COAL LIQUEFACTION

1. Introduction

Liquefaction is the generic term for converting coal to fuels and chemicals (see also FUELS, SYNTHETIC, GASEOUS FUELS; FUELS, SYNTHETIC, LIQUID FUELS). Coal (qv) has been described variously, depending on the context, as "nature's dump" and "nature's storehouse." The reason is that while the primary constituents of coal

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are carbon and hydrogen, one also finds oxygen, sulfur, and nitrogen (generally classified as "heteroatoms"). Lesser amounts of many other elements can be detected (as inorganic oxides, or "mineral matter") as well. All methods for converting coal to fuels, and most methods of converting coal to chemicals, require both an increase in the hydrogen/carbon (H/C) ratio (from ~0.2 to ~2, order of magnitude, both molar) and removal of sulfur, nitrogen, and the other elements.

Coal can be converted to liquid and gaseous fuels and chemicals by two different processing routes, normally termed "direct" and "indirect." Direct liquefaction processes result in primary products (liquids or solids) of molecular weight greater than, or of the order of magnitude of, the fuels and chemicals desired. Catalysts may be used. Secondary processing is usually required to form fuels and chemicals. Some direct liquefaction schemes also involve chemical pretreatment of the coal. Other schemes involve a second feed source, generally heavy fractions of petroleum (coal–oil coprocessing), sometimes recyclable wastes (coal–waste coprocessing). In indirect liquefaction (IL) processes, on the other hand, the first step is always gasification of coal to synthesis gas ("syngas," $CO + H_2$), and this is followed by additional steps in which the syngas is catalytically recombined to form hydrocarbons and/or oxygenates.

In the 1990s, the US Department of Energy (USDOE) considered catalytic two-stage liquefaction and coal/oil and coal–waste coprocessing as the two major elements of its direct coal liquefaction (DCL) program. Major elements of the indirect coal liquefaction program were advanced Fischer-Tropsch technology for transportation fuels and processes for oxygenated fuel additives and high value chemicals. At the turn of the century, USDOE's Vision 21 Concept has as a goal the development of a suite of "modules" that can be interconnected to design a plant that takes advantage of local resources and supply local needs. The object is for the plant to be able to use one or more fuel types (coal, natural gas, biomass, petroleum coke from oil refineries, waste from municipalities) and, coupled with carbon sequestration techniques, to produce multiple products (one or more of electricity, heat, fuels, chemicals, hydrogen) at high efficiencies with no emission of greenhouse gases (1).

Reviews of coal liquefaction may be found in (2–5). Below, the processing schemes for DCL, including some of the research results on catalytic DCL since the 1990s, are discussed first followed by coprocessing schemes. This is followed by a discussion of indirect coal liquefaction.

2. Direct Coal Liquefaction

From the above, there are two chemical concerns in DCL—introduction of hydrogen to the parent coal molecule, and removal of heteroatoms (nitrogen, sulfur, and oxygen) and mineral matter. A third concern is the transport of solid and slurry-phase material. Though a physical rather than a chemical problem, it has ramifications in the economics of commercial–scale plant design.

Hydrogenation (hydroprocessing, hydrorefining, solvent refining, or hydroliquefaction) and pyrolysis are the two means used for DCL. In hydrogenation, the organic components of coal are dissolved under a moderate-to-high hydrogen pressure using a solvent, generally a coal-derived heavy aromatic material (6).

Here the primary reactions are a combination of homogeneous thermal cracking (ie, free-radical generation) and heterogeneous hydrogenation (involving hydroaromatics in the slurry vehicle and/or the coal itself as hydrogen-transfer agents). Rapid and efficient capping of the primary free radicals generated by heating is thought to be necessary in order to prevent retrogressive reactions leading to formation of solid char (7). Other theories of coal liquefaction suggest that hydrogen can engender reactions involving scission of strong bonds in the coal macromolecule, and hence can act as an active bond-cleaving agent rather than simply a passive radical quencher (8). Typically, the object of hydrogenation is to maximize the yield of distillate fractions that can subsequently be converted into fuels. [Distillate materials comprise the naphtha fraction, typically boiling between C_5 and 420°F (215°C) plus the middle distillate fraction, typically between 300 and 700°F (150–370°C), with the exact cuts depending on product specifications.]

Pyrolysis normally involves heating in an inert or reducing atmosphere and produces char and oil, and often a low-BTU gas. The relative proportion of char to the other products can be quite high, hence the rationale for liquefaction by pyrolysis is often not production of coal-derived distillate materials but rather the solid. Hydropyrolysis (heating in the presence of hydrogen) and/or pyrolysis under conditions of rapid heating can, however, generate yields of distillate products significantly in excess of the volatile matter content of the starting coal.

2.1. Hydrogenation. *Early Work.* Bergius was awarded the Nobel Prize for chemistry in 1931 based on his pioneering work on DCL (9). The work of I. G. Farben on the Bergius process led to the development of a two-stage direct-hydrogenation liquefaction process. Here, primary coal solubilization was carried out in the first stage using added disposable catalysts in bubble-column reactors. Distillate materials were subsequently catalytically upgraded to liquid transportation fuels using supported hydrotreating/hydrocracking catalysts in fixed-bed reactors (10). The Bergius process was significant in the years of World War II but fell into disuse due to the decreasing price of crude. In the 1960s, interest was rekindled when oil prices increased and a better understanding of the fundamentals of hydrogen donation made solvent refining more attractive as a DCL technique (6).

Solvent-Refined Coal Process. Work in the mid-1960s by the Spencer Chemical Co. (11) and during the 1970s by its successor, the Gulf Chemical Corp. (now Chevron) led to two solvent-refined coal (SRC) processing schemes: SRC-I for production of low ash solid boiler fuels and SRC-II for distillates, eg, "syncrude."

A schematic flow diagram for the SRC-I process is shown in Figure 1. Coal is first slurried in a recycle solvent, then preheated and finally reacted in a bubble column-type reactor at 450°C in the presence of gaseous hydrogen. Because of the high reactivities of the coals tested, primarily eastern U.S. high- and medium-volatile bituminous coals, no catalysts were added and the reaction was carried out at pressures as low as 6.9 MPa (1000 psig). Mean residence time in the reactor was reported to be on the order of 30 min. Solids were removed by use of either rotary pressure precoat filters or hydroclones. SRC yields, computed as the mass of SRC-I per mass of moisture- and ash-free (maf) coal exclusive of light hydrocarbon gas make, of ~60% were achieved.

