TRENDS IN RESEARCH AND DEVELOPMENT OF COAL CONVERSION TO
LIQUID FUELS AND BASIC CHEMICALS IN EUROPE

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Abstract - Three principal aspects - scientific, technical and
economic ones - are encountered in the future use of coal as a
raw material for the production of non-polluting liquid and
gaseous fuels and basic organic chemicals. The economic aspect
is the most decisive one, and it is not yet in favour of the
processes of coal conversion in question in most instances.
However, relative economy of these processes is going to im-
prove in the future.
The range of production costs varies widely, particularly with
costs of the feed coal available in a country and also to a less-
er extend with the process to be applied and with various local
factors. Appropriate economic calculations have thererore to be
made for each particular situation separately. The properties
of the coal available can vary considerably and are important
because of technical reasons mainly concerning the process to
be applied.
Widespread scientific and technical research and development in
the field of coal conversion have been reinitiated during the
last years and already produced a number of new suggestions, new
processes and modifications of well-known ones. The hydrogenative
and extractive conversion of coal to valuable liquids is one
main route, which is also presently aimed at the production
of aromatic chemicals. The other main route concerns the gasifi-
cation of coal and the production of fuels and various chemicals
from the synthesis gas. Fischer-Tropsch reactions as a means for
producing aliphatic chemicals are under development, as well as
other conversions starting from synthesis gas or methanol as a
feed material. In addition pyrolytic treatment of coal before its
use in power stations or gasifiers can be another source for
liquid and gaseous fuels and chemicals. The relations and deve-
lopments outlined in this abstract will be treated in some detail
in the lecture, preferably with respect to examples of scientific
and technical progress. Development of coal technology is also
performed in industrialized countries with minor coal reserves
or a high coal price level as a general contribution to energy
supply problems and as the basis of technology export.

INTRODUCTION

Conversion of coal to liquid hydrocarbons through hydrogenation of coal or coal
tar (Bergius-Pier processes) and through hydrogenation of carbon monoxide ob-
tained by coal gasification (Fischer-Tropsch processes) was applied particular-
ly during the period 193o to 1945. The total annual capacity of the plants
amounted to ca. 4 million tons of liquid products from coal hydrogenation and
ca. 1 million tons from the Fischer-Tropsch Synthesis (1). About 1/4 of the
Fischer-Tropsch capacity was installed outside of Germany. Today, commercial
conversion of coal to liquid hydrocarbons is performed only in Fischer-Tropsch
plants with a total capacity of ca. 3oo.ooo tons/a, run by Sasol (RSA) (2).

The economic feasibility of coal-to-oil conversion depends particularly on the
oil-to-coal-price ratio, and this has considerably increased during the past
few years and will probably increase still further. Processes of oil-from-coal
production seem to have reached today the level of economic performance in some
favoured situations. Resources of coal are estimated to be approximately 1o
times larger than those of mineral oil. Figure 1 shows a prognostic diagram
of the world mineral oil and coal production.
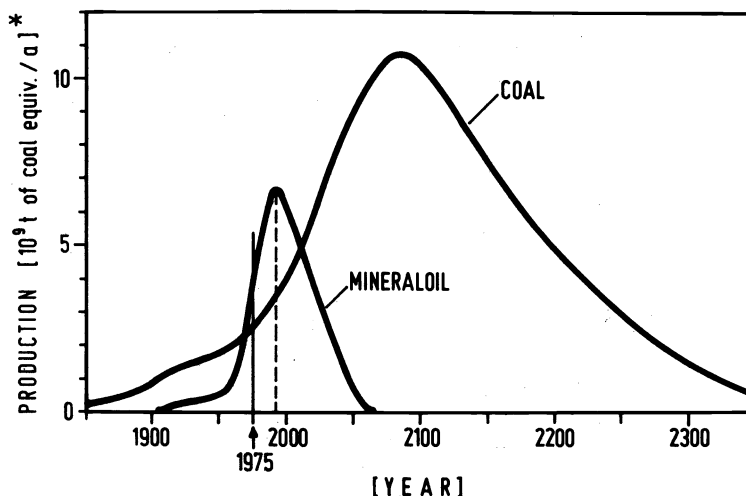
PROGNOSTIC WORLD PRODUCTION OF COAL AND MINERALOIL

*1 TON OF COAL EQUIVALENT TAKEN AS 7000 kcal/kg (or 28700 kJ/kg)

Fig. 1.

One can notice that the maximum of mineral oil consumption is expected to
occur already in about 15 years' time (3,4). Successive substitution of miner-
al oil by coal will have to be realized even earlier. Therefore the solution
of scientific and technological problems arising in this connection has to be
regarded as an urgently demanding task of fundamental importance for any
country.

Since 1973 a government program of energy research is being developed in West
Germany. One main topic concerns processes of coal conversion, the individual
points being

        -   gasification of coal;

        -   liquefaction of coal;

        -   electric energy production from coal;

        -   further processes of coal conversion.

The financial volume of the various projects amounted to 477 million DM in
1976, the contributions of the branches mentioned above being 264, 97, 84 and
32 million DM, respectively (5)(Fig. 2). In addition, projects of coal conver-
sion are performed within the regional program of Nordrhein-Westfalen.

These branches of coal conversion are strongly interrelated. De-
velopment of gasification processes is very important for coal liquefaction
also because production of hydrogen for direct coal hydrogenation or of syn-
thesis gas for the Fischer-Tropsch process contribute decisively to technolo-
gical as well as economical feasibility of coal liquefaction.

Degasification i.e. pyrolysis of coal, as a first step during coal
utilization in power stations, could also produce appreciable quantities of
liquid tar products which can be regarded as a special crude oil from coal.
Production of this material could be very large when generally degasified coal
instead of original coal would be used in thermal power stations.

Additional benefits for coal gasification and thus for Fischer-Tropsch synthe-
this or coal hydrogenation are expected from the use of thermal energy from
nuclear power stations for the endothermic reactions of coal gasification with
steam (1,6,7).

Development of technologies of coal liquefaction in Germany at present aims
particularly at the production of basic aliphatic and aromatic chemicals in-
stead of or in addition to the production of liquid fuels.

ENERGY RESEARCH PROGRAM OF COAL CONVERSION OF THE GERMAN FEDERAL REPUBLIC		
BRANCH	FINANCIAL VOLUME OF SCHEDULED PROJECTS (1976)	AVERAGE DEGREE OF SPONSORSHIP
1.1 GASIFICATION	$264 \cdot 10^6$ DM	51 %
1.2 LIQUEFACTION	$97 \cdot 10^6$ DM	83 %
1.3 ELECTR. ENERGY PROD.	$84 \cdot 10^6$ DM	50 %
1.4 FURTHER PROCESSES	$32 \cdot 10^6$ DM	65 %
	$477 \cdot 10^6$ DM	58 %

Fig. 2.

