and (4) the Solvent-Refined Coal process (SRC-II) operated jointly by Gulf, Ruhrkohle and Steag, described by Dr Schmid.

In the F.R.G. the IG Farben process is being modified in various ways. Ruhrkohle/Veba-Öl as well as Saarbergwerke are working on processes based on hard coal while Rheinbraun is studying the liquefaction of lignite.

After gasification and hydrogenation, we come to the third future focal point of coal chemistry, the further development of synthesis gas (syngas) chemistry.

The industrially established syngas-based processes – ammonia and methanol production – would hardly require any modification on conversion from oil to coal. Economics alone will determine the date of the change over. In the U.S.A., the situation is such that coal's position is becoming more and more favourable. The commercial breakthrough is expected in this decade.

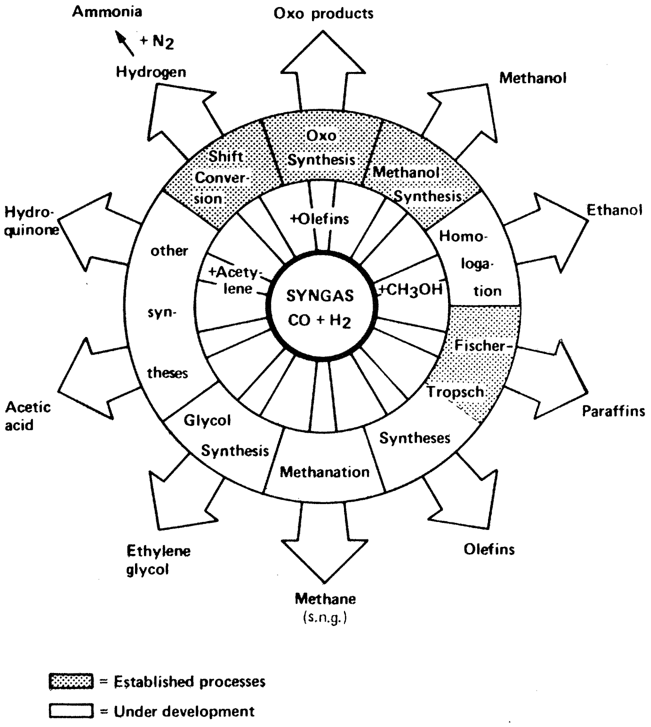


Figure 10. Future development of synthesis gas chemistry.

Figure 10 depicts other possibilities for the future development of syngas chemistry. Conversion of established processes (shaded) to coal-based synthesis gas would present no problems, no development work would even be necessary if coal gasification processes of the second generation were to be employed.

Methanol production and ammonia manufacture are examples of established processes. In addition, the Oxo synthesis presents a route to aldehydes from a syngas–olefin feedstock.

These industrial syntheses possess considerable industrial significance. The Oxo alcohols, which have a world production of 4,5 Mt, are used as plasticizer precursors, solvents and detergent feedstocks. The annual world production of methanol is even greater, at around 12 Mt.

The Fischer–Tropsch synthesis (also shaded), which is currently operated in South Africa to produce paraffins, does not require any conversion as it has always been based on coal. Present development work on the Fischer–Tropsch synthesis (unshaded) aims at altering the product spectrum towards olefins, in particular light olefins (C_2–C_4), with special catalysts. Even today, it is possible to produce a yield of 70 g light olefins cubic metre of $CO + H_2$ at s.t.p., corresponding to a selectivity of around 35%.

There is also an indirect route to the production of light olefins from syngas, i.e. the manufacture of oxygen-containing precursors by a modified Fischer–Tropsch process. Methanol is of particular interest. Two pathways are possible. The first is the homologation of methanol with synthesis gas to ethanol, which would then be dehydrated to ethylene in a third stage. Mobil is working on another potential route via dimethyl ether followed by dehydration. At present, neither process is sufficiently selective.

Various projects are devoted to combining the Fischer–Tropsch process with a thermal cracking process, leading to olefin production. The results show that this process is competitive with the other syngas-based processes for olefin production. The naphtha feedstock could be obtained from the Fischer–Tropsch entrained-bed synthesis. This process variant would produce a high yield of gasoline along with considerable amounts of ethylene and propylene.

Other synthetic routes currently being developed lead to the production of ethylene glycol, acetic acid and hydroquinone.

The methanation of syngas should also not be neglected as it presents a route to s.n.g. production.

These examples may help to stress the expected future significance of syngas chemistry.

To summarize, it can be said that at present the production of 'coal-oil' by coal hydrogenation is noticeably more expensive than by coal gasification. Theoretically at least, gasification processes that utilize h.t.r. heat are most economically attractive. The price of coal is of course the most important factor. If one compares the cost of manufacturing coal-oil and coal-based syngas with crude oil and oil-based syngas then it can be readily appreciated that the coal-based processes are still unable to compete with their oil-based counterparts. Nevertheless, the cost of coal-based syngas is very near the break-even point. If it proves feasible to use nuclear process heat from h.t.rs for coal gasification, then gas could be obtained from German coal around 20% cheaper than at present. Although we can reckon with a more marked increase in the cost of oil than of coal, it is extremely difficult to assess the point at which coal-based processes will be economically viable. However, it is reasonable to expect that chemicals from coal via syngas will be economically competitive in the 1980s.

Aside from economic considerations, there is also political value in coal-based chemistry, because it secures supply of raw materials for important sectors of the chemical industry and reduces the risks from relying on imports.

Far-sighted planning in research and technology will be necessary to achieve the aim of utilizing native resources to a wider and increased extent in this decade. This means that not only will industrial and academic scientists have to make a supreme effort but important decisions by statesmen will be required.

Discussion

J. M. Solbett (*Humphreys & Glasgow Ltd, London, U.K.*). Professor Falbe mentioned that the price of coal was the key factor in the economics of coal conversion. However, all conversion processes are inevitably much more complex than equivalent oil processing schemes, thus requiring far greater investment. I believe that it is this relatively high cost of coal conversion plants that controls their economic viability rather than the price of coal. Would the author care to comment on this?

J. Falbe. Of course, high investment costs have to be considered. However, I cannot agree that *all* coal conversion plants are much more complex than the corresponding oil processing schemes. For instance, the coal-gasification processes of Texaco and Shell–Koppers can be performed with a greater degree of simplicity than some of the original 'first-generation' coal gasification processes or other not so highly developed coal conversion technologies.

J. M. Thomas, F.R.S. (*Department of Physical Chemistry, University of Cambridge, U.K.*). In the figure consisting of concentric circles centred upon $CO + H_2$, Professor Falbe summarized the variety of important chemical feedstocks that may be synthesized from syngas. Many of these reactions – the production of paraffins, olefins, methanol, etc. – are already well worked out, and efficient catalysts are at hand. For those reactions that are under development, e.g. the synthesis of hydroquinone, glycol and acetic acid, it would be of interest, from the viewpoint of the academic chemist at least, to know the most desirable conditions which one would like to achieve for these syntheses. Would it, for instance, be better to go for homogeneous rather than heterogeneous catalysts? Is it best, knowing what is done at present in Fischer–Tropsch, for example, to go for high-pressure–high-temperature catalytic reactions? What kinds of catalyst would, in the opinion of Professor Falbe, prove ideal from the industrial standpoint?

J. Falbe. It is difficult to provide an answer to this question. However, I believe the primary aim is to seek a catalyst of high selectivity rather than to commit oneself to a certain – homogeneous or heterogeneous – application phase. As far as the technical considerations are concerned, both cases are equally desirable: the industrial Fischer–Tropsch synthesis is heterogeneously catalysed, the several variations of hydroformylation as prototypes of a syngas chemistry are homogeneously catalysed. It is probably not incorrect to assume that the various processes and the corresponding application phases will be retained in the future. For the various applications of syngas chemistry this means that the modified Fischer–Tropsch syntheses, methanation or methanol synthesis will probably be heterogeneous reactions, and homologization or glycol synthesis as 'Oxo-analogous' reactions will probably be homogeneous.