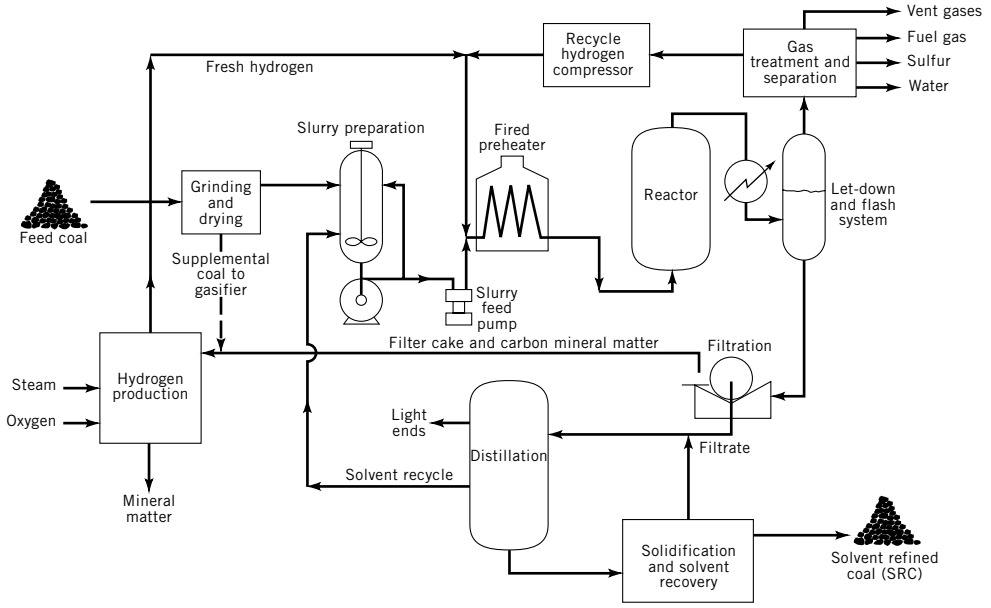


Fig. 1. SRC process. The reactor operated at 450°C and 6.9 MPa (1000 psig).

Ash removal was quite high by this process and, depending on the forms of sulfur in the parent coal (inorganic/organic), sulfur reduction was also substantial. Data for a Kentucky No. 9 high pyrite, eastern U.S. coal showed SRC-I/parent-coal weight percent ratios for total sulfur as 0.22 and for mineral matter as 0.0095. The heating-value ratio was 1.2.

The SRC-I technology was tested at a large-scale (50 t/day) demonstration plant in Fort Lewis, Washington, commissioned in 1974. This plant operated for several years, but severe problems were encountered, primarily with solvent balance and with operation and reliability of the solids-separation portion of the facility (12). The final design for this facility differs from Figure 1 in that an expanded-bed hydrocracking unit was added as a second-stage reactor to increase the yield of distillate material (13). Total solids [SRC plus two-stage liquefaction (TSL) solids] were reduced to ~27% by this modification, resulting in an increase in distillate materials. Bench-scale testing of the hydrocracking step indicated that the naphtha fraction, C_5 to 420°F (215°C), would be low in sulfur (0.01 wt%) but high in nitrogen (~0.1%). Severe hydrotreating of this material would be required before refining into gasoline via catalytic reforming. An overall thermal efficiency (defined loosely as the energy capable of being generated by combustion of product from a unit weight of feed per energy generated by combustion of a unit weight of feed) of this proposed facility was calculated to be 70%.

The SRC-II process, shown in Figure 2, was developed in order to minimize the production of solids from the SRC-I coal-processing scheme. The principal variations were incorporation of a recycle loop for the heavy ends of the primary liquefaction process and imposition of more severe conditions during

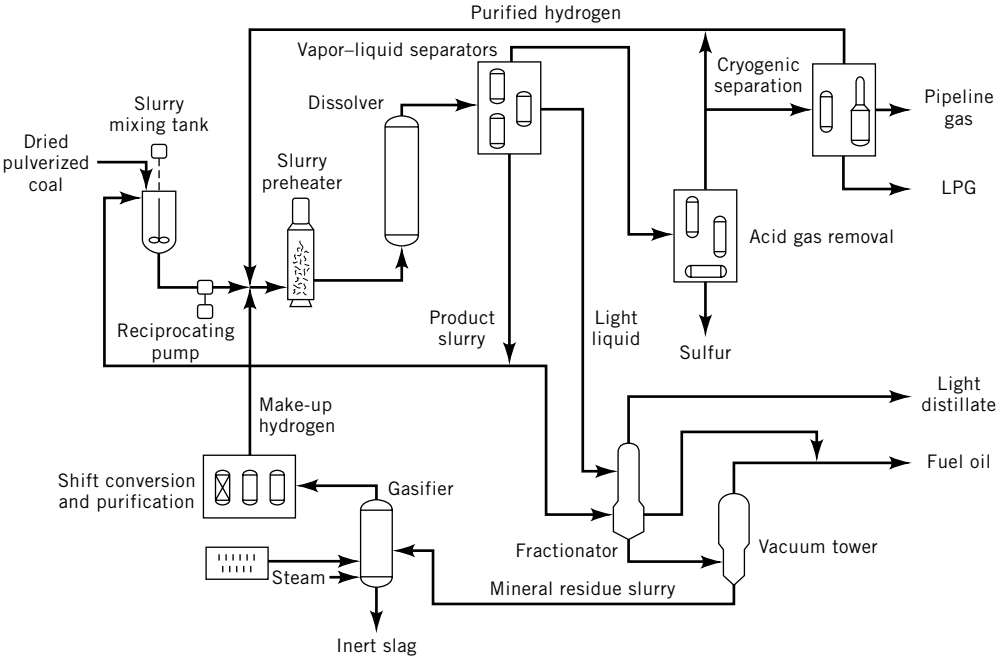


Fig. 2. SRC-II process where LPG is liquefied petroleum gas.

hydrogenation (5). It was quickly realized that minerals concentrated in this recycle stream served as heterogeneous hydrogenation catalysts that aid in the production of distillate. In particular, pyrrhotites, Fe_xS_y (where x and y are ~ 1), nonstoichiometric iron sulfides produced by reduction of iron pyrite (FeS_2), were identified as being especially important. Pyrite was subsequently added for cases where the inherent pyrite content of the coal was low (14,15). Yields of some of the primary liquefaction products formed when pyrite is added to a slurry containing a moderately reactive but relatively low pyrite coal are given in Table 1.

A yield comparison between the products of the SRC-I and SRC-II processes is given in Table 2.

Table 1. **Yield[a] for Addition of Pyrite to Coal[b]**

	Pyrite addition, wt%		
Product	0.0	3.0	7.5
light hydrocarbon gases[c]	16.6	17.1	17.6
naphtha	7.3	9.4	11.4
total oil	37.5	40.9	44.7
SRC	29.8	27.5	23.5
insoluble organic matter	5.9	5.3	5.2

[a]Based on wt% maf coal.
[b]Pittsburgh seam bituminous coal from West Virginia containing 0.9 wt% pyrite.
[c]Up to C_4.

Table 2. **Comparison between Products of the SRC-I and SRC-II Processes**[a]

Process	SRC-I	SRC-II
Product yield, wt %		
C_1–C_4	10.5	16.1
total oil	25.9	38.9
SRC solids	42.7	21.0
insoluble organic matter	4.1	5.1
H_2[b]	−2.4	−5.6

[a]High-volatile Kentucky bituminous coal.
[b]The negative sign indicates that hydrogen is being consumed.

Changing the process configuration to SRC-II was successful in producing ∼50% additional oil. However, a large increase in light hydrocarbon gas make accompanied this increase, with an attendant reduction in hydrogen utilization efficiency. Problems persisted using many coals, particularly subbituminous coals (4).