As domestic bituminous coal is very expensive, production of valuable compounds might at first allow an economical use of coal as a raw material. Today in West Germany organic chemicals are almost completely derived from mineral oil. The argument of a possible future technology export is also of importance for the development of processes of coal conversion.

GENERAL ECONOMIC INTERRELATIONS, PROPERTIES OF THE FEED COAL AND PRINCIPAL ROUTES OF COAL LIQUEFACTION

Calculations of economic feasibility have been performed for various processes and products of coal conversion, for different prices of coal and special local situations. The price of the feed coal is the dominating and mostly decisive parameter. Its percentual contribution to production costs e.g. of gasoline via the Fischer-Tropsch synthesis ranges from about 25 % in the case of a very cheap coal, as available in the Republic of South Africa (ca. 1.15 DM/10^6 kcal), to about 32 % in cases of cheap coal, as available in the USA or Australia (ca. 2.5 DM/10^6 kcal), to about 45 % in the case of relatively cheap "Braun-kohle" in West Germany (5.0 DM/10^6 kcal), to almost 60 % to 70 % in West Germany for types of minor quality (10 DM/10^6 kcal) and high-quality bituminous coal (18 DM/10^6 kcal) as normally mined in the Ruhr region of West Germany (1,8) (Fig. 3). According to the large differences in coal prices, today production of liquid fuels from coal is economically feasible in South Africa; it seems to be almost feasible in the USA or Australia, and it is at present beyond the economic level with "Braunkohle" and even more with bituminous coal as a raw material in West Germany (1,8). In accordance with these statements, large industrial projects with coal as a raw material are being realized in South Africa (9,10) (a 2-million ton/a capacity Fischer-Tropsch plant, a ca. 320.000 ton/a ammonia plant including the Koppers-Totzek coal gasification process, a 300.000 ton/a carbide plant for acetylene production, and a large complex of coal degasification using the COED-process as a primary step in a power station, which will thus produce several million tons of hydrocarbon liquids from coal per year as byproducts of electrical energy from coal).

In the USA several processes of coal conversion are in a state between pilot plant and demonstration plant operation. Main aspects of coal conversion in the USA are the production of non-polluting fuels such as methane or a bituminous extract with low sulfur content.

Australia seriously considers the build-up of a first industrial plant for the production of liquid fuels from coal via the Fischer-Tropsch process.

ESTIMATED CONTRIBUTIONS OF COAL COSTS TO TOTAL PRODUCTION COSTS
AND TOTAL PRODUCTION COSTS PER TON OF GASOLINE FROM COAL VIA
FISCHER-TROPSCH-SYNTHESIS   (JAN.1974)

APPROXIMATE PRICES OF FEED COAL ON A THERMAL BASIS [DM/10^6 kcal; DM/4,2·10^6 kJ]	PERCENTAGE OF COAL COSTS RELATED TO THE TOTAL PRODUCTION COSTS (FISCHER-TROPSCH-SYNTHES.)	APPROXIMATE PRODUCTION COSTS PER TON OF GASOLINE [DM/ton]
1,5 SASOL , R.S.A.	25 %	290
2,5 USA , AUSTRALIA	32 %	340
5 „BRAUNKOHLE", W-GERMANY	45 %	420
10 – 18 BITUMINOUS COAL, W-GERMANY	60-70%	580 – 850

Fig. 3.

In Europe the state of development of coal-gasification processes in general
is more advanced than that of liquefaction processes. Laboratory and pilot
plant experiments in West Germany aim at demonstration plant operation in a
few years' time; however, it is still with financial support from the energy
research program.

In a recent detailed expertise of Union Rheinische Braunkohlen-Kraftstoff AG,
Wesseling (6) concerning the economics of a production of low molecular weight
olefins and other chemicals through known techniques of the Fischer-Tropsch
synthesis, average costs of about 8oo DM per ton of the desired products have
been calculated. The coal price was taken as 7 DM/1o^6 kcal. The ratio of pro-
duction costs to the prices of obtainable products was found within the range
of about 1.6 to 3.3 for the 12 processes regarded.

Production costs for only a low-sulfur heavy fuel oil from coal are substan-
tially lower than those of the valuable products mentioned above. These have
been calculated as 31o - 35o DM/t in 1975 using a coal price of 13o DM/t (11),
and the production of this material in the USA is said to be already economi-
cal

The choice of any process of coal conversion depends on the properties of
the feed coal. Coal with a high ash content is better suited for gasification
and hence for Fischer-Tropsch synthesis than for direct hydrogenation. From
such types of coal appreciable yields of tars can be obtained by low tempera-
ture carbonization, and this may be further hydrogenated to yield motor fuels o:
organic chemicals. More than half of the plant capacity of coal hydrogenation
before 1945 was run with coal tars. Bituminous coal with a high content of
volatile matter is suited for direct hydrogenation, extraction or hydrogena-
tive extraction. The coal reactivity is increased by its pyrite content.

The principal routes of coal liquefaction are outlined in Fig. 4. The Fischer-
Tropsch synthesis works with the purified synthesis gas from coal. The products
are separated from the tail gas. Selectivity can be adjusted within a wide
range. The product compounds are generally aliphatic and may be recovered as
motor fuels, olefins, paraffinic hydrocarbons, alcohols, waxes and fuel gas.

Direct hydrogenation of coal yields valuable liquid products and a residue
of solid matter and non evaporable asphaltenes. These may, for example, be se-
parated by means of distillation. The distillate oil can be processed further
by hydrogenation (hydrofining operation) in gas phase or mixed phase processes
to yield naphtha (or motor fuels), aromatic chemicals and some gaseous by-
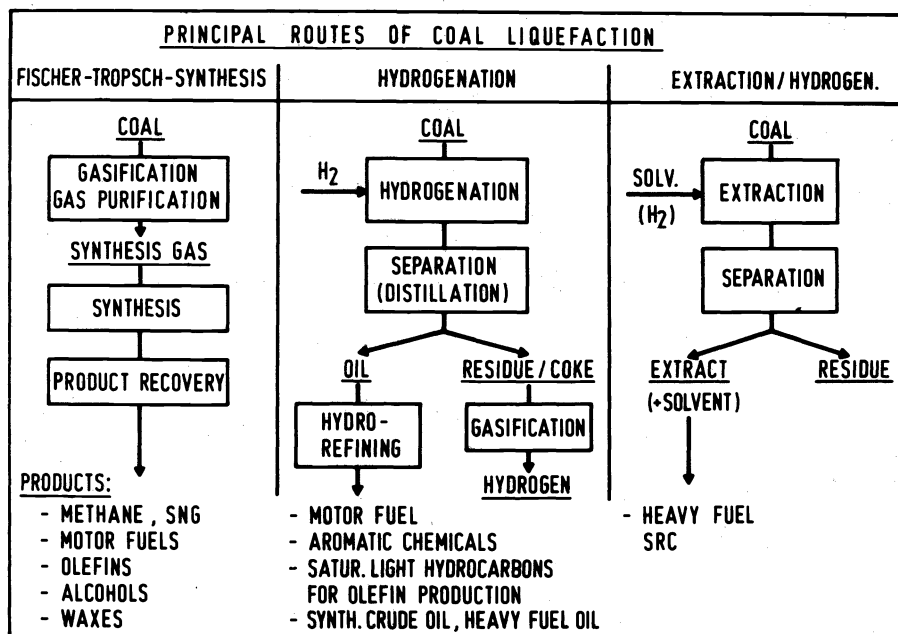products. Hydrogen can be produced from the residue.

