Other Hydrogenation Processes

The USBM is developing a process in which yields of three barrels of oil per ton of coal are obtained and H_2 consumption is 1000 scf per barrel of product oil.(49) The major difficulty with the process is the high pressure drop with attendant high recycle pumping requirements. A summary of typical operating conditions and product properties is given in Table 9. The catalyst is a fixed-bed cobalt molybdate/silica alumina which, it is claimed, retains good activity over long, though unspecified, periods due to the turbulence produced by high hydrogen throughput. Dwell time for the coal slurry is short, less than 14 minutes, allowing for a relatively high throughput. The product is intended for use as a low-sulfur fuel oil and apparently not for refining to gasoline for which the C/H ratio is evidently too low. The sulfur is, as usual, removed as hydrogen sulfide and may be converted to elemental sulfur by the Claus process.

This study has been conducted on so small a scale that the mechanical problems are probably not yet obvious. At 50 lb/hr pilot plant is expected to be operable soon, using a 1-inch ID by 60-ft reactor, and a 4-inch reactor to handle 5 to 8 tons/day is planned for one to two years hence. Cost estimates for this process have not yet been made.

A second process under study at USBM uses CO and liquid H_2O (under high pressure and moderate temperature), but it does not work well on bituminous coals. On the more reactive lignites the process is much more attractive. A possible area for further research is obviously research on suitable catalysts for bituminous systems. The USBM is also doing some work on generating oils from urban wastes, manure, wood, and the like by reaction with CO and H_2O, but this effort is not considered to be of high interest, at least for the present.

Another technique for coal hydrogenation under study by the USBM is electrochemical reduction. In one study, coals with 70 to 75 percent carbon gave a 45 to 50 percent yield of soluble products which was increased by preoxidation.(50) The soluble products appeared to consist mostly of benzenoid compounds.

Wender(51) describes the electrochemical reduction of coal in the presence of LiCl and ethylenediamine. It was possible to add 53 atoms of hydrogen per 100 atoms of carbon to a coal containing 91 percent carbon. Current efficiencies are only 10 to 20 percent. For this system, the reaction of $2\ Li^+ + 2e^- \rightarrow 2Li^\circ$ is believed to form solvated Li° at the cathode, which reacts with the hydrocarbon and amine; thus, the lithium cation is used catalytically in carrying out the reduction. Given(52) found that large-scale electrolysis of solvent extracts of coals, in the presence of phenols, resulted in the addition of larger amounts of H_2 than when phenol was absent.

Recent work at the USBM has also demonstrated that ethanol containing hexamethylphosphoramide can be used for generating solvated electrons in reducing coal. The ultimate goal is to find an aqueous system for this reduction.

Schulman Patent. One hydrogen-consuming reaction in coal liquefaction is the conversion of the oxygen in coal to water.(53) It would, in view of the cost of H_2, be economically preferable to eliminate this oxygen as CO_2. Such a process is claimed in an Esso patent describing a two-stage process which first uses a hydrogen-donor solvent extraction then catalytic hydrogenation. The first stage noncatalytically eliminates about 80 percent of the oxygen equally as CO_2 and H_2O while the normal ratio for these by-products is a disadvantageous 1:5. The process reportedly converts about 90 percent of the coal but product properties and analysis are not specified. The hydrogen donor solvent is identified as tetralin. This is clearly not a practical nor fully developed process but it may point the way to economies in H_2 consumption.

TABLE 9. RESULTS OF HYDRODESULFURIZATION OF MIDDLE KITTANING NO. 6 SEAM COAL IN RECYCLE OIL(49)

Experimental Conditions:
Reactor: 5/16-inch ID x 68 ft long
Catalyst: Silica-promoted cobalt molybdate
Temperature: 450 C
Pressure: 2,000 psi
Liquid feed: 30 coal + 70 recycle oil
Liquid feed throughput: 140 $lb/hr/ft^3$ reactor volume
Gas recycle rate: 500 scfh

A. Gross Results	
Sulfur in feed coal, wt pct	3.00
Sulfur in centrifuged oil, wt pct	0.31
Yield, bbl oil/ton coal maf	3.0
B. Analyses of Centrifuged Product Oil	
Solvent Analysis, Wt Pct	
Organic benzene insolubles	11.6
Ash	1.3
Asphaltene	24.4
Oils	62.7
Elemental analysis (ash-free basis), wt pct	
Carbon	89.6
Hydrogen	7.6
Nitrogen	0.9
Sulfur	0.31
Oxygen (by difference)	1.6
Range of specific gravity, 60/60 F	1.126-1.141
Range of viscosity, SSF at 180 F	75-204
Calorific value, Btu/lb	16,840
C. Analyses of Residue (Centrifuge Cake)	
Solvent Analysis, Wt Pct	
Organic benzene insolubles	33.1
Ash	27.7
Asphaltenes	9.0
Oil	30.2
Sulfur content, wt pct	2.10

Hoffman Patent. An attempt to eliminate H_2 generation as a separate operation is dependent on a two-component catalyst, and relatively low pressures (<500 psi).(54) Presumably, the introduction of coal and steam leads first to the formation of H_2 and CO (Na_2CO_3 catalyst) which then react in a Fischer-Tropsch-type fluidized bed reaction (iron oxide catalyst) to produce the products. Temperatures of about 540 C are maintained. A heat balance is claimed in which the endothermal first reaction is balanced by the exothermal second reaction. The overall conversion of carbon is 77 percent and the product mixture contains about 25 percent gaseous hydrocarbons, 50 percent liquid fuels, and 15 percent hydroxy compounds. The disclosure lacks specificity on some aspects of the process, e.g., the sulfur content of the product, but if it is actually workable, it does contain some attractive features: the elimination of an H_2 production step, the use of relatively low pressures and the heat balance achieved between reactions. These features in combination could markedly reduce costs and make a lower yield of oil acceptable.

Schraeder Process. This process minimizes the use of H_2 by being rather selective for the production of aromatics.(55, 56) Powdered coal is subjected to a rather high temperature (ca. 800 C) under about 2000 psig of H_2 with or without use of a catalyst (molybdenum) and without use of a vehicle oil. Reaction time is very short, about 2 minutes, and the fact that the liquid portion of the product is of low viscosity is said to aid in solids separation. However, the yield of hydrocarbon gas is higher than for most liquefaction processes. The sulfur content of the product is not discussed. It has been reported(57) that further study of this procedure is in progress at City College in New York.

Tin Chloride Hydrogenation. The University of Utah has taken alternate approaches to the catalytic hydrogenation of coal.(58) In one scheme coal is sprayed with an aqueous solution of granular $SnCl_2$ (6 weight percent of coal feed) then dried. The coal is mixed with high-temperature char in a 1:1 ratio then fed into a reactor operating at 515 C and 2000 psig hydrogen pressure. The dry feed is introduced into a 2-inch ID by 48-inch-high reactor at a rate of 10 grams/minute plus 15 liters H_2/minute. Other process variations are also under study.