Exxon Donor Solvent Process. A schematic flow diagram for the Exxon Donor Solvent (EDS) process is shown in Figure 3. The principal modification in

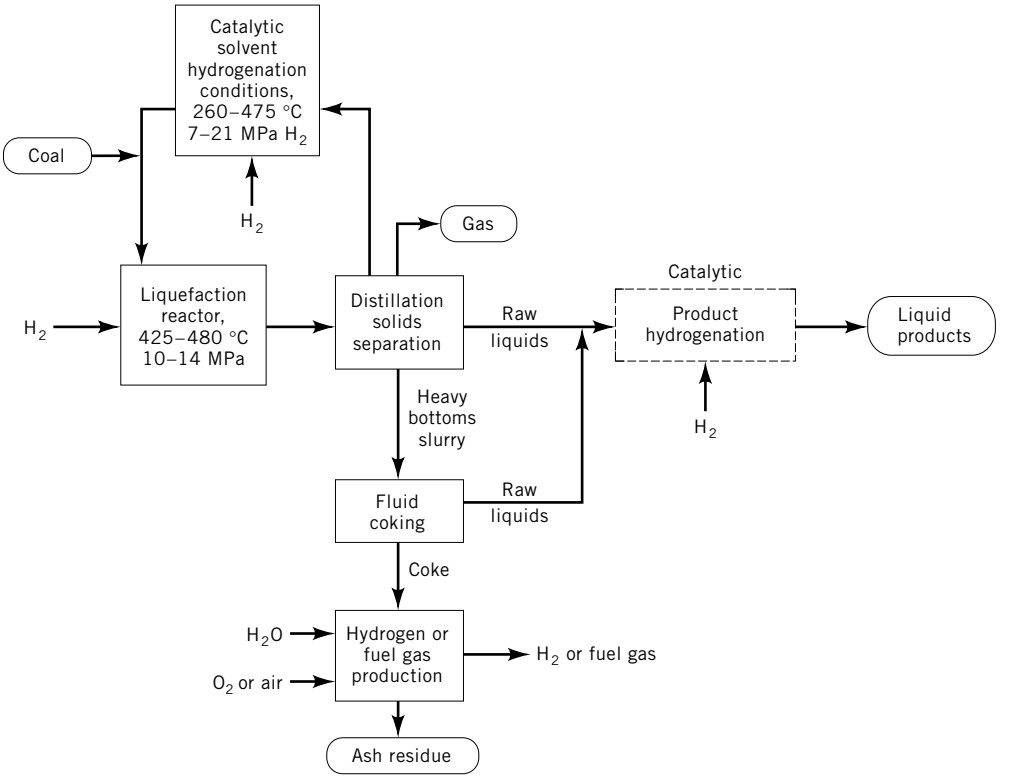


Fig. 3. Exxon Donor Solvent process. To convert MPa to psi, multiply by 145.

this technology was the incorporation of a fixed-bed catalytic hydrogenating unit for the recycle solvent stream. This additional unit was required to keep the hydrogen donating/shuttling capacity of the recycle solvent oil at an acceptably high value (16). The use of bottoms slurry recycle to increase the solvent "make" fraction by taking advantage of the catalytic properties of minerals was also investigated, and improved yields in the bottoms recycle mode were generally reported. Recycle of this fraction was also reported to improve operability of the process dramatically, especially using low rank coals where viscosity of the bottoms stream was a significant problem (17). The primary liquefaction part of the reaction system operated at temperatures of 425–480°C and pressures of 10–14 MPa (1450–2030 psi), using mean residence times in the range of 15 min–2 h, depending on coal reactivity and process configuration. Operation at these conditions required significant advances in hardware, such as the design of a slurry let-down valve, required to reduce the pressure of the let-down slurry (15% solids) from 14 to 1 MPa at 450°C (18).

Operation of the EDS process was demonstrated in a 230 t/day unit in Baytown, Texas that started up in 1980 and was dismantled in late 1982. Exxon (now ExxonMobil) was the first to investigate the suitability of a wide range of different U.S. coals for conversion. Data on the response of a variety of coals to once-through and bottoms-recycle operations are shown in Figure 4. Figure 5 presents typical liquefaction product distributions for the system operated both with and without the Flexicoking (fluidized-bed coking) option.

H-Coal. A significantly different scheme for DCL, developed by Hydrocarbon Research Inc. (HRI; now Hydrocarbon Technologies Inc., HTI; as of August

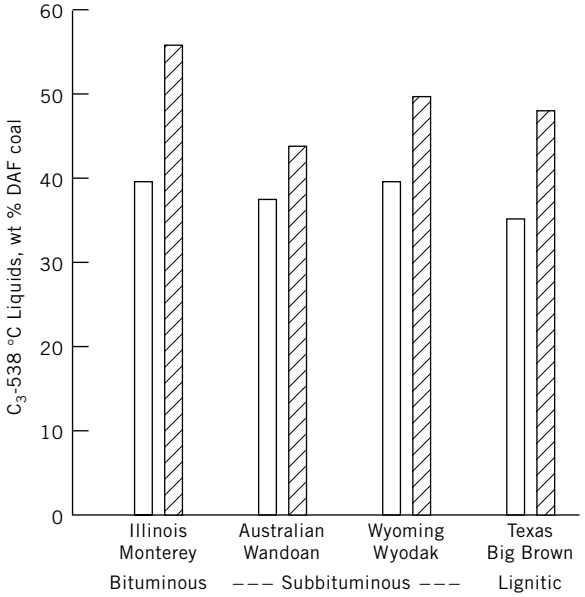


Fig. 4. Product yields for EDS process on (open) once-through basis and (shaded) bottoms-recycle basis for various types of coal. DAF = dry, ash-free. C_3–538 °C = a boiling fraction.

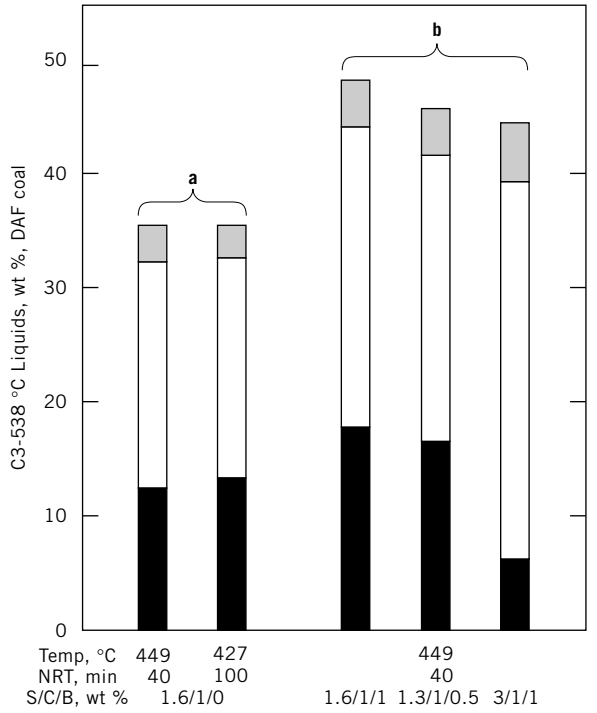


Fig. 5. Product yields for the EDS process in a 34-kg/day pilot plant **a** with, and **b** without, the Flexicoking option. Gray bars represent gas, clear bars represent naphtha, and dark bars represent oil. The pressure for the once-through process is 10.3 MPa, for the recycle 13.8 MPa. NRT, nominal residence time; S/C/B, solvent/coal/bottoms. To convert MPa to psi, multiply by 145.