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│            PRINCIPAL  ROUTES  OF  COAL  LIQUEFACTION                     │
├─────────────────────────┬─────────────────────┬────────────────────────┤
│ FISCHER-TROPSCH-SYNTHESIS│     HYDROGENATION   │  EXTRACTION/HYDROGEN.   │
├─────────────────────────┼─────────────────────┼────────────────────────┤
│          COAL           │        COAL         │         COAL            │
│    ┌──────────────┐     │  H2 ┌─────────────┐ │  SOLV. ┌────────────┐   │
│    │ GASIFICATION │     │ ──▶│HYDROGENATION│ │  ───▶ │ EXTRACTION │    │
│    │GAS PURIFICATION│   │    └─────────────┘ │  (H2)  └────────────┘   │
│    └──────────────┘     │    ┌─────────────┐ │        ┌────────────┐   │
│     SYNTHESIS GAS       │    │ SEPARATION  │ │        │ SEPARATION │    │
│    ┌──────────────┐     │    │(DISTILLATION)│ │        └────────────┘   │
│    │  SYNTHESIS   │     │    └─────────────┘ │                         │
│    └──────────────┘     │   OIL    RESIDUE/COKE│  EXTRACT      RESIDUE  │
│    ┌──────────────┐     │ ┌─────┐ ┌──────────┐│  (+SOLVENT)             │
│    │PRODUCT RECOVERY│   │ │HYDRO-│ │GASIFICATION││                       │
│    └──────────────┘     │ │REFINING│ └──────────┘│                      │
│                         │ └─────┘    HYDROGEN  │                        │
│ PRODUCTS:               │                      │                        │
│   - METHANE, SNG        │ - MOTOR FUEL         │ - HEAVY FUEL           │
│   - MOTOR FUELS         │ - AROMATIC CHEMICALS │   SRC                  │
│   - OLEFINS             │ - SATUR. LIGHT HYDROCARBONS│                  │
│   - ALCOHOLS            │   FOR OLEFIN PRODUCTION│                       │
│   - WAXES               │ - SYNTH.CRUDE OIL, HEAVY FUEL OIL│            │
└─────────────────────────┴─────────────────────┴────────────────────────┘
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Fig. 4.

Extractive processing of coal can be favourably performed with hydrogen trans-
ferring solvents. The extract, a heavy fuel with low sulfur content, has to be
separated from the residual matter.

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┌──────────────────────────────────────────────────────────────────────┐
│             COMBINED  PROCESSES  OF  COAL  LIQUEFACTION                  │
│                                                                         │
│  COAL ┌──────────────┐                                                  │
│  ────▶│ LOW TEMPER.  │────▶ FUEL GAS                                    │
│       │ CARBONISATION│                                                  │
│       └──────────────┘                                                  │
│          │         │                                                    │
│       TAR+OIL      COKE                                                  │
│  H2      │          │         ┌────────────┐                            │
│ ───▶┌──────────────┐│┌──────────┐│ GASIFICATION│  H2 FOR TAR           │
│     │ HYDROREFINING │││ POWER    ││└────────────┘  HYDROGEN.            │
│     └──────────────┘││ STATION  ││                                      │
│                     │└──────────┘│  SYNTHESIS GAS                       │
│                     │            │  ┌──────────────┐                    │
│                     │            │  │FISCHER-TROPSCH-│                   │
│                     │            │  │SYNTHESIS      │                    │
│                     │            │  └──────────────┘                    │
│ PRODUCTS: LIQUID FUELS   ELECTR. ENERGY   ALIPHAT. CHEMICALS            │
│           AROM. CHEMICALS (STEAM)         LIQUID FUELS                  │
│           (FUEL GAS)                      FUEL.GAS                      │
└──────────────────────────────────────────────────────────────────────┘
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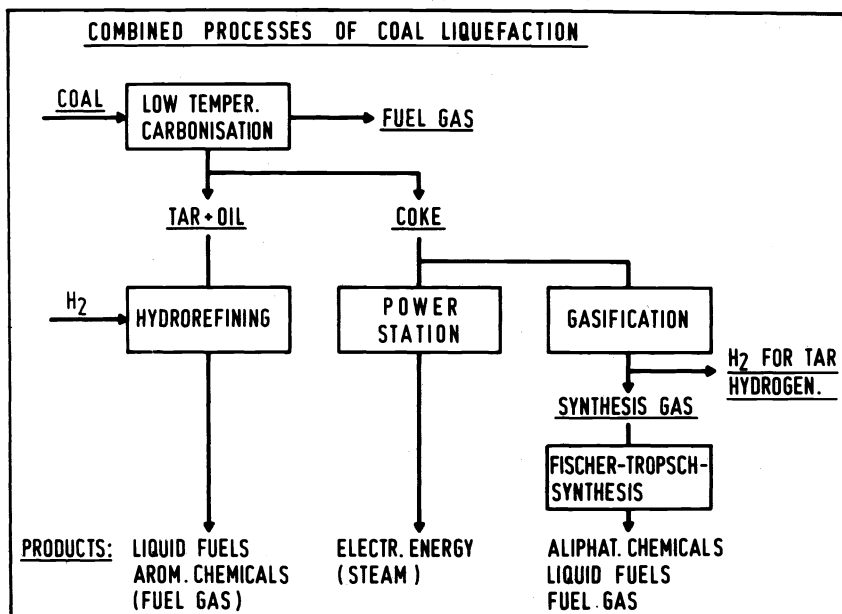
Fig. 5.

A fourth combined version is shown in Fig. 5. Low-temperature carbonization
of the coal yields tar, oils, coke and a fuel gas. Tar and oil will be pro-
cessed by hydrorefining to, for example, motor fuels and aromatics. The coke
can be used for energy and steam production. However, the coke can also be
gasified to yield hydrogen for the processes of hydrogenation or to yield syn-
thesis gas for a Fischer-Tropsch plant. This scheme is very flexible and the

.optimum relative size of the individual process units will be governed by the
spectrum of products desired, the relative economy of the routes in question
and the properties of the feed coal.

SYNTHESIS GAS AND HYDROGEN PRODUCTION

Production of synthesis gas from coal for the Fischer-Tropsch process affords
almost half of the total plant capital required (1,12). For direct hydrogena-
tion of coal and further conversion of the products, the production of hydro-
gen is also an important process step. Any progress in coal gasification is
therefore beneficial for processes of coal liquefaction. New optimum routes
of direct coal hydrogenation have been developed on the basis of present avail-
able gasification technology applicable on the residue of coal hydrogenation.