Battelle Hydrogenation. Experiments were carried out at BCL from 1963 to 1968 on hydrogenation of coal and shale at 480 C and 445 psig hydrogen pressure.(59) The catalyst-to-coal ratio used in the batch "retesting" experiments was 3:1, while residence time was 3.27 hours. Yield of liquid products was only 20 percent, but the sulfur content of the coal had been reduced to 0.13 percent.

Active Studies by Oil Companies. Industry is highly interested in both liquid and gaseous coal conversion processes. Kennecott Copper bought Peabody Coal several years ago and within a year began staffing a coal laboratory in Lexington, Massachusetts. It is reported that they are joining one group interested in low-Btu gas. Their other interests have not been published.

The oil industry has invested heavily in research related to coal properties. Exxon, Shell, Texaco, and Universal Oil Products have for years maintained discrete, byt apparently large, efforts in coal conversion. In addition, Exxon worked with CCC in their early low temperature catalysis investigations and have more recently participated in the H-Coal consortium.

ARCO also has a long-standing interest in coal conversion. They have made a feasibility and economic study on the H-Coal process for the OCR. They also belong to the H-Coal consortium. They recently made a policy statement saying that they would have a commercial synthetic fuels plant started by 1976, apparently using oil shale or tar sands, which they investigated earlier with others.

Gulf Oil has nursed and promoted solvent-refined-fuel studies through their subsidiaries, Spencer Chemical Company and Pittsburgh and Midway Coal Mining Company. Gulf has also indicated interest in using waste heat from nuclear power plants to convert coal. Gulf has carried out fixed-bed catalytic hydrogenation at Harmarville, and an analysis of a product sample is shown in Table 10. Gulf Oil has also been a partner in the H-Coal consortium. They are also involved in coal liquefaction with Penn State on a $265,000 grant award just announced by Research Applied to National Needs (RANN), a division of NSF for a one-year period, which may be renewed at the end of that time. Although it is known that coals are not equally suitable for liquefaction, it is not yet understood how the oil yield, pumpability of the oil, and its sulfur content depend on the type of coal. It is the purpose of the Penn State research to find out how these characteristics of the oil product change with the nature of the various coals found throughout the country. Collaboration with Gulf will make possible the testing of a large number of selected coals under conditions that closely approximate those in a full-scale commercial plant. Research by the Penn State group has been supported for some years by a contract with the OCR. Objectives of this work have been to obtain samples of coals from all the principal seams in the major coal areas of the U.S. and to determine for these a wide variety of characterization data that may bear on behavior in conversion processes. This data base will be used in the new project.

TABLE 10. TENTATIVE LIQUEFACTION PRODUCT SPECIFICATIONS

"It is envisioned that ultimately the liquid products derived from coal may be tailored to satisfy a variety of applications, including those served by distillates and residuals. The nature of catalytic coal liquid can be judged from the following properties which were obtained from an unrefined liquid product using a western subbituminous coal."

Gravity: API	9.0	Sulfur: %	0.04
Sp. Gr. 60/60	1.007	Water: %	0.8
Lb/gal 60 F	8.39	Ash, D482: %	0.02
Viscosity, SUS		Btu/lb	19,120
100 F	49.1	Btu/gal	160,400
210 F	32.3		

Continental Oil through its subsidiary, CCC, has considerable background in coal conversion, discussed above. They were a member of the H-Coal consortium, but have recently dropped out. Currently they are assisting Southern Services with their pilot-plant efforts. They are also investigating several aspects of their synthetic fuel process which developed from the Project Gasoline data and are actively looking for partners who also are interested in building and operating a demonstration (1000 tons/hr) extraction plant.

Sun Oil has considerable background in synthetic fuels, including an operating tar sands plant in Alberta, Canada. They were partners in the oil shale experiments at Rifle, Colorado, and are in the H-Coal consortium.

Chemical Production

It seems fairly certain that the hydrogenation of coal to form synthetic crudes that can be processed by present refinery techniques will be a significant source of hydrocarbons within 10-20 years. However, need for this technology is almost upon us now. It is thus important to optimize current hydrogenation processes so that high yields of the most economically desirable products can be predetermined and to investigate new ideas needed for converting coal into synthetic products. In this regard, emphasis should be placed on the utilization of the entire coal structure (e.g., using nitrogen compounds) during the conversion of coal to synthetic crude. There is not much current technology to review in this area. The output of a hypothetical hydrogen facility is shown in Table 11.

Of the compounds present in liquid products from hydrogenation of coal and tar, a large number have been identified in the distillable liquid-phase oil but many are still unknown. All of these compounds are by-products since the hydrogenation process has been operated primarily to produce liquid fuels. However, even in the early plants, propane, butane, and pentane were recovered from coal by hydrogenation. Phenols and sulfur also were recovered from gaseous and liquid products. Polynuclear aromatic compounds and tar bases were considered profitable by-products, and their recovery was under study. Recently, chemicals produced by hydrogenation of coal have received more attention; however, this subject, particularly the market for these chemicals when produced on a large scale, still needs extensive study. It is not possible to discuss in detail all the various chemicals that can be derived from coal, and the impact on the general economy that each would have if it were to be removed from the chemicals market. An overview, however, seems to be justified. Shown below are the specific compounds that could be obtained by appropriate modification of structures that are inherent in coal:

Olefins	Aromatics	Other
Ethylene	Benzene	Tar Acids
Propylene	Toluene	Hydrogen
Butadiene	Xylene	Sulfur
Butylene	Durene	Ammonia
Acetylene	Pseudocumene	
	Naphthalene	

Examining ethylene specifically is a worthwhile exercise. This material is now derived from 4 major sources:

1. Dehydrogenation of ethane
2. Cracking of propane

TABLE 11. CHEMICALS AND FUELS FROM A COAL-HYDROGENATION PLANT WITH A DAILY PRODUCTION CAPACITY OF 30,000 BARRELS*

Products	Production, bbl/day	Weight-Percent of Total Product
Tar acids:		
Phenol	428	1.9
o-Cresol	48	0.2
m- and p-Cresol	530	2.4
Xylenols	374	1.6
Total	1,380	6.1
Aromatics:		
Benzene	2,210	8.2
Toluene	3,770	13.9
Xylenes	4,190	15.4
Ethylbenzenes	750	2.8
Naphthalene	790	3.7
Mixed aromatics	1,780	6.8
Total	13,490	50.8
Liquefied petroleum gas	7,300	16.4
Gasoline:		
Motor	5,260	15.6
Aviation	3,660	11.1
Total	8,920	26.7
Grand total	31,090	100.00

*This plant could also produce 450 tons of $(NH_4)_2SO_4$ and 89 tons of H_2SO_4 per day.

3. Separation of refinery off-gases
4. Cracking of heavier hydrocarbons.

The principal use of ethylene is, of course, to make the polymer polyethylene which is now selling at the rate of about 3 x 10^9 lb/year. Other important uses are in the production of:

Material	Estimated Amount, 10^6 lb
1. Ethylene Glycol (antifreeze)	1000
2. Polyester Fibers	600
3. Surfactants	400

Material	Estimated Amount
4. Ethanolamines (rust inhibitors)	250
5. Ethyl Alcohol	350
6. Ethylene-Propylene Rubber	100
7. Styrene	750
8. Vinyl Chloride	unknown
9. Ethylene Dichloride	unknown

It is not difficult to determine from the above list the impact the removal of ethylene from the chemical market would have on the economy and the way of life we have grown accustomed to. The same type of case could be made for all the chemical intermediates now derived from petroleum. For instance, propylene is now used in the following applications.