2001, a wholly owned subsidiary of Headwaters Inc), was based on research and development on the H-Oil ebullated bed catalytic reactor for hydrotreating and hydrocracking heavy oil. The heart of this process is the reactor, where coal, catalyst, solvent, and hydrogen are all present in the same vessel (Fig. 6). The reactor is maintained in a "bubbling" or ebullated, ie, well-mixed, state by internal agitation coupled with the action of the gas bubbling through the fluid. This process was piloted by the then HRI and Ashland Synthetic Fuels, Inc. in a 600 t/day pilot plant adjacent to Ashland's refinery in Catlettsburg, Kentucky (12) . The process consists of slurry preparation followed by catalytic hydrogenation/hydrocracking at 450°C and 15 MPa (2200 psi) in the ebullated bed reactor (Fig. 7).

A principal focus of this project was research and development for catalysts that were tolerant of the coal-derived mineral matter in the reactor. Typical early catalysts showed rapid deactivation because of coking and loss of surface area, presumably from pore–mouth blockage by coke and metals laydown. Coke buildups of 20–25 wt% and surface area reductions from 300 m^2/g for the fresh catalyst to 25 m^2/g for the aged catalyst were reported after only 5 days on stream (19). Although one of the primary advantages of the H-Coal processing scheme was the ability to add and withdraw catalyst continuously from the reactor in

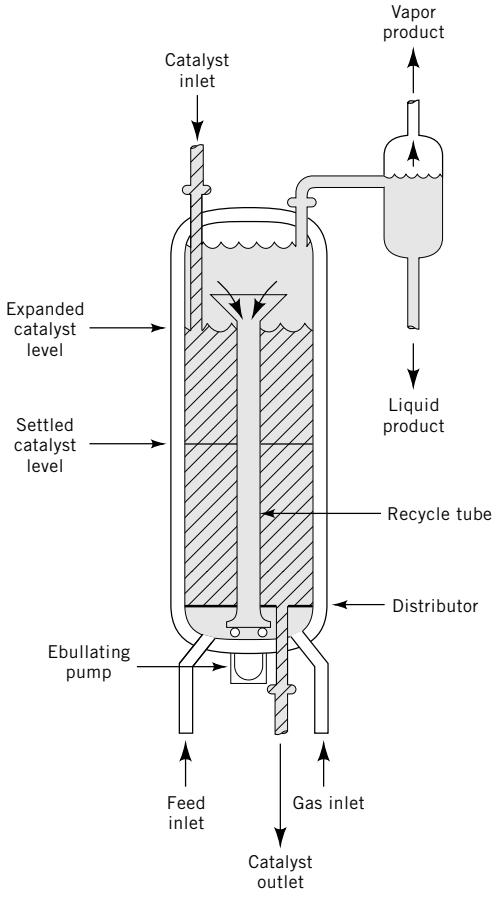


Fig. 6. H-Coal ebullating-bed reactor.

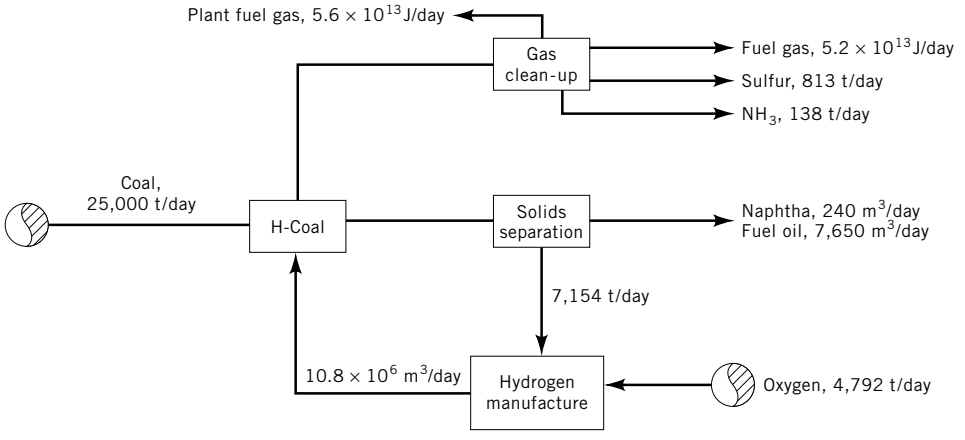


Fig. 7. H-Coal process using Illinois No. 6 coal. To convert J to Btu, multiply by 6.48×10^{-4}. To convert m^3 to bbl, multiply by 6.29. To convert m^3 to standard cubic feet (scf), multiply by 35.3.

order to maintain a stable level of activity, catalyst replacement and consumption rates were unacceptably high under these conditions.

In a later version, two reactors were used, coupled closely together, one operating at 400°C and the other at 420–425°C. The catalyst was also changed, from a cobalt–molybdenum/alumina to a nickel–molybdenum on bimodal alumina (4). Catalyst was added to both reactors, and ash was not removed between reactors. The deasher feed, now from the second reactor, was sufficently light that the deasher previously used could be replaced by a (simpler) pressure filter. In this Catalytic Two-Stage Liquefaction (CTSL) process, conversion was increased and hydrogen was more efficiently used (5,20).

Wilsonville Coal-Liquefaction Facility. Beginning in 1973, a 6 t/day coal liquefaction pilot plant was built in Wilsonville, Alabama by the Edison Electric Institute (EEI) and Southern Company Services. The Electric Power Research Institute (EPRI) assumed project sponsorship in late 1973, and USDOE became the primary sponsor in 1976. Amoco Oil Co. (now BP) joined the project in 1984. The purpose of the Wilsonville Advanced Coal Liquefaction R&D facility was to provide a flexible but reasonably large-scale pilot plant where effects of coal type and processing, ie, reactor configuration, could be tested and evaluated. Research on the Kerr–McGee critical solvent deashing (CSD) technology (also termed the Residual Oil Solvent Extraction, or ROSE, process) was also carried out, resulting in the development of alternative methods for solids removal from primary liquefaction products. Because of the role of Wilsonville in consistently demonstrating success or failure of a large number of concepts, many of whom were initialized elsewhere, particular attention should be paid to the results from this facility.

The plant began operation in 1974 in the SRC-I mode, but evolved to a two-stage operation utilizing two ebullating bed catalytic reactors (21). Initial efforts in TSL focused on catalytic upgrading of the thermal products, or Nonintegrated Two-Stage Liquefaction (NTSL). This configuration, termed nonintegrated because the coal-derived resid hydrocracking step did not interact with the primary thermal part of the plant, was excessively inefficient because of high hydrogen consumptions associated with the thermal part of the operation.