In Fig. 6 current projects of development of synthesis gas and hydrogen pro-
duction are mentioned (4,5). The well-known Lurgi-Pressure-Gasification of
Coal with oxygen and steam in a fixed bed is being increased in throughput by
increasing the diameter of the reactor from 3.7 to 5 m and by other means.
The maximum gasification pressure shall be elevated from 30 to 100 bar so that,
for instance, organic byproducts can react with hydrogen to yield methane. By-
products such as tar and phenols will also be converted to synthesis gas and to
methane in the gasification zone. Higher efficiency of the process shall be
obtained by operating at higher temperatures; however, new constructions for
removal of the ash in a liquid state instead of in a solid state have, there-
fore to be developed (5).

CURRENT PROJECTS OF COAL GASIFICATION FOR SYNTHESIS GAS PRODUCTION	
PROCESS	INTENTIONS OF DEVELOPMENT
LURGI (RUHRGAS, RUHRKOHLE, STEAG) FIXED BED	· INCREASE IN REACTOR DIAMETER (3.7→5m) · INCREASE IN PRESSURE (30→80(100) bar) · REDUCTION OF BYPRODUCTS (TAR, PHENOLS) · INCREASE IN TEMPERATURE, LIQU. ASH REMOVAL
KOPPERS-TOTZEK (SHELL) ENTRAINED PHASE	· APPLICATION OF PRESSURE (1→15 bar)
TEXACO (RUHRCHEMIE, RUHRKOHLE) ENTRAINED PHASE - PRESSURE GASIFICATION	· GASIFICATION OF COAL AND VARIOUS OTHER FEEDS, E.G. RESIDUE OF COAL HYDROGENATION
RUMMEL - OTTO / SAARBERGWERKE ENTRAINED PHASE, LIQUID ASH	· COAL GASIFICATION AT 25 bar
ALLOTHERMIC FLUID BED GASIFICATION OF COAL WITH STEAM AND PROCESS HEAT FROM A NUCLEAR POWER STATION (BERGBAUFORSCHUNG)	

Fig. 6.

The Koppers-Totzek-Process of coal gasification with oxygen in an entrained
phase, the ash being in liquid state at reaction temperature, is being develo-
ped by Koppers and Shell to operate at a pressure of 15 bar (5).

The Texaco-Process for pressure gasification of preferably heavy liquid fuels
is developed for processing of coal and also of residues from coal hydrogena-
tion in a cooperation of Texaco, Ruhrchemie and Ruhrkohle AG (5).

Another process of coal gasification, the Rummel-Otto-Process, in which the
burning mixture of fine coal particles with oxygen and steam is directed to
the surface of the liquid ash at the bottom of the reactor, is going to be
developed by the firms Otto and Saarbergwerke for operation at a pressure of
25 bar (5).

It is common to these four projects that future processes of coal gasification are generally thought to operate at relatively high pressure, and at the reaction temperature to be above the melting point of the ash (e.g. $1500^{\circ}C$). The throughput has to be high and the production of an individual gasifier to be large because of the great amounts of coal which are expected to be converted in the future. Finally, <u>allothermic gasification of coal</u> with steam in a fluid bed, using external heat, is mentioned. This heat shall be supplied in future from a High-Temperature-Gas-Cooled Nuclear Reactor by means of heat exchange with helium as the medium for heat transfer (5).

Processes of high-temperature coal gasification generally produce gases with a high CO content. Synthesis gases with less carbon monoxide or pure hydrogen are obtained through the water gas shift reaction and absorption of the CO_2.

HYDROGENATION AND EXTRACTION OF COAL

Treatment with hydrogen at high pressure and with solvents, mostly in the presence of catalysts, converts coal more or less completely to oil. The properties of these oils range from a material which melts at about $200^{\circ}C$ - a heavy fuel with low sulfur and ash content to light boiling hydrocarbons in the gasoline range. In addition, a residue rich in ash and rich in poorly reactive asphaltenes and gaseous compounds are obtained. As compared with former application of coal hydrogenation, modern processes have to observe the demands of environment protection. Whereas formerly hydrogen was produced from valuable coke, modern gasification technologies allow the hydrogen to be produced from almost any carbonaceous material and also from the residue of coal hydrogenation. Reactive bituminous coals with a high content of volatile matter are best suited for hydrogenation. A high ash content of a coal reduces the efficiency of hydrogenation considerably.

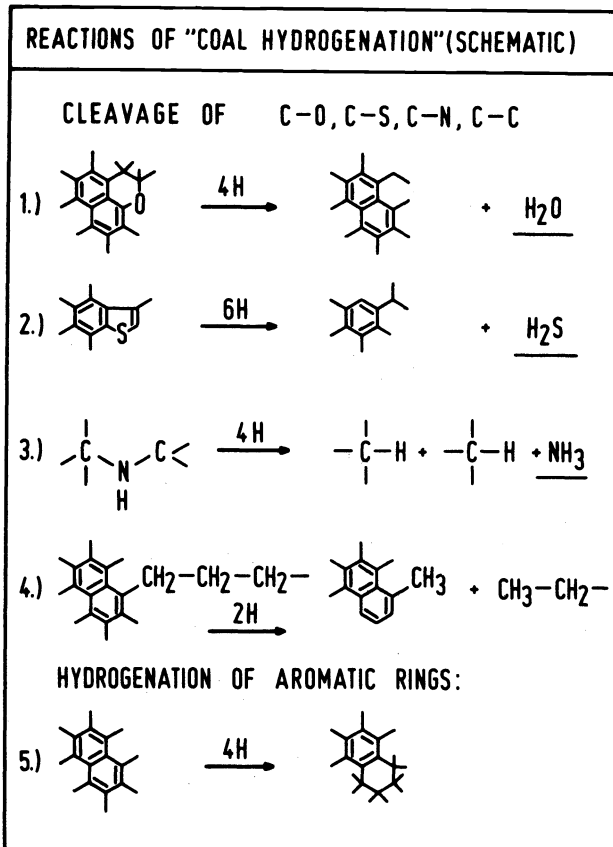Some main <u>reactions in coal hydrogenation</u> are schematically shown in Fig. 7.

Fig. 7.

The bonds between carbon and oxygen, sulfur or nitrogen are commonly more
reactive than the carbon/carbon bonds. Hence hydrogen is initially preferable
consumed by reactions which produce water, hydrogen sulfide and ammonia and
hereby reduce the molecular weight and increase the solubility of the coal
considerably. Under more severe conditions carbon/carbon bonds are also hydro-
genatively split leading to aromatic ring saturation.