1. Polypropylene
2. Isopropanol
3. Acrylonitrile (Orlon)
4. Propylene oxide
5. Epichlorohydrin (Epoxy resins)
6. Glycerine

Although the volume of propylene used is not as great as that of ethylene, it still can be estimated at 8-10 x 10^9 lb/year for all applications.

A dramatic way of placing a single material in proper perspective is shown in Figure 11. This shows the progression of toluene through a disproportionation reaction to yield benzene and xylenes. The product tree from these compounds progressing to end products is in no way complete. One could easily double or triple the amount of branching. However, it does show the dependency of many industries on a single compound which can be derived from coal.

If coal can be used as a source of chemicals, an estimate of yield can be made from currently available data. Assuming that each 100 pounds of coal will yield 36 pounds of liquids via hydrogenation and that from this one can derive 11 pounds of chemicals, the following estimates of yields can be made.(48) The figures are based on a plant hydrogenating 10 x 10^9 lb/year.

Chemical	10^6 Lb/Year
Benzene	100
Toluene	300
Ethylbenzene	100
Xylenes	200
Cumene	20

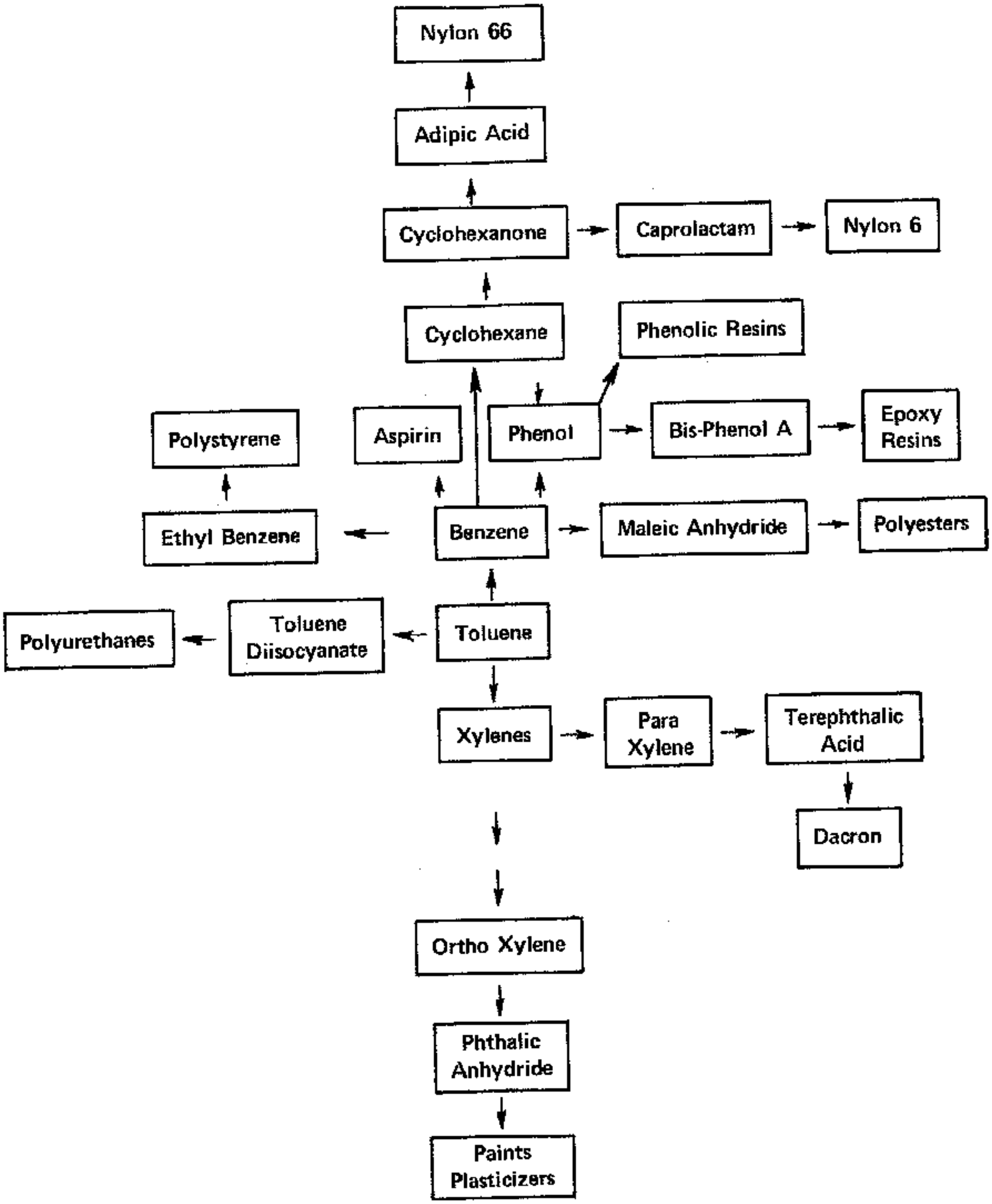


FIGURE 11. PARTIAL LIST OF PRODUCTS STEMMING FROM TOLUENE

Chemical	10^6 lb/Year
Durene	20
Naphthalene	100
Phenol	100
Cresols	100

It is also believed that economics could best be served by building a plant to process 100,000 tons/day. One can immediately see that coal could indeed become the major source of organic chemicals with sufficient research to solve certain immediate and long range problems.

Economic Evaluation

Cost estimates for catalytic coal liquefaction were made for two representative processes: H-Coal and CONSOL. In each case, primary cost data were obtained from the literature(37, 44) and the appropriate scaling factors were used to cost a plant having a total product output of 9.6×10^9 Btu/hr. The H-Coal process produces a low-sulfur, synthetic crude oil with a heating value of about 18,000 Btu/lb. The CONSOL process produces a product mix consisting of 63.7 percent liquid product fuel with a heating value of 18,600 Btu/lb, 17.0 percent naphtha with a heating value of 19,600 Btu/lb, and 19.3 percent fuel gas with a heating value of 20,600 Btu/lb. The weighted average heating value of the product mixture is 19,200 Btu/lb. The range of capital and operating cost estimates for the catalytic liquefaction processes using various types of coal are listed in Table 12. The lowest costs are for Eastern, low-sulfur coal, while the highest costs are for Western lignite.

TABLE 12. EXPECTED RANGE OF COSTS FOR CATALYTIC COAL LIQUEFACTION PROCESSES USING VARIOUS TYPES OF COAL

Process	Capital Cost Range, 10^6 \$	Operating Cost Range(a), ¢/10^6 Btu
"A"	233 - 391	33.8 - 67.9
"B"	189 - 318	27.0 - 54.4

(a) Does not include cost of coal.