In Integrated Two-Stage Liquefaction (ITSL), a short contact-time thermal reactor was close coupled to an ebullated-bed catalytic reactor and process solvent was generated by distillation of the hydrocracked products. The thermal resid produced in the ITSL at short contact times was more reactive toward expanded-bed hydrocracking, thus permitting operation of the ebullated bed reactor at lower severity and minimizing gas make (22). Results on liquefaction of an Illinois No. 6 high-volatile bituminous coal using both the NTSL and ITSL modes at Wilsonville are shown in Table 3 (23).

Coal throughput, ie, space velocity per unit reactor volume, was substantially improved in going to the ITSL mode. The higher reactivity of the coal-derived resid permitted operation of the hydrocracker at lower temperature; this would be expected to reduce the rate of coke lay-down on catalyst, and to improve hydrogen utilization efficiency by minimizing formation of light hydrocarbon gases (higher distillate selectivity). A 35% increased yield of C_4^+ distillate was obtained.

Table 3. **Operating Conditions and Yields at Wilsonville Plant**[a]

	Mode of Operation[b]				
parameter	NTSL	ITSL	RITSL	CC–ITSL	CTSL
run number	241CD	7242BC; 243JK/244B	247D	250D	250G (a)
catalyst	Armak	Shell 324M	Shell 324M	Amocat IC	Amocat
Thermal stage					
average reactor temperature, °C	429	460;432	432	440	443
coal space velocity at temp >371°C, kg/m^3	320	690;450	430	320	320
pressure, MPa[c]	15	17;10–17	17	17	17
Catalytic stage					
average reactor temperature, °C	416	382	377	399	399
space velocity catalyst[d], h^{-1}	1.7	1.0	0.9	2.08	2.23
catalyst age resid/cat	260–387	278–441; 380–850	446–671	697–786	346–439
Yields[e]					
C_1–C_3 gas	7	4;6	6	7	8
C_4^+ distillate	40	54;59	62	64	63
resid	23	8;6	3	2	5
hydrogen consumption	4.2	4.9;5.1	6.1	6.1	6.4
Other					
hydrogen efficiency, C_4^+ distillate/H_2 consumed	9.5	11;11.5	10.2	10.5	9.8
distillate selectivity, C_2–C_3/C_4^+ distillate	0.18	0.07;0.10	0.10	0.11	0.12
energy content of feed coal reject to ash concentrate, %	20	24;20–23	22	23	16

[a]Illinois No. 6 coal.
[b]See text for term definition.
[c]To convert MPa to psi, multiply by 145.
[d]On a wt of feed per wt of catalyst basis.
[e]Wt% on a maf coal basis.

Also explored were Reconfigured Integrated Two-Stage Liquefaction (RITSL), where solvent deashing was practiced after the hydrocracking step, and Close-Coupled Integrated Two-Stage Liquefaction (CC–ITSL), where the two reactors (thermal/catalytic) were linked directly without any intervening processing steps (24,25). Typical results for these processes are also shown in Table 3. Incremental improvements in distillate yield and selectivity were realized by changing the process configuration, but at the expense of increased hydrogen consumption.

From 1985 to 1992, process development at Wilsonville focused on development of a Catalytic/Catalytic Two-Stage Liquefaction (CTSL) scheme utilizing ebulating-bed catalytic reactors in both stages. Initial work (26) indicated that distillate yields as high as 78% could be obtained by operating the first stage at low severity (399°C) and by using a large-pore bimodal NiMo catalyst having a mean micropore diameter in the 11.5–12.5-nm range. Results in the CTSL mode for three different coals are shown in Table 4. These data show the significant improvement in distillate production that can be achieved by use of catalyst in both stages, but (again) at the cost of increasing levels of hydrogen consumption.

Table 4. **Operating Conditions and Yields at Wilsonville for Three Coals in CTSL Mode**

	Coal type		
Parameter	Illinois No. 6	Ohio 6[a]	Wyodak
run number	253A	254G	251-IIIB
catalyst	Shell 317	Shell 317	Shell 324
First stage			
average reactor temperature, °C	432	433	441
inlet hydrogen partial pressure, MPa[c]	14.1	15.0	17.3
feed space velocity, h^{-1}	4.8	4.3	3.5
pressure, MPa[b]	17.9	18.8	17.9
catalyst age, resid/catalyst	150–350	1003–1124	760–1040
Second stage			
average reactor temperature, °C	404	421	382
space velocity, feed/catalyst, h^{-1}	4.3	4.2	2.3
catalyst age, resid/catalyst	100–250	1166–1334	371–510
Yield[c]			
C_1–C_3 gas	6	8	11
C_4^+ distillate	70	78	60
resid	–1	–1	+2
hydrogen consumption	6.8	6.9	7.7
Other			
hydrogen efficiency, C_4^+ distillate/H_2 consumed	10.3	11.3	7.8
distillate selectivity, C_1–C_3/C_4^+ distillate	0.08	0.11	0.18
energy content of feed coal rejected to ash concentrate, %	20	10	15

[a]Approximately 6% ash.
[b]To convert MPa to psi, multiply by 145.
[c]Wt% on a maf coal basis.

Block diagrams of NTSL, ITSL, RITSL CC–ITSL, and CTSL operations at Wilsonville are given in Figure 8. The Wilsonville Advanced Liquefaction R&D facility was shut down in early 1992 and was decommissioned shortly thereafter.

NEDOL. The Japanese NEDOL process and the German Kohleoel process (below) are considered to be demonstrated and suitable for commercialization by their companies. NEDOL is similar to the EDS process. However, a catalyst is used ("natural" pyrite of mean particle size 0.7 μ) with the hydrogenated recycle solvents. A pilot plant has been reported to be successfully functioning at 150 t/day (27). A 2500-t/day plant operating at mild reaction conditions, 16.8–18.8 MPa and 450°C, has been simulated (28). The pilot-plant schematic is shown in Figure 9.

Kohleoel-Integrated Gross Oil Refining (IGOR+). Ruhrkohle and VEBA Oel have collaborated on this process. In the primary reactor, conditions are maintained at 30 MPa and 470°C, and an iron oxide catalyst is used. Products are separated hot, and the vapor products are hydrotreated at 30 MPa and 350–420°C. The liquid from the first separator is recycled as part of the solvent. Liquid from the second separator is distilled at atmospheric pressure to yield a light oil and a medium oil. The process schematic is shown in Figure 10 (29). Process yields are shown in Table 5.