The production of a heavy fuel of low sulfur and ash content by extraction or
extractive hydrogenation of coal appears very costly in Europe; however, this
route is attractive in the USA. In these processes the reaction conditions are
relatively mild. The extract and the residue are separated by means of filtra-
tion or centrifugation. The main product, solvent refined coal (SRC), will be
used in power stations. However, it can eventually be refined further. Inter-
national cooperation has become very important today in the field of energy
technology. Cheaply produced solvent refined coal might be transported from
the USA to Europe in the future. A financial and technical participation of
the consortium of RAG/STEAG in the demonstration plant development and opera-
tion of the Gulf-SRC-Projects has therefore been conceived (5).

Non-hydrogenative extraction of coal, sometimes at a supercritical state of
the solvent, has been performed in Great Britain during the past years (13,14).

As already stated, activities in coal hydrogenation in West Germany particu-
larly focus on processes which will finally yield preferably basic chemicals
and raw materials for the chemical industry, namely individual aromatic hydrocar-
bons and mixtures of saturated hydrocarbons in C_2-C_4 and the gasoline range to
be used as feed for an olefin production. One interesting possibility arises
from the IG-process as formerly industrially applied. However, a substantially
lower pressure will be possible because now it will not be the intention to
transform also the poorly reactive asphaltenes to valuable liquids. The resi-
due of hydrogenation will serve as the source of hydrogen in a process of par-
tial combustion at about 8o - 1oo bar (Fig. 8).

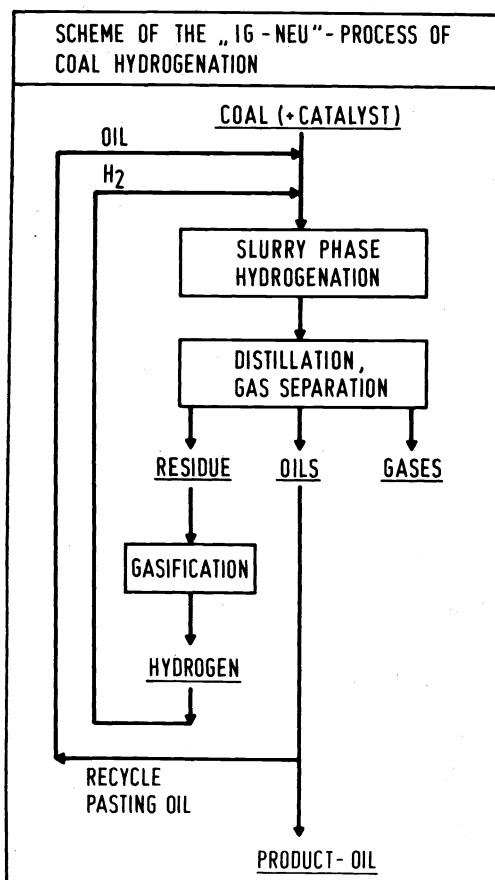SCHEME OF THE „IG-NEU"-PROCESS OF COAL HYDROGENATION

Fig. 8.

The residue of this coal hydrogenation in a slurry phase is obtained from the reaction mixture by means of distillation under vacuum and remains in a liquid state at elevated temperature, so that it can be pumped to the gasification unit. The initial slurry of coal particles and oil will be prepared with a distillate product oil. Hence the level of asphaltenes in the reaction mixture remains low. The further refining of the product oil can be performed in principally known processes; however, these have to be adapted to the new feed stocks. A comparison of this "IG-NEU" process with the classic IG way of coal hydrogenation is given in Fig. 9 on the basis of a feed stream of 1oo t/h of coal (15). The pressure will be only 3oo instead of 7oo bar, the reactor volume required 133 instead of 16o m^3, hydrogen consumption only 5.5 t/h instead of 7.3 t/h and the undesired yield of gases only 16 t/h instead of 2o t/h. The yield of oils is about 13% lower i.e.53 instead of 6o.9 t/h. However, in the old process additional valuable coke was consumed for hydrogen production, whereas in the new process no residue of hydrogenation has to be handled except for gasification. Hence all steps of the process are technologically feasible and no particular problems of environment protection arise. Fundamental work on coal hydrogenation in pilot plants is presently performed by Bergbauforschung in Essen (5) and Saarbergwerke in Saarbrücken (5,16). A small pilot plant with a capacity of 3 tons of coal per day is going to be erected by Saarbergwerke (5). A coal hydrogenation plant with a capacity of about 1oo tons of coal per day will probably be built within a few years time in the Ruhr-Coal district.

COMPARISON BETWEEN THE "IG-NEU" PROCESS AND THE CLASSIC IG - PROCESS

	IG-CLASSIC	IG-NEU
FEED COAL , WAF, t/h	100	100
PRESSURE , bar	~700	~300
TEMPERATURE , °C	~475	~475
VOLUME OF REACTOR REQUIRED, m^3	160	133
RECYCLE PASTING OIL :	RESIDUAL OIL	DISTILLED OIL
H_2 CONSUMED , t/h	7.3	5.5
H_2 PRODUCED FROM		
COKE	7.3	—
TOPPED RESIDUE	—	4.14
PRODUCTS , t/h		
LIQU.: GASOLINE	12.1	11.0
MIDDLE OIL	31.4	19.0
HEAVY OIL (DISTIL.)	17.4	23.0
	60.9	53.0
HYDROCARBON GASES		
METHANE	5.3	4.2
ETHANE	4.9	3.9
PROPANE	6.3	5.0
BUTANE	3.5	2.9
	20.0	16.0

Fig. 9.

It is also possible to recover phenols and multiring aromatics from the liquid products of coal hydrogenation. However, normally the primary distillates will be directly processed further in gas phase and mixed phase hydrogenative operations in fixed bed catalytical reactors.

Final yields (related to 1ooo kg of coal; moisture and ash free) of aromatics
and of aliphatic hydrocarbons which might be used as raw materials for organic
chemicals are given in table 1. These can be obtained in consecutively working
processes of slurry phase coal hydrogenation and further hydrogenation of the
distillates in fixed bed reactors.

The yields of almost only chemicals from 1ooo kg of coal (moisture and ash
free) as to be obtained from a further combination with pyrolysis of the satu-
rated hydrocarbon products of coal hydrogenation are listed in table 2. Addi-
tional improvements of these yields can be expected to be obtained due to
continued development of coal hydrogenation.

Table 1.   Yields of basic aromatic chemicals and of saturated hydrocarbons
           used as raw material for olefin production, to be obtained through
           hydrogenation of 1000 kg of coal (moisture and ash free).

	kg of products
Basic chemicals	
Benzene	45
Toluene	77
Xylenes	61
Higher Aromatics	2o
	2o3
Raw materials for olefin production	
Ethane	65
Propane	85
Butanes	55
Naphtha	21o
	415
Methane	67
	685

Table 2.   Yields of predominantly basic organic chemicals to be ob-
           tained from 1000 kg of coal (moisture and ash free) through
           processes of coal hydrogenation and from pyrolysis of hydro-
           carbons.