Fischer-Tropsch Processes and Related Syntheses

In concept, the Fischer-Tropsch processes entail two major steps:

1. Production of synthesis gas, $CO + H_2$, from coke or coal
2. Catalytic reaction of that gas to form hydrocarbons.

Although the process was intended as a means for manufacture of liquid hydrocarbons, variations in the conditions of the catalytic reactor led to major yields of CH_4, liquid hydrocarbons, waxes, and oxygenated products.(31) The production of synthesis gas from coal usually is accomplished by the water-gas reaction

$$C + H_2O \rightleftarrows CO + H_2$$

followed by the water-gas shift

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

to increase the ratio of H_2/CO obtained. For the conventional Fischer-Tropsch process this ratio is about 2, but the production of liquid fuels by hydrogenation of carbon oxides is not limited to this high ratio. Further, interaction processes between coal and H_2O can lead directly to hydrocarbons rather than to CO and H_2 as shown for the water-gas reaction. For these reasons the Fischer-Tropsch synthesis is properly viewed against the background of the technical feasibilities for these alternative and competing reaction systems. In this study, the ensemble of these reaction processes is summarized for the purpose of deriving conclusions and recommendations with the highest degree of technological leverage.

There are a fairly large number of organic and inorganic reaction possibilities in the Fischer-Tropsch and related syntheses. Some do not occur under a chosen set of reaction conditions because the free energy changes are positive and sizable yields cannot be expected. Others are thermodynamically possible under the chosen conditions but do not occur to any appreciable extent for kinetic reasons. The balance obtained among those reactions that are possible is controlled by choice of reaction conditions and of the catalyst used.

The opportunities and limitations for the related syntheses under consideration can be discussed by consideration of the reactions listed in Table 13. The three classifications shown, hydrogenation of CO, hydrogenation of CO_2, and reactions with water vapor, identify the scope of this discussion.

Thermodynamic Limitations

Equilibrium constants for typical Fischer-Tropsch reactions of the systems A and B in Table 13 can be written as

$$(K_{eq})_A = \frac{P_{C_nH_{2n+2}} \quad P^n_{H_2O}}{P^{2n+1}_{H_2} \quad P^n_{CO}} \quad \text{and } (K_{eq})_B = \frac{P_{C_nH_{2n+2}} \quad P^n_{CO_2}}{P^{n+1}_{H_2} \quad P^{2n}_{CO}} ,$$

using the coefficients listed for the hydrocarbon syntheses in that table.(60) Similar equilibria can be written for the other reactions. The value of each equilibrium constant can be obtained from the free energy change for each reaction

$$- \Delta F° = RT \ln K_{eq}$$

in which it is seen that the equilibrium constant is > 1 when $\Delta F° < 0$. It is difficult to specify the value of an equilibrium constant below which the yield of the reaction is insignificant because of the large and various values of n that are involved. For this reason the reactions will be compared by noting the conditions for each under which $\Delta F°<0$ and hence the conditions where sizable yields are possible.

All of the reactions tested, other than those forming C, and the water-gas shift, show a decrease in the number of moles present as the products are formed and hence are favored by increasing pressure. This is illustrated by rewriting the equilibrium constant for the A series as

$$P^{2n}(K_{eq})_A = \frac{N_{C_nH_{2n+2}} \quad N^n_{H_2O}}{N^{2+1}_{H_2} \quad N^n_{CO}} ,$$

where the products and reactants are given in mole fractions, N, and P is the total pressure in atmospheres.

The conditions favorable to each of the reaction systems under consideration can be visualized with the help of Figure 12. The solid lines represent the free energies for hydrocarbon formation at one atmosphere by system A in which the by-product is H_2O. The large spread in position of the lines reflects the differences in favorability for the various hydrocarbons. For products other than the low molecular weight paraffins, reaction temperatures at one atmosphere must be held below about 450 C for sizable yields. The dotted line representing the water-gas shift reaction shows a negative $\Delta F°$ at all temperatures below 800 C so that the equilibrium position for the shift reaction is favorable at all temperatures below that limit. This is of considerable importance since the free energies for hydrocarbon production by system B can be derived by adding together algebraically the $\Delta F°$ values shown for the hydrocarbon concerned and that shown for the water-gas shift. This leads to the conclusion that the reactions of system B in which CO_2 is the by-product have more negative $\Delta F°$ values than those of system A and hence may be regarded as more favorable thermodynamically.

On the other hand the $\Delta F°$ values for reactions of system C, in which hydrocarbons are obtained by hydrogenation of CO_2, are obtained by subtraction of the $\Delta F°$ value for the water-gas reaction from that for the hydrocarbon so that the processes of hydrocarbon formation by this system are somewhat less favorable than system A although still capable of appreciable yields. In Figure 12a the line marked C represents the free energy for production of free carbon by the reverse of the water-gas reaction. The large negative free energies shown for free carbon indicates that carbon production is thermodynamically favored over most hydrocarbons in the temperature range of interest. The degree to which carbon is actually formed is determined in practice by the catalyst selectivity.

Figure 12b shows that large yields of alcohols, except methanol, are thermodynamically possible under the usual Fischer-Tropsch conditions for hydrogenation of CO. A similarly favorable situation is shown in Figure 12c for the reaction of CO and steam to form hydrocarbons.

A contrasting circumstance is shown in Figure 12d for the reaction of steam with carbon (graphite) in which the $\Delta F°$ values show most hydrocarbon yields to be

TABLE 13. TABULATION[(a)] OF REACTIONS FOR HYDROGENATION OF CO AND RELATED PROCESSES(60)

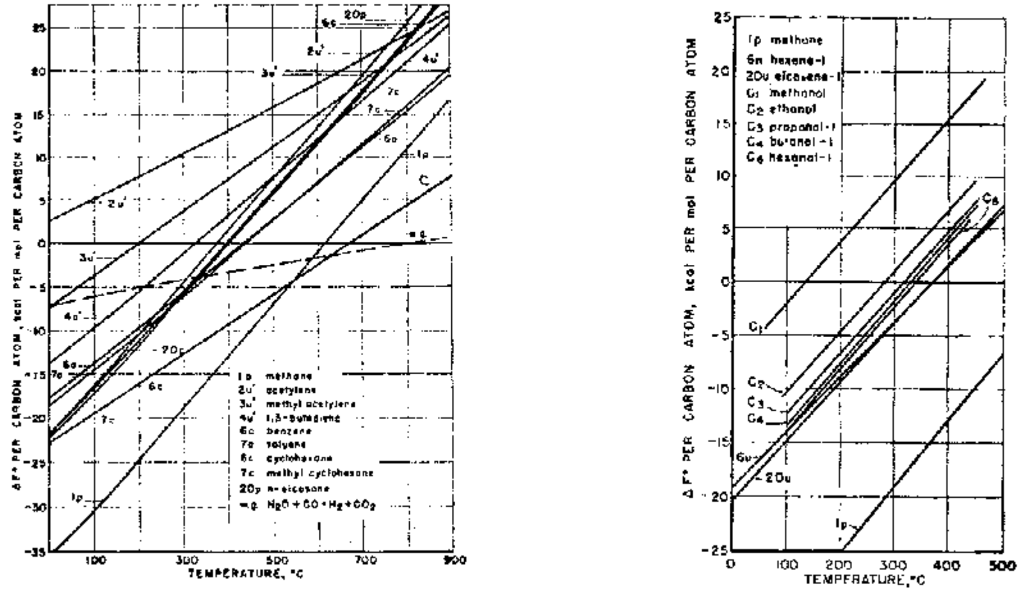
Reaction Designation	REACTANTS (b)					PRODUCTS (b)					
	C_g	H_2	CO	H_2O	CO_2	C_g	H_2	C_nH_{2n+2}	C_nH_{2n+1}	H_2O	CO_2
Hydrogenation of CO											
A1		2n+1	n					1		n	
A2		2n	n						1	n-1	
A3		1	1			1				1	
B1 (c)		n+1	2n					1			n
B2 (c)		n+1	2n-1						1		n-1
B3			2			1					1
Hydrogenation of CO_2											
C1		3n+1			n			1		2n	
D1		3n			n				1	2n-1	
Reactions with Water Vapor											
E1			1	1			1				1
E2			3n+1	n+1				1			2n+1
F1	3/2n+1/2			n+1				1			1/2(n+1)