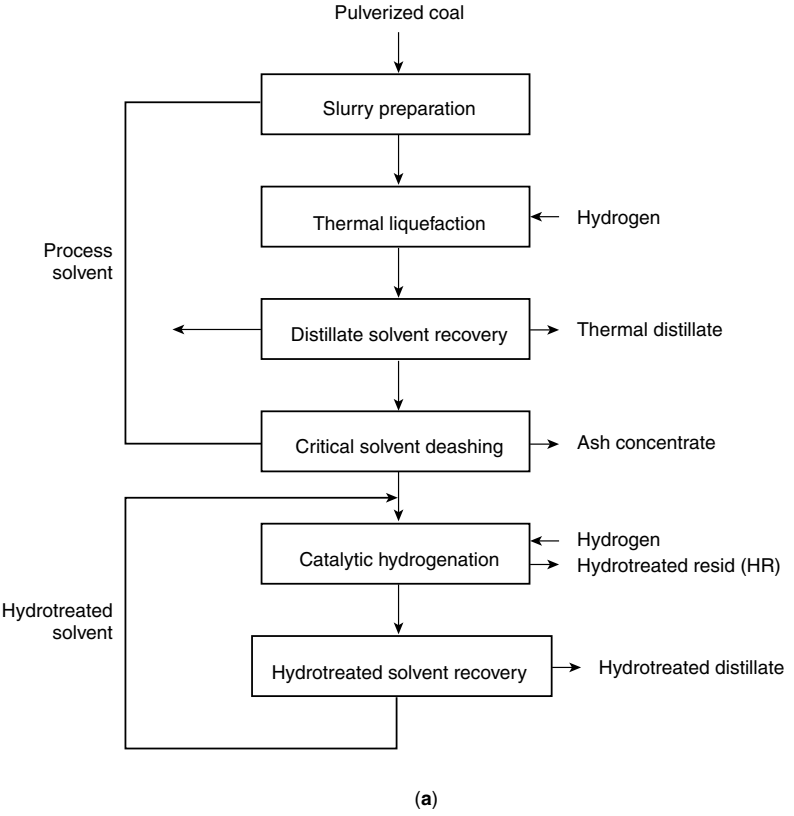
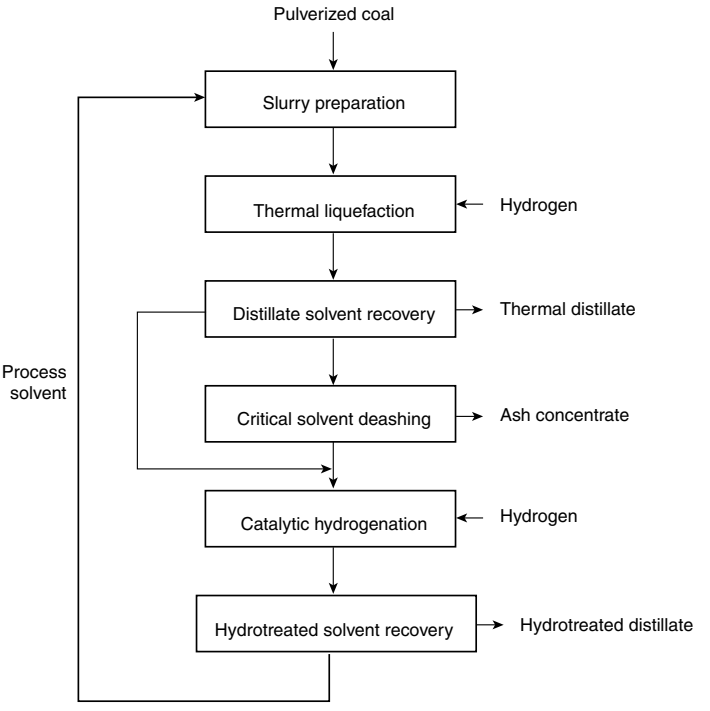


Fig. 8. Block diagrams for (**a**) NTSL, (**b**) ITSL, (**c**) RITSL, (**d**) CC-ITSL, and (**e**) CTSL operations at Wilsonville (4).



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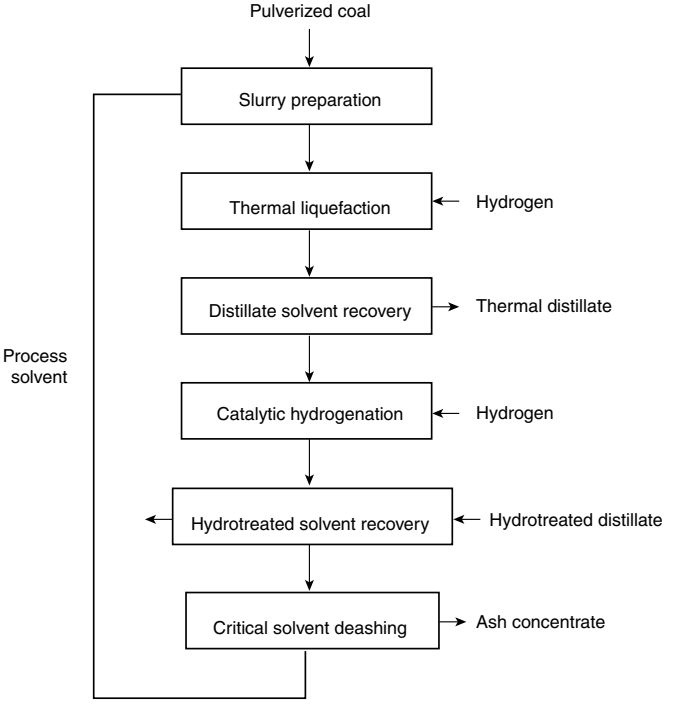
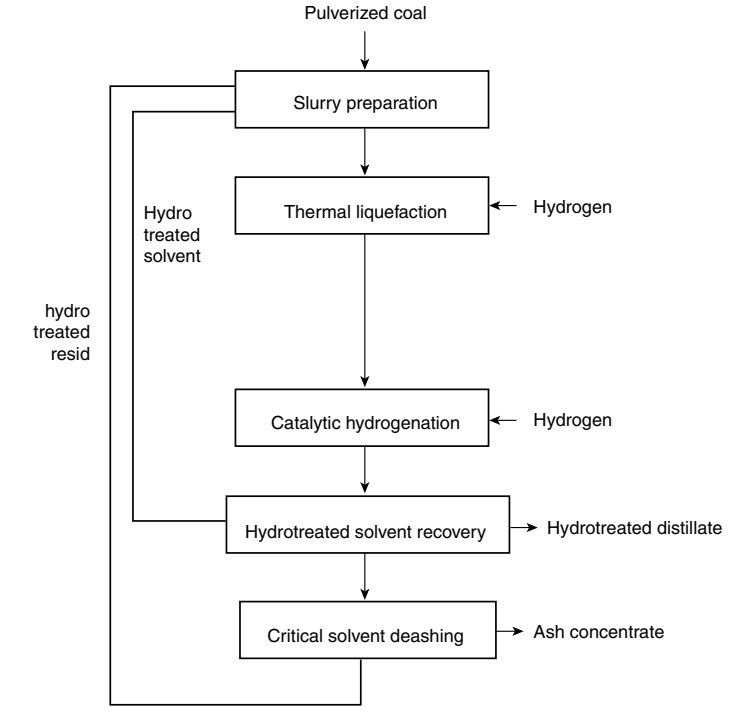


(**c**)

Fig. 8 (*Continued*)