Product	Yield, kg		Σ
	Hydrogenation	Pyrolysis	
Hydrogen	–	8	8
Methane	67	67	134
Ethylene	–	177	177
Propane	–	57	57
Butadiene	–	14	14
Butenes	–	13	13
i-Butane	14	–	14
Benzene	45	13	58
Toluene	77	1o	87
Xylenes	61	3	64
Styrene	–	2	2
Motor gasoline	2o	29	49
Fuel oil (internal use)	–	8	8
	284	4o1	685

Of general interest are also the activities of Lurgi and other corporations to develop opti-
mum routes of tar hydrogenation (5) because tars, obtained in various processes of coal pyro-
lysis and gasification, may become important resources for chemicals and fuels.

FISCHER-TROPSCH SYNTHESIS AND RELATED PROCESSES

The high level of coal prices in Europe has directed also the development acti-
vity in the field of Fischer-Tropsch synthesis towards the selective formation
of valuable organic chemicals. Low molecular weight olefins $C_2 - C_4$, alcohols,
α-olefins and polymethylen are the mainly desired products. Selectivity shifts
in the Fischer-Tropsch system are complicated due to the complexity of the re-
action. The main features of product selectivity can be characterized as
follows (Fig. 10).

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PRODUCT SELECTIVITY OF THE FISCHER-TROPSCH-SYNTH.

- CHAIN LENGTH;

  MAIN REACTION OF CHAIN FORMATION E.G.:

  $$3\,CO + 6\,H_2 \longrightarrow -CH_2-CH_2-CH_2- + 3\,H_2O$$

- METHYL BRANCHING : $-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-$

- PARAFFINS   : $-CH_2-CH_2-CH_3$

- OLEFINS   : $-CH_2-CH=CH_2$

  $-CH=CH-CH_3$

- ALCOHOLS   : $-CH_2-CH_2-CH_2-OH$

- ALDEHYDES, KETONES, ACIDS, ESTERS

</div>
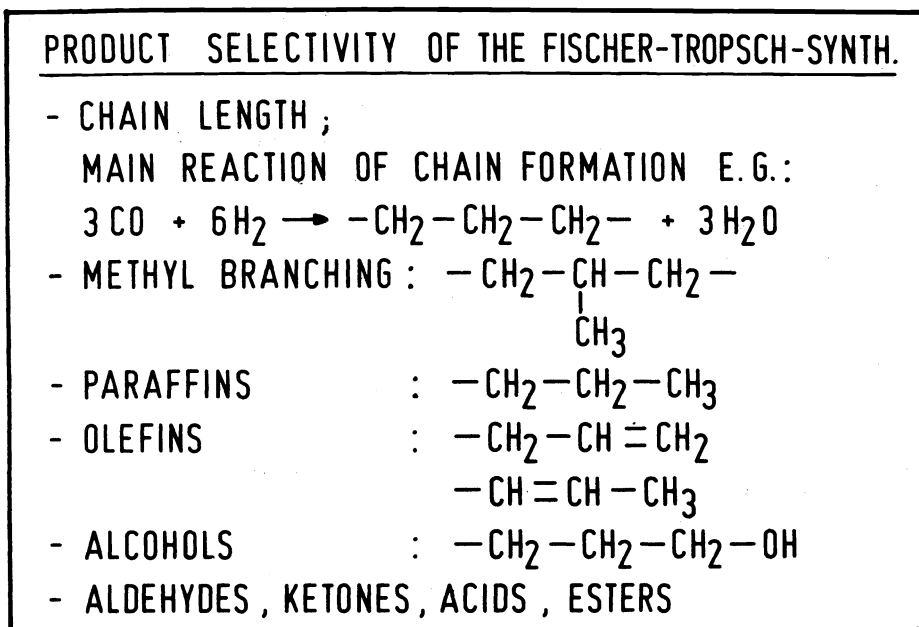
Fig. 10.

The fundamental reaction is that of growth of aliphatic chains from CO and H_2
at the catalyst surface. In a situation of high selectivity this growth re-
action can produce polymers with molar masses of, for example, one million.
This is possible with active ruthenium catalysts at low reaction temperature
of about 100°C and high pressure of about 1000 bar (17,18). On the other hand,
only methane is produced from CO and H_2 with nickel catalysts at about 250°C
and higher temperatures. Formation of small molecules without excessive methane
selectivity can be obtained best with iron catalysts. In dependence of the re-
action conditions some methyl branching in the products is observed. The mole-
cules are desorbed from the catalyst surface as paraffins, olefins (mainly α-
and β-olefins), alcohols (preferably n-alcanols-(1)) and some aldehydes, ke-
tones, acids and esters. The selectivity of the reaction is strongly depen-
dent on catalyst properties as well as on reaction conditions (18).

A survey of catalysts, reaction conditions and products is given in Fig. 11.
The active metals are particularly iron, cobalt, nickel and ruthenium. Iron,
cobalt and nickel catalysts have been successfully promoted, but not ruthenium
catalysts. Iron is the most flexible catalyst metal and is used in technical
operations. The products can range from predominantly gases to predominantly
light boiling liquids, to paraffin waxes as the main fraction.

The intention of more selectively performing Fischer-Tropsch reactions
is thought to be realized on the basis of an improved understanding of the
individual steps in the complex network of interconnected reactions (19).

CATALYSTS, REACTION CONDITIONS AND PRODUCTS OF THE FISCHER - TROPSCH - SYNTHESIS				
CATALYST		TEMP.-RANGE [°C]	PRESS.-RANGE [bar]	MAIN PRODUCTS
METAL	SUPPORT, PROMOTOR			
IRON	ALUMINA, SILICA KIESELGUHR, MgO K$_2$O, Na$_2$O, Cu	220 - 370	10 - 40	1) PARAFFINWAX (MIDDLE DISTILLATES, GASOLINE, GASES) 2) MIDDLE DISTILLATES (PARAFFINWAX, GASOLINE, GASES) 3) GASOLINE, OLEFINIC GASES (METHANE) 4,5) n-OLEFINS, n-ALCOHOLS
COBALT	KIESELGUHR, MgO, ThO$_2$	180 - 205	1 - 15	MIDDLE DISTILLATES, GASOLINE PARAFFINWAX, GASES
NICKEL	KIESELGUHR MgO, ThO$_2$	180 - 200	1	GASOLINE, MIDDLE DISTILLATES, PARAFFINWAX (METHANE)
RUTHENIUM	NONE	110 - 150	200 - 1000	POLYMETHYLENE (PARAFFINWAX, DISTILLATES)

Fig. 11.