(a) The quantities tabulated are the coefficients of the products and reactants in the designated process.

(b) C_g=graphite; C_nH_{2n+2}=saturated hydrocarbon; $C_nH_{2n+1}OH$=alcohol.

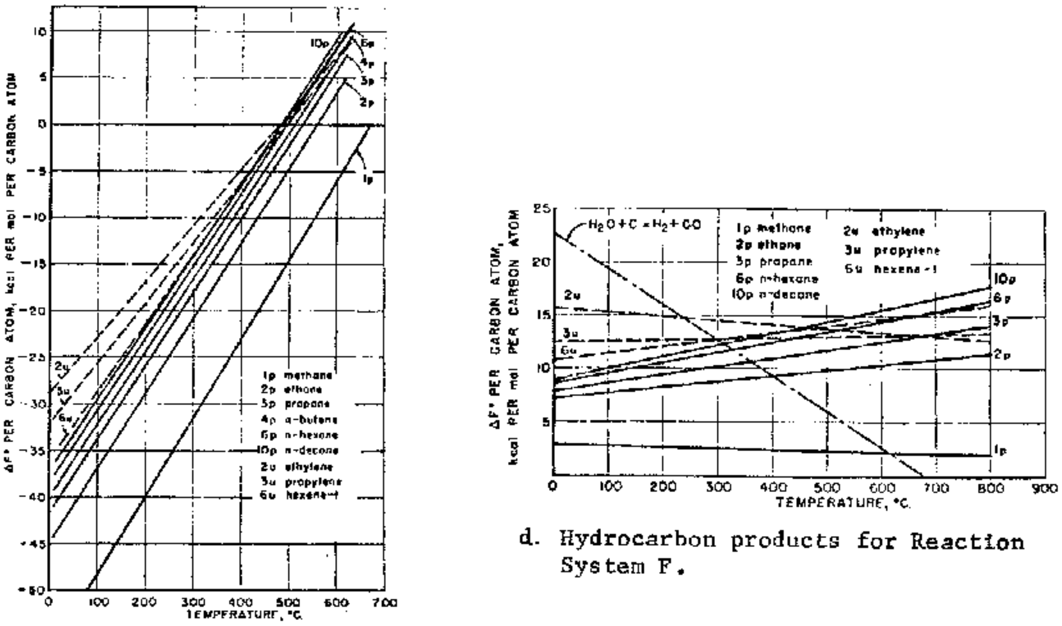
(c) Note that A1+n(E1)=B1 A2+(n-1)E1=B2
A1-n(E1)=C1 A2-(n-1)E1=D1

so that the position of the water gas shift, E1, determines the thermodynamic equilibria among the various processes for hydrocarbon or alcohol production.



a. Hydrocarbon products for Reaction Systems A,B,C.

b. Alcohol products for Reaction System D.



c. Hydrocarbon products for Reaction System E.

d. Hydrocarbon products for Reaction System F.

FIGURE 12. STANDARD FREE ENERGIES OF FORMATION OF VARIOUS PRODUCTS BY THE SELECTED REACTION SYSTEMS(60)

unfavorable. However, coal is much more reactive than graphite and, for some coals, reactions of this kind may be thermodynamically favorable.

Kinetics and Catalysis

Sabatier reported(61) the production of methane by hydrogenation of CO over nickel, cobalt, and palladium catalysts as early as 1905; by hydrogenation of carbon at high pressures and above 500 C over nickel and nickel oxide catalysts in 1913; and by hydrogenation of CO_2 at ordinary pressure at 450 C in 1913. At about this same time (1913 and 1914) Badische Analin and Soda Fabrik obtained patents for the production of a variety of organic compounds, such as alcohol, aldehydes, etc., by hydrogenation of CO at 100 to 200 atmospheres and 300 to 400 C over catalysts containing cobalt and osmium oxides.(62) The early experiments by Fischer and Tropsch in 1923 provided the principal impetus for further development of these reactions in their disclosure of the formation of oxygenated organic molecules by hydrogenation of CO at 100 atmospheres and above, and the formation of hydrocarbons at low pressures, in the range of 5 to 10 atm. Since that time, the work that has been published on these reactions is voluminous, and a number of books have been devoted to the subject.

Hydrogenation of Carbon Monoxide. Studies on the mechanism of Fischer-Tropsch syntheses can, for convenience, be discussed from three different points of view:

1. The adsorption of CO and H_2 on the catalyst surface
2. The kinetics of the synthesis
3. The formation of product nuclei and their growth on the catalyst surface to the final higher molecular weight products.

The following summary of the kinetics and mechanisms from these three points of view is extracted from the review by Emmett.(63)

1. The information available relative to the adsorption of H_2-CO on iron catalysts, can be very simply summarized. In the Fischer-Tropsch synthesis range of 200 to 325 C, iron readily chemisorbs both H_2 and CO. Iron oxide, on the other hand, seems to chemisorb only H_2, whereas iron carbide chemisorbs H_2, but in the temperature range of 0 to 100 C holds very little CO on its surface. It seems likely, therefore, that the active catalyst surface which must chemisorb both H_2 and CO probably consists primarily of iron, though the possibility exists that a mixture of iron carbide and iron oxide might operate by the former adsorbing H_2 and the latter adsorbing CO.
2. The kinetics of catalytic reactions have traditionally been helpful in interpreting the mechanism by which a reaction takes place. In this instance, however, because of the complicated nature of the reactions, the kinetic information falls far short of providing any lucid picture of the way in which synthesis takes place. Kinetic calculations have, however, been very helpful in throwing light on the details of chain growth on the catalyst surface as reflected in the distribution of compounds with respect to carbon number in the products, and also distribu-

tion with respect to chain branching for a given molecular-weight hydrocarbon.