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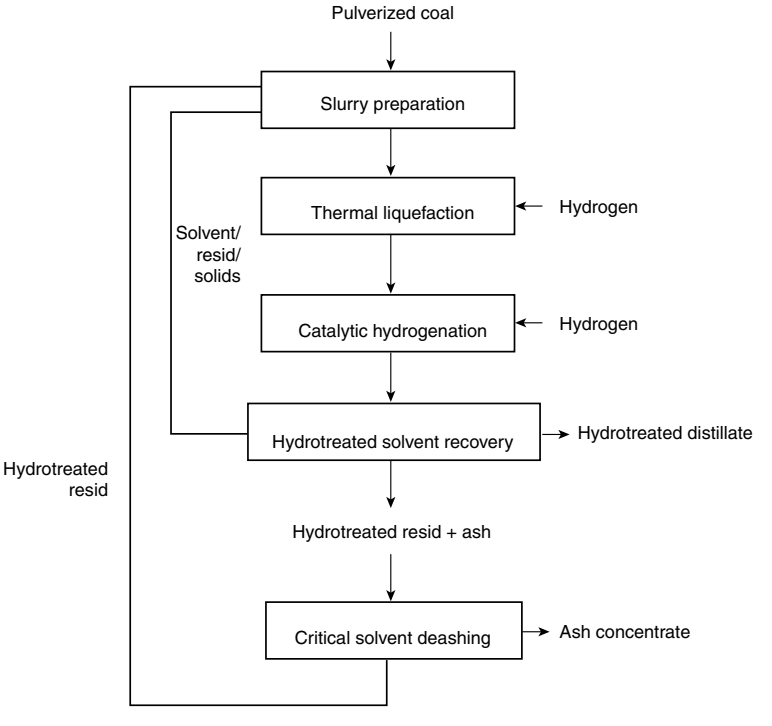

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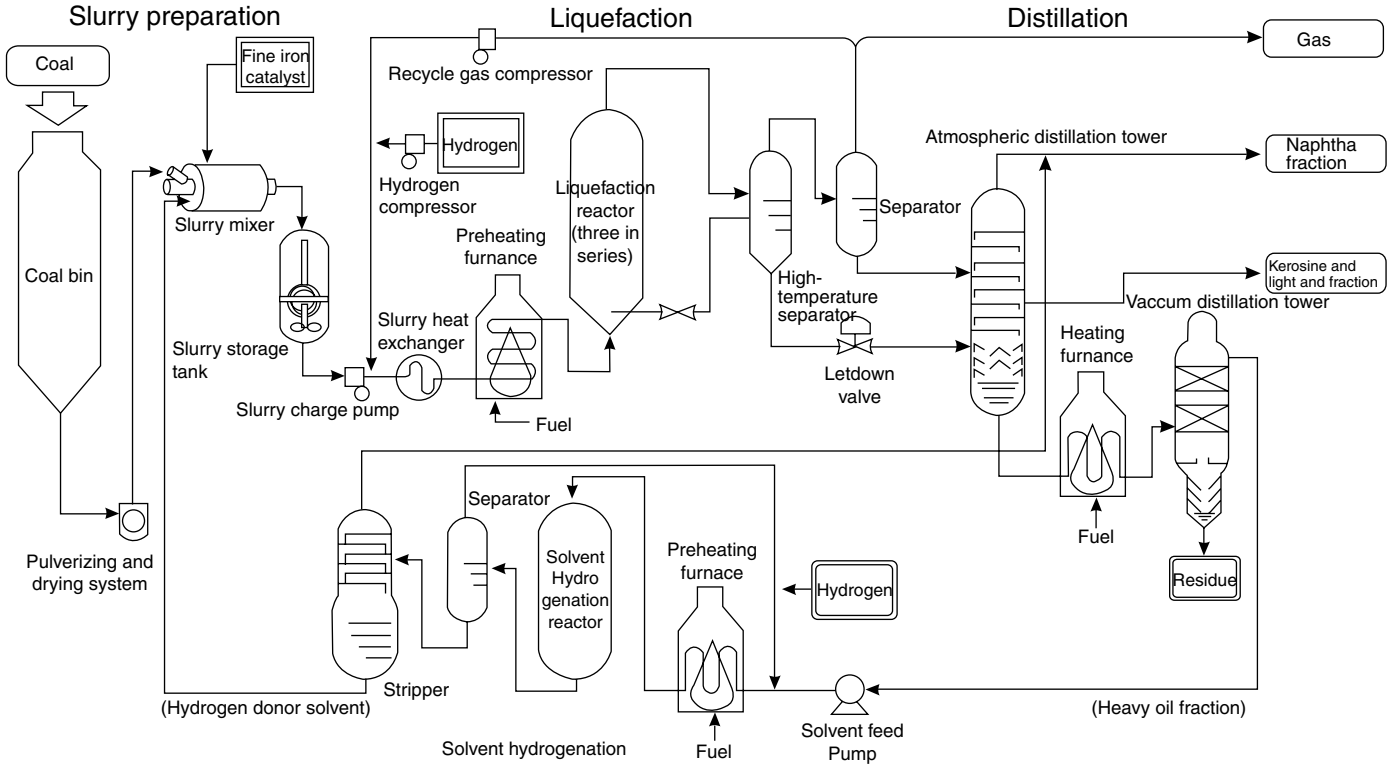


Fig. 9. Schematic of NEDOL Pilot Plant. Reprinted from K. Hirano, Ref. 27 with permission from Elsevier Science.

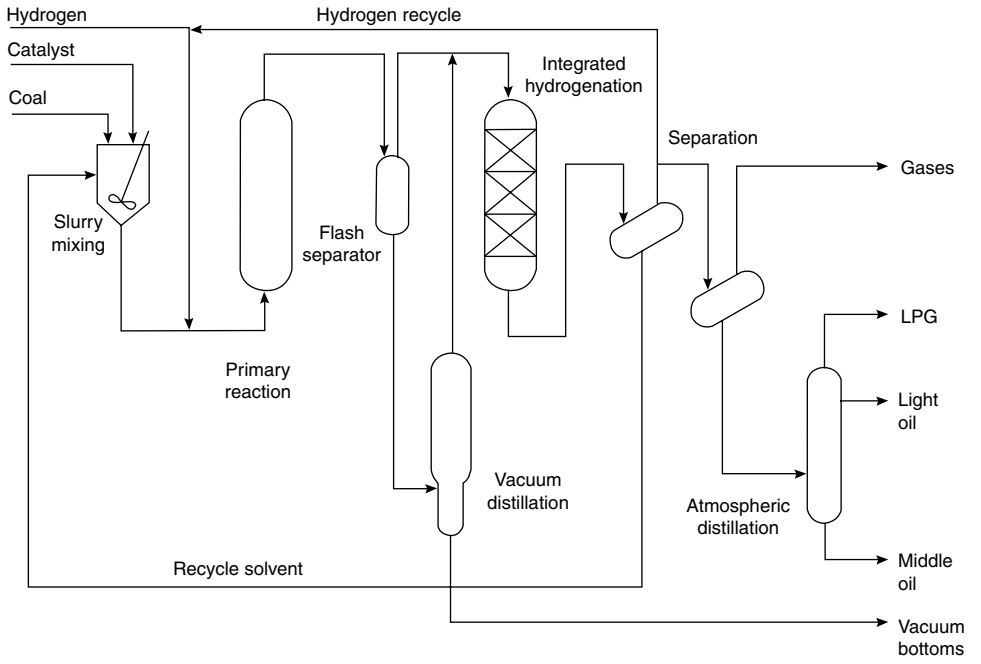


Fig. 10. Schematic for Kohleoel Process (29).