Figure 12 shows the __reaction sequence__ for the prolongation by one CH$_2$ group of a growing chain at the catalyst surface and the various product desorption reactions according to Pichler, Schulz and Zein El Deen (20).
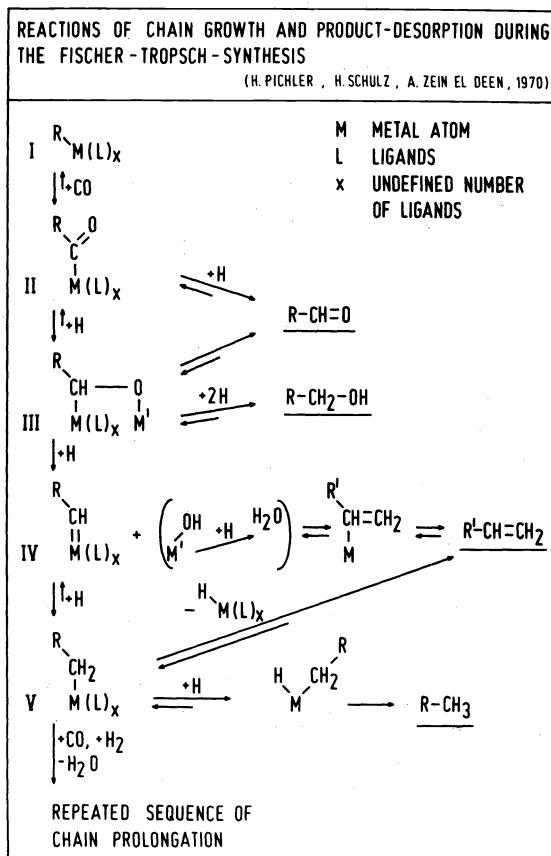
Fig. 12.

Chain growth takes place as a ligand reaction between alkyl group and carbon monoxide. The resulting acyl group reacts with hydrogen in steps with one H-atom. The intermediates of this reduction sequence can be desorbed as aldehydes, alcohols, olefins or paraffins. Many of these reactions are reversible. The relative rate of these reactions, which generally govern selectivity, are affected by various means. A parameter, which strongly influences the general surface state and product selectivity, is the carbon monoxide partial pressure. The real system of reactions is far more complicated than shown in Fig. 12. Distinct reaction paths have recently been found by tracer experiments and radio-gaschromatography (19,20,21,22). It is obvious from this reaction scheme that changes in reaction parameters will simultaneously affect more than one or two of these individual reactions, and therefore desired selectivity changes are expected to be obtained through complicated optimizing procedures regarding the catalyst as well as the reaction conditions.

Main characteristics of product selectivity are

- average chain length;
- chain branching;
- olefin/paraffin ratio;
- alcohol formation;
- carbon deposition and
- methane formation (19).

General trends of changes of these characteristics of selectivity are reported in Fig. 13. One can notice, for example, that an increase in reaction temperature will reduce the average molecule size, increase the number of methyl side groups, favour the deposition of carbon on the catalyst surface and increase the methane selectivity. The olefin/paraffin ratio during one run decreases with increasing temperature; however, products with a high olefin content can be obtained at a high level of reaction temperature with appropriate catalysts. As shown in the figure, also total pressure, H_2/CO-ratio of the synthesis gas, degree of conversion, space velocity and alkalization of iron catalysts have a marked influence on the features of selectivity.

FISCHER - TROPSCH SYNTHESIS ; TRENDS OF SELECTIVITY CHANGES						
PARAMETER TO BE IN- CREASED	CHARAKTERISTICS OF PRODUCT SELECTIVITY					
	AVERAGE CHAIN LENGTH	CHAIN BRANCHING	OLEFIN/ PARAFFIN- RATIO	ALCOHOL SELECTIVITY	CARBON DEPOSITION	METHANE SELECTIVITY
TEMPERATURE	- - -	+ +	+ , -	(-)	+ +	+ +
PRESSURE	+ +	- -	~	+ +	~	-
H_2/CO - RATIO	- -	+ +	- -	- -	- -	+ +
DEGREE OF CONV.	~	~	- -	- -	+	(+)
SPACE VELOCITY	~	~	+ +	+ +	~	(-)
ALKALIS. OF IRON CATALYSTS	+ +	- -	+ +	+	+	-

+++, ++, +   INCREASE WITH INCREASING PARAMETER
---, --, -   DECREASE   "   "   "
~   MORE COMPLEX RELATION ; LESS PRONOUNCED DEPENDENCY

Fig. 13.
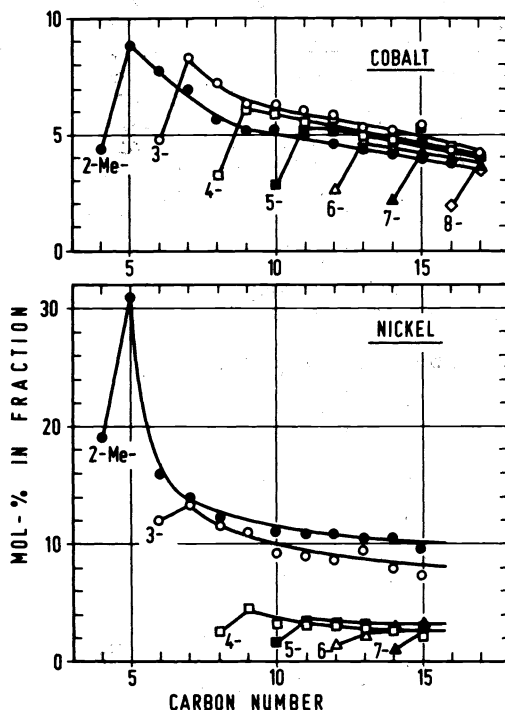
DISTRIBUTION OF MONOMETHYL BRANCHED HYDROCARBONS IN
PRODUCTS FROM NORMAL PRESSURE SYNTHESIS WITH COBALT
AND NICKEL CATALYSTS. (190°C, 1 bar, $H_2/CO = 2:1$, SPACE-
VELOCITY 100 h^{-1}, 100 Co : 18 ThO_2 : 100 KIESELGUHR AND
100 Ni : 18 ThO_2 : 100 KIESELGUHR)

Fig. 14.

As an example of the sophisticated selectivity interrelations in Fig. 14 the
content of methyl branched compounds as dependence of carbon number is shown
for one product obtained with a cobalt catalyst and another one obtained with
a nickel catalyst (19). These diagrams and their change with reaction condi-
tions obviously represent a wealth of information about the catalytic system
and the type of reactions at the active sites.

In 1970 an expertise from Pichler and coworkers (1) evaluated the various
technical and economical aspects of a liquid fuel production from coal in West
Germany. Since then the oil to coal price ratio has increased remarkably. A
detailed new expertise concerning the possibilities of a production of alipha-
tic chemicals via the Fischer-Tropsch route has been elaborated by the "Union
Rheinische Braunkohlen AG" (Fig. 15). Some of the results are reported in the
table. Twelve processes had been selected and compared on the basis of a pro-
duction of 2.5·10^6 t/a of products C_2^+ and of a coal price of 7 DM/t. All pro-
cesses operate with iron catalysts. Fixed bed reactors, entrained phase and
fluid bed reactors, and also liquid phase recirculating and suspension reac-
tors have been taken into account.