3. In considering the nature of the growth processes for conversion of the original nuclei to higher molecular weight products, the following assumptions have been successful in predicting the observed distribution of products:

   a. Addition of single carbon atoms may take place at only one end of growing chains on the catalyst surface.

   b. Addition may take place on adjacent-to-end carbon atoms subject to the restriction that this addition does not occur if a carbon atom is already attached to three other carbon atoms.

   c. Upon addition to an end carbon, the rate of growth through the intermediate may be represented by a first-order rate constant α with respect to the concentration of the growth chain on the surface.

   d. On addition of CO, the growing group passes through intermediate structure and finally forms an intermediate similar to the first but containing an additional C-atom. From these intermediates, alcohols, aldehydes, olefins, and paraffins may desorb and appear as products.

   e. For addition to an adjacent-to-end carbon, the rate of growth may be represented by a similar first-order constant β.

   f. The rate of desorption is characterized by a first-order rate constant γ with respect to growing chains on the surface.

   g. For chain species n, the rates of chain growth at the end and the adjacent-to-end carbon atoms and the rate of desorption may be represented respectively by αC_n, and γC_n, where C_n is a molar concentration of the chain n on the catalyst surface.

   An essential feature of their method of calculation is the assumption that for steady-state conditions, the concentration of any growing intermediate will remain constant and thus, its rate of formation will equal its rate of growth plus its rate of desorption.

Thus, for growth of straight chains

$$\alpha C_n = (\alpha + \beta + \gamma) C_{n+1}$$

$$\frac{C_{n+1}}{C_n} = \frac{\alpha}{\alpha+\beta+\gamma} = \frac{R_{n+1}}{R_n} = a$$

and for growth of branched chains

$$\beta C_n = C^{\ell}_{n+1} (\alpha + \gamma)$$

$$\frac{C^{\ell}_{n+1}}{C_n} = \frac{\beta}{\alpha+\gamma} = \frac{R^{\ell}_{n+1}}{R_n} = b$$

It is suggested(63) that a and b are constants in the steady state so that f = b/a = a new constant. On this basis the distribution of hydrocarbons by chain length would be as shown in Table 14, and the agreement of this theory with observed results is shown for two different assumptions in Table 15. Such treatments have successfully represented the distribution of hydrocarbons from n =2 to n = 20 for cabalt catalyst systems, and from n = 2 to n = 14 for iron catalyst systems. These considerations indicate the steady-state relationships that control hydrocarbon or alcohol chain growth on Fischer-Tropsch catalysts and hence the product distribution that characterizes the synthesis.

Experience has shown that alcohol production increases at the expense of hydrocarbon production as the pressure is increased in the range from about 10 to 150 atmospheres. It is believed that the terminal carbon at the growth end holds an OH group in its surface-complex configuration, and alternative routes for hydrogenation to desorb a hydrocarbon or alcohol are postulated.

Hydrogenation of Carbon Dioxide. The experience with various mixtures of H_2 and CO_2 or $H_2 + CO + CO_2$ indicates a number of serious shortcomings in this reaction system for production of hydrocarbons other than methane.(64) Thus

1. Mixtures of $4H_2/1CO_2$ and $1H_2/4CO_2$ on cobalt and nickel catalysts, at temperatures between 150 and 300 C have generally shown only CH_4 production with little or no higher hydrocarbons and waxes produced.
2. Some liquid hydrocarbons are produced in mixtures of H_2 with CO and CO_2, but the liquid is due to the hydrogenation of CO which is apparently not at all inhibited by the presence of CO_2. The hydrogenation of CO_2 on cobalt or nickel catalysts apparently proceeds only after all CO is consumed.
3. Most iron catalysts are inactive for hydrogenation of CO_2 at atmospheric pressure but the water-gas shift reaction proceeds readily.
4. The addition of 1 or 2 percent K_2CO_3 to various catalysts, including ruthenium, increases somewhat the yield of liquid hydrocarbons. Rubidium additions are also effective, but sodium and lithium produce only CH_4.
5. Because of the ease of CO hydrogenation, the concentration of CO in reacting mixtures of $CO_2 + H_2$ is always low, with CO/H_2 perhaps as small as 1:400. This ratio strongly favors CH_4 production over all other hydrocarbons, and so the stepwise reduction of CO_2 to CO and hydrocarbons leads to little more than CH_4.

TABLE 14. ISOMER AND CARBON-NUMBER DISTRIBUTIONS IN TERMS OF a AND f(60)

	Carbon Chain	Relative Isomer Composition	Relative Carbon-Number Distribution, moles
C_2		1	1
C_3		1	2a
C_4	n-C_4	1	$2a^2(1 + f)$
	2-Methyl-C_3	f	
C_5	n-C_5	1	$2a^3(1 + 2f)$
	2-Methyl-C_4	2f	
C_6	n-C_6	1	$2a^4(1 + 3f + f^2)$
	2-Methyl-C_5	2f	
	3-Methyl-C_5	f	
	2,3-Dimethyl-C_4	f^2	
C_7	n-C_7	1	$2a^5(1 + 4f + 3f^2)$
	2-Methyl-C_6	2f	
	3-Methyl-C_6	2f	
	2,3-Dimethyl-C_5	$2f^2$	
	2,4-Dimethyl-C_5	f^2	
C_8	n-C_8	1	$2a^6(1 + 5f + 6f^2 + f^3)$
	2-Methyl-C_7	2f	
	3-Methyl-C_7	2f	
	4-Methyl-C_7	f	
	2,3-Dimethyl-C_6	$2f^2$	
	2,4-Dimethyl-C_6	$2f^2$	
	3,4-Dimethyl-C_6	f^2	
	2,5-Dimethyl-C_6	f^2	
	2,3,4-Trimethyl-C_5	f^3	

TABLE 15. CALCULATED CHAIN STRUCTURES OF HYDROCARBONS FROM IRON CATALYSTS (60)

		Mole Percent in Fraction		
	Carbon Chain	Observed	Weller and Friedel	Anderson, Friedel, and Storch
			a = 0.890 b = 0.110	f = 0.115
C_4	n-C_4	89.4	94.2	89.7
	2-Methyl-C_3	10.6	5.8	10.3
C_5	n-C_5	81.2	83.8	81.3
	2-Methyl-C_4	18.8	16.2	18.7
C_6	n-C_6	78.8	74.7	73.5
	2-Methyl-C_5	11.2	14.4	16.9
	3-Methyl-C_5	9.5	10.3	8.5
	2,3-Dimethyl-C_4	0.4	0.6	0.9
C_7	n-C_7	66.0	66.4	66.0
	2-Methyl-C_6	13.1	12.8	15.4
	3-Methyl-C_6	19.1	18.4	15.4
	2,3-Dimethyl-C_5	1.6	1.8	1.7
	2,4-Dimethyl-C_5	0.3	0.6	0.8
C_8	n-C_8	61.0	59.2	60.5
	Monomethyl Isomers	36.4	36.0	34.7
	Dimethyl Isomers	2.6	4.8	4.8

Reactions With Water Vapor.(71, 72) The water-gas shift

$$CO + H_2O \rightarrow CO_2 + H_2$$

occurs readily over catalysts employed for Fischer-Tropsch and related reactions, and its velocity appears to increase with the concentrations of both H_2O and CO. For this reason, CO_2 production is a common result in reaction systems where both reactants are present. However, a second reaction process, that of hydrocarbon synthesis,

$$3CO + H_2O \rightarrow (-CH_2-) + 2CO_2,$$

has been readily demonstrated and offers considerable merit for further investigation. In a series of publications published in 1951 and 1952, Koelbel and Englehardt(65) demonstrated a number of interesting features of this synthesis route, and recently, in 1970 and 1971, Smolyaninov(66) has continued the investigation in the USSR. The salient points are as follows:

1. Working conditions and product yields (Koelbel)(65)
    - Temperature: 150 to 400 C, preferably 200 to 260 C
    - Pressure: 1 atmosphere and above
    - Space velocities: Up to 1000 hr^{-1}
    - H_2O/CO use ratio: 1/3 to 1/2
    - Catalyst: Fe, Co, Ni, and others
    - H_2O conversion: > 90 percent
    - CO conversion: > 90 percent
    - Yields: At least up to 216 g hydrocarbon and oxygenated material per cu m CO converted
    - Products: Paraffin hydrocarbons, hard waxes, up to 60 percent olefins in total product, up to 40 percent oxygenated compounds.
2. The heat of reaction for $CO + H_2O$ is 59.8 kcal per mole per C atom for hexane production. This is about 20 kcal per mole per C atom greater than that for the Fischer-Tropsch synthesis using $2H_2 + CO$.
3. The free energy change for the reaction of $CO + H_2O$ is more negative than for the Fischer-Tropsch synthesis.
4. The equilibrium constant for hexane production from $CO + H_2O$ approaches 1 at about 500 C so that sizable yields of hydrocarbon are possible up to this temperature.
5. Yields of olefins are high for C_2 species and pass through a minimum at about the C_7 hydrocarbon level.

    Thus if $K = \frac{\text{olefin}}{\text{paraffin}}$, then according to Smolyaninov(66), $K = 7$ (approximately for ethylene/ethane, falls to about 0.1 for the heptene/heptane fraction, and rises again to about 0.5 for the C_8 and C_{10} fractions).

6. The selectivity of a catalyst for synthesis of hydrocarbons versus the water-gas shift can be described by the ratio $\frac{(-CH_2-)}{H_2}$, which is about 90 for cobalt catalysts and about 10 for iron catalysts at 240 C, contact time = 0.08 seconds, approximately (Smolyaninov).(66)

Koelbel(65) viewed the process as consisting of two steps

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

$$\begin{array}{ll} 2CO + H_2 \rightarrow (-CH_2-) + CO_2 \ ; & (2) \\ \hline 3CO + H_2O \rightarrow (-CH_2-) + 2CO_2 & (\text{sum}) \end{array}$$

however, Smolyaninov(66) questions the identification of these two reactions as separate stages in the overall process.

The theoretical yield of hydrocarbon $(-CH_2-)$ would be 208 g/cu m CO converted. The yield of 216 g/cu m quoted by Koelbel,(65) and the maximum of 250 g/cu m CO reported by Smolyaninov(66) probably represent the increased product mass that results because of the formation of oxygenated products. In either case, the optimum conversion to hydrocarbons and oxygenated materials appears to be very high.

Although the reaction of water vapor with graphite to yield hydrocarbons is unfavorable at all temperatures of interest, the reactions of water vapor with coal may be anticipated to be far more favorable. Thus Smolyaninov(66) estimated the equilibrium constant for 36 reactions in which saturated hydrocarbons are caused to react with water to yield smaller molecular weight hydrocarbons, CO_2 and H_2. The various constants show that sizable yields of these reactions might occur above about 300-400 C. These results may be expected to support the conclusion that the various hydrocarbon linkages in some coals can be hydrolyzed in similar processes to yield liquid and gaseous hydrocarbons.

Experimental evidence on this possibility is sparse (see Hoffman(54)) and easily confused with the combined pyrolyses and water-gas processes that might otherwise occur.

In each case, the reactions of water vapor discussed in this section represent processes that are otherwise accomplished by separate water-gas shift and synthesis reactors in conventional Fischer-Tropsch processes. The direct conversion of coal or CO to hydrocarbons by reaction with H_2O clearly represents alternatives to the more conventional processes.

Production of Liquid Hydrocarbons. Fischer and Tropsch first described their work on the hydrogenation of CO over iron alkali catalysts in 1923.(31) Pilot-plant operations were started in 1932, and the next year Ruhrchemie undertook construction of a plant of 1,000-ton-per-year capacity. This was followed in 1936 by a 30,000-ton plant; by 1937, over 500,000-ton-per-year capacity had been started in Germany, plus one plant in France. These were all atmospheric-pressure cobalt-catalyst units.

By 1939, nine Fischer-Tropsch plants had been erected in Germany with a total rated output of 740,000 tons per year - about 16,000 barrels per stream day. No further plants were erected nor major increases in capacity made during the war; all expansion was in coal-hydrogenation capacity. As a result, toward the end of the war Fischer-Tropsch accounted for less than 20 percent of German synthetic-oil production.(67-69) All plants operated on cobalt catalyst; about 75 percent (based on production) at atmospheric pressure; 25 percent at medium pressure (7-20 atm).

The synthesis gas was usually made from coke in standard water-gas generators and used at atmospheric or low pressures; high-pressure purification methods were not attractive. Because of the use of coke-oven gas in many plants, the presence of resin formers in the gas needed special attention.

Hydrogen sulfide was reduced to about 0.4 grain per 100 cubic feet by passage through beds of iron oxide at ordinary temperatures. The organic sulfur was removed by passage through beds of Luxmasse (a hydrated iron oxide recovered in aluminum production) plus soda ash at temperatures of 175-250 C, with about 0.2 percent O_2 in the gas. A freshly charged bed (60 tons) was placed second in line, moved up to first after about six weeks, and recharged after staying six weeks in first position. During the total cycle, a tower charge could treat about 11.5 million cubic feet per ton of material. Sulfur removed could be 5 to 61 tons per cycle. Residual sulfur in the gas was about 0.2 grain per cubic feet.

The purified gas passed directly to the atmospheric-pressure synthesis section and, after compression, to medium-pressure synthesis. The catalyst used in both was a reduced cobalt promoted with thoria and magnesia, supported on Kieselguhr (a diatomaceous earth).

For synthesis at atmospheric pressure, the catalyst was packed in rectangular boxes (16 x 8 x 5 feet) containing bundles of 600 horizontal tubes expanded into vertical steel sheets 7 mm apart. The catalyst occupied the space between the vertical sheets which, together with the tubes, served as surface for transfer of heat to water flowing through the tubes. Total cooling surface was over 40,000 sq ft, and catalyst capacity was about 3-1/2 tons. The production of such a unit was 12 to 15 barrels a day.

For synthesis at 5 to 15 atmospheres a different reaction vessel was used. It consisted of a vertical cylinder 23 feet high with an inside diameter of 9 feet containing 2100 tubes. Each of the tubes was fitted with a concentric inner tube with the catalyst packed in the annulus. The inside tube and the external surface of the outer tube were water cooled. The synthesis gas flowed through the annulus. Such a vessel contained about 2-1/2 tons of catalyst and had some 20,000 square feet of cooling surface.

The current commercial plant of South African Coal, Oil, and Gas Corporation at Sasolburg, Union of South Africa, has aroused widespread interest since it started operations in 1955. It combines Lurgi gasification, Rectisol gas purification, a modern Ruhrchemie-Lurgi synthesis unit, oxygen-steam reforming of light hydrocarbons and a Kellogg suspended-catalyst gasoline-synthesis unit.

Subbituminous coal from a nearby mine is used for power plant and as a feed to a battery of Lurgi gasifiers operating at 380 psi. Consumption for gas production is about 3000 tons/day (63 percent moisture- and ash-free coal). Raw Lurgi gas is made at a rate of 162 x 10^6 cu ft/day, and by inference, the oxygen production is of the order of 1500 tons a day.

Liquor from the gasification unit is processed for the recovery of phenol and $(NH_4)_2SO_4$ with the hydrocarbon condensate processed for recovery of aromatic light oils, creosote, and tar. Raw gas is scrubbed with cold methanol by the Rectisol process to remove CO_2, H_2S, organic sulfur, and other impurities. The purified gas is used for both the fixed-bed and the Kellogg synthesis units.

The Ruhrchemie-Lurgi synthesis is a development of the middle-pressure Fischer-Tropsch process.(70) The reactor is in essence a vertical boiler containing 2000 tubes about 40 feet long by 2 inches in outside diameter. Catalyst is packed in the tubes, at approximately 1400 cu ft/reactor. Production rate is 50 metric tons (about 400 bbl)/reactor/day. The Sasol plant has five such reactors in which steam is produced at about 300 psi.

The process variations investigated during World War II and the early postwar years were directed toward several widely recognized shortcomings.

1. Sensitivity of the catalyst performance to temperature changes required a prohibitively large investment in steel for cooling surface in the catalytic reactor of the original German atmospheric and low-pressure processes.
2. The average molecular weight of the hydrocarbon product gradually decreased with on-stream time due to catalyst composition instabilities.
3. The accumulation of waxes, formed during the synthesis, made frequent catalyst regeneration necessary.
4. Synthesis gas had to be carefully purified to minimize accumulations of catalyst poisons such as H_2S, and organic sulfur compounds.

The original catalyst, cobalt-thoria-Kieselguhr, is operated at about 190 to 2000 tubes about 40 feet long by 2 inches in outside diameter. Catalyst is packed in the tubes, at approximately 1400 cubic feet per reactor. Production rate is 50 metric activity, sometimes in fluidized systems, in which the reaction occurs in gas or oil that is rapidly recycled through the reactor at low conversions per pass. In this way the fluid is used as coolant to replace the difficult cooling requirements of the original design. These variations have culminated in changes typified by modern Sasol plant (Lurgi Unit):

1. Higher pressure (25 versus 7 to 10 atm)
2. Higher temperature (430 versus 360 F for fresh catalyst)
3. Iron versus cobalt catalyst
4. Higher H_2/CO ratio (2.1 versus 1.6 for middle pressure processes and 2.0 for the original atmospheric process)
5. Higher specific rates (500 versus 60 to 100 cu ft feed gas/hr cu ft catalyst)
6. Larger diameter catalyst beds (44 versus 7 to 10 mm).

This Sasol process is shown schematically in Figure 13.

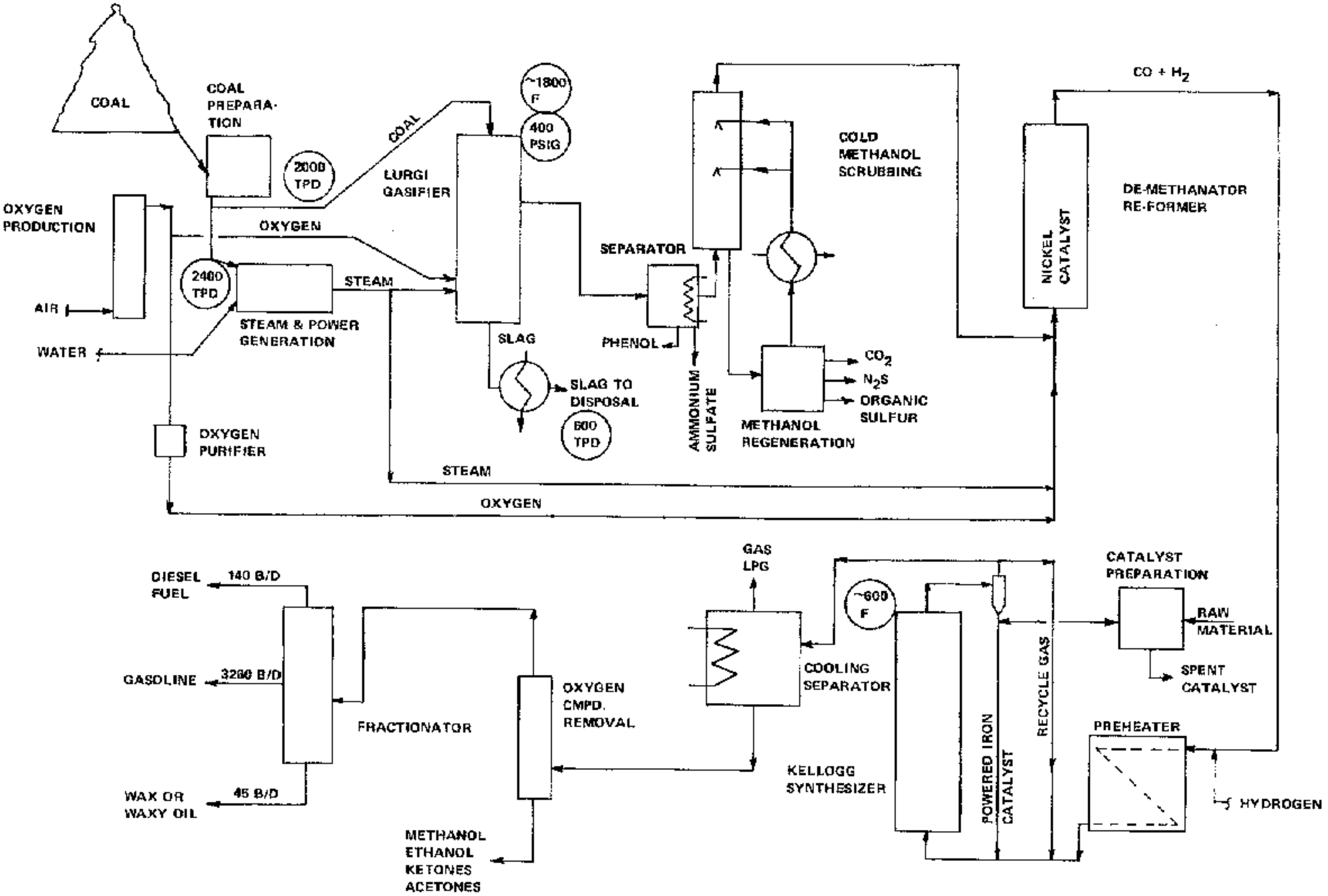


FIGURE 13. FISCHER-TROPSCH PROCESS SASOL PLANT, SOUTH AFRICA COMMERCIAL PRACTICE