Other Processes. Other variations of catalytic and noncatalytic coal liquefaction schemes have also been developed. A 2.5-t/day pilot plant was operated for 4 years by the National Coal Board in the United Kingdom at Point of Ayr in Wales, but has since been decommissioned (29,30). The Catalytic Coal Liquids (CCL) process (31) reacted a coal–oil slurry with hydrogen over baskets containing a proprietary catalyst developed by then—Gulf Oil (now a part of Chevron), reportedly unaffected by coal ash. The Consolidation Synthetic Fuels (CSF) process used a complicated multistage operation in place of the second-stage hydrogenation/fractionation typically carried out in TSL processes (32).

Table 5. **Yields and Product Quality for the Kohleoel Process**[a]

Process yields	Yield	
hydrocarbon gases (C1–C4)	19.0	
light oil (C5–200°C)	25.3	
medium oil (200–325°C)	32.6	
unreacted coal and pitch	22.1	
Product quality	**Light oil**	**Medium oil**
hydrogen (%)	13.6	11.9
nitrogen (ppm)	39	174
oxygen (ppm)	153	84
sulfur (ppm)	12	<5
density (kg m^{-3})	772	912

[a]Prosper coal (German bituminous).

Table 6. **Effect of Emulsified Mo Catalyst on Product Distribution**[a]

Mo added, ppm	216	108	0
Product			
gases and light oil, wt %	33.3	32.6	17.6
hexane-soluble oil, wt %	22.2	26.6	5.4
asphaltenes[b]	23.4	21.1	50.3
hydrogen consumed[c]	6.1	6.1	4.4

[a]Pittsburgh No. 8 bituminous coal, 400°C, 13.7 MPa.
[b]Defined as toluene-soluble, hexane-insoluble material.
[c]kg H_2/100 kg maf coal.

The Brown Coal Liquefaction process was developed by NEDOL to handle very low rank coals with high moisture levels, such as those found in Australia (29). The China Coal Research Institute has comissioned feasibility studies, pilot plants and demonstration units for DCL from Germany, Japan and HTI, to use various Chinese coals.

Bench-Scale Research on Catalysts for DCL. Bench-scale test results are generally looked upon with skepticism because it is not clear how they relate to processes going on in industrial-scale reactors. However, Xu and co-workers (33) compared various types of bench-scale reactors and found that results similar to those from a large-scale ebullated-bed reactor could be obtained from a microautoclave reactor shaken at 400 cpm and containing a steel ball for efficient mixing.

While materials like zinc chloride were tested as catalysts for DCL (34), most catalytic research employed expensive materials such as molybdenum or cheap, disposible materials such as iron. The increase in conversion using an emulsified molybdenum catalyst is shown in Table 6. However, the costs and recovery of such material posed problems.

In the 1990s, USDOE started a consolidated program where various iron-based catalysts were used in bench-scale tests in different laboratories. Standard coals DECS-6 or DECS-17, chosen for their extremely low iron content, were used for the bench-scale tests.

Researchers at the University of Pittsburgh used finely divided sulfated iron oxides for the direct liquefaction of coal (36). Figure 11 shows results (37) from liquefaction runs using DECS-17 with a series of anion-modified iron(III) oxides and monoclinic pyrrhotite (Fe_7S_8) as catalysts (0.35 wt% Fe relative to coal). The overall conversion of coal (defined as product soluble in methylene chloride, MC, as a fraction of the initial coal) and the yield of oil (defined as MC-soluble, pentane-soluble product as a fraction of the initial coal) are both significantly smaller for the unmodified iron oxide. Using the sulfated iron oxide and the sulfated iron hydroxide results in conversions and yields comparable to modifying the iron oxide with 5% tungstate or 5% molybdate anions, and all are comparable to using pyrrhotite alone.

A series of catalysts were made at West Virginia University by preparing and disproportionating ferric sulfide (Fe_2S_3) under various conditions. The disproportionation is assumed to lead to an intimate mixture of pyrite, nonstoichiometric pyrrhotite and elemental sulfur (38). The catalysts are extremely sensitive

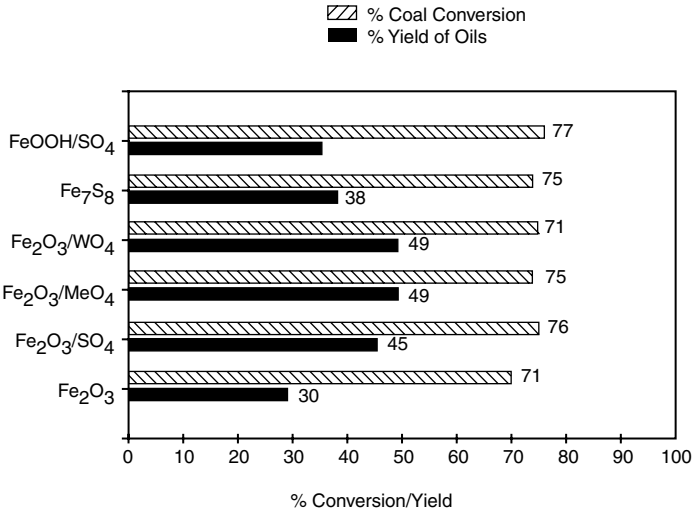
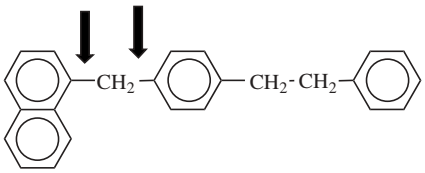


Fig. 11. Activities of iron(III) oxides, modified by small amounts of different anions. DECS- 17 coal, 400°C, 6.9 MPa (1000 psig) hydrogen pressure (cold). 300-mL stirred batch autoclave, 1200 rpm, 60 min, tetralin/coal = 3, Fe/coal = 0.35 wt%. Reprinted Ref. 37 from V. R. Pradhan, J. Hu, J. W. Tierney, and I. Wender, with permission of the American Chemical Society.

to air or oxygen. The materials can be made as small particles by preparing *in situ* on the coal surfaces (39), or in an aerosol reactor (40), or using surfactants (41). The *in situ* technique generally works best. Figure 12 shows the effect of various amounts of *in situ* impregnated catalyst on conversion [tetrahydrofuran(THF) soluble] and oil + gas yield (THF soluble, hexane soluble). Addition of second metals as sulfides sometimes leads to alloys, but with little improvement in conversion or yield (42).

Researchers at Pacific Northwest Laboratory developed techniques (43) for generating iron-based catalysts in large quantities using flow-through techniques termed Rapid Thermal Decomposition of Solutions (RTDS) and Modified Reverse