The product distribution varies widely between 13 and 63 wt % in the fraction
$C_2 - C_4$ and 19 to 83 wt % in the fraction C_5 . The contents of oxygenates
range from 3 to 47 % of weight, the contents of olefins, as given in the
fraction C_4, from 19 to 84 wt %. The economical evaluation, last column in
the figure, shows the factor by which the production costs are higher than
the prices to be obtained for the chemicals produced. At present this factor
is between 1.6 to about 3.3 for the 12 processes regarded.

PROCESS	WT.-% OF PROD. C_2^+			WT.-% OLEF. i-C_4- FRACTION	COSTS OF PRODUCTION PRICE TO BE OBTAINED
	HC C_2-C_4	HC C_5^+	0-COMP.		
1) FIXED BED (TUBE-REACT.) (LURGI-RUHRCHEMIE)	13	83	4	55	2.0
2) CATALYST LAYERS (LURGI)	25	69	6	60	1.8
3) FIXED BED, HOT GAS RECYCLE 7C,(BUR.O.MIN.)	32	59	9	68	2.3
4) FIXED BED, HOT GAS RECYCLE 20A,(BUR.O.MIN.)	77	19	4	19	3.3
5) ENTRAINED PHASE (SYNTHOL N,(SASOL)	37	57	6	82	1.8
6) ENTRAINED PHASE SYNTHOL L,(SASOL)	63	34	3	66	2.1
7) FLUID BED (HYDROCOL)	38	54	8	83	1.9
8) FLUID BED Fe-NITRID (BUR.O.MIN.)	39	14	47	51	1.9
9) LIQU.PHASE, SUSPENS.„B" (RHEINPREUSSEN-KOPPERS)	20	77	3	80	1.8
10) LIQU.PHASE, SUSPENS.„L" (RHEINPREUSSEN-KOPPERS)	31	66	3	76	1.9
11) CIRCUL.OIL,Fe-TURNINGS (BUR.O.MIN.)	35	52	13	84	1.6
12) CIRCUL.OIL, Fe-NITRID (BUR.O.MIN.)	30	56	14	60	2.1

COMPARISON OF FISCHER-TROPSCH-PROCESSES FOR THE PRODUCTION OF CHEMICALS FROM $CO + H_2$
R. KÜHN AND M. ELSTNER, 1977

Fig. 15.

An important project concerns catalyst development which is performed by Ruhr-chemie, Oberhausen (5). Some attractive results of this development in the direction of the selective formation of low molecular weight olefins from CO and H_2 have been published (Fig. 16)(23). These data show values of C_2-C_4 seletivity of more than 50 % at relatively high values of total yields. Particularly propene can be obtained with a maximum selectivity of about 25 %. According to the patent literature, sintered iron catalysts modified with, for example, V_2O_5, ZnO and K_2CO_3 have been used (24).

Technical development of the production of chemicals via the Fischer-Tropsch process has been undertaken by Schering AG (5). A first expertise of feasibility has been prepared. A pilot plant with a synthesis gas throughput of 10.000 m^3/h (ca. 30 t/d of desired products) is proposed to be erected.

In competition with the Fischer-Tropsch route of coal conversion to liquid fuels and organic chemicals other processes, which start from synthesis gas, have to be regarded (Fig. 17). The implications of a use of methanol as motor fuel have been studied in detail (25). Methanol has been converted, in a new process with zeolite catalysts, to mainly aromatic hydrocarbons (26). Another interesting reaction with synthesis gas is that of homologizing alcohols, e.g. that of methanol to ethanol (27).

CONCLUSION

Processes of coal conversion to liquid and gaseous fuels and organic chemicals attract increasing attention. At present specially favourable situations allow economic operation of such processes. However, in only 10 years the economy can be in favour of processes of coal conversion in a number of instances. Development of the corresponding processes is therefore an urgently important task. The examples mentioned in this paper show significant technical progress in various cases and planned activities for finding solutions of the problems of liquid fuels and chemicals supply which will have to be envisaged in the near future.

RESULTS OF NEW RUHRCHEMIE FISCHER-TROPSCH-EXPERIMENTS FOR THE SELECTIVE FORMATION OF LOW MOLECULAR WEIGHT OLEFINS FROM CO AND H_2

B. CORNILS , B. BÜSSEMEIER , C.D. FROHNING , 1977

PROMOTED SINTERED IRON CATALYSTS

	FIXED BED / GASPHASE			SUSPENSION
	I	II	III	
TEMPERATURE , °C	360	340	280	350
PRESSURE , bar	10	10	10	20
CO / H_2 , Vol/Vol	1	1	1	1
YIELD OF HYDRO-CARBONS , g/m³	200	152	124	155

PRODUCT SELECTIVITY , % OF C IN ORGANIC COMPOUNDS

CH_4	9,8	11,8	15,2	16,5
C_2H_4	5,8 ⎫	10,9 ⎫	17,5 ⎫	16,2 ⎫
C_3H_6	7,2 ⎬ 18,8	17,0 ⎬ 38,8	26,2 ⎬ 57,7	18,2 ⎬ 46,9
C_4H_8	5,8 ⎭	10,9 ⎭	14,0 ⎭	11,5 ⎭
(C_5H_{10})				(5,4)
$C_2 - C_4$ SATT.	3,9	5,3	6,7	
($C_2 - C_5$ SATT.)				(17,5)
C_5^+	67,5	44,1	20,4	
(C_6^+)				(14,7)
	100,0	100,0	100,0	100,0

Fig. 16.

SYNTHESIS GAS CONSUMING PROCESSES

1) METHANOL SYNTHESIS

$$CO + 2 H_2 \longrightarrow CH_3OH$$

2) OLEFIN HYDROFORMYLATION

$$R-CH=CH_2 + CO + H_2 \longrightarrow R-CH_2-CH_2-CHO$$

3) METHANATION

$$CO + 3 H_2 \longrightarrow CH_4 + H_2O$$

4) ALCOHOL CARBONYLATION (MONSANTO)

$$CH_3OH + CO \longrightarrow CH_3COOH$$

5) HYDROCARBONS FROM METHANOL (MOBIL OIL)

$$CH_3OH \xrightarrow{\text{ZEOLITE}} HYDROCARBONS (GASOLINE) + H_2O$$

6) HOMOLOGUOUS ALCOHOLS

$$CH_3OH + CO + 2 H_2 \longrightarrow C_2H_5OH + H_2O$$

7) GLYCOL FROM SYNTHESIS GAS (UNION CARBIDE)

$$2 CO + 3 H_2 \longrightarrow CH_2OH-CH_2OH$$

8) DERIVED FISCHER-TROPSCH PROCESSES:

ETHANOL , ALCOHOL MIXTURES, POLYMETHYLENE , n-OLEFINS.

Fig. 17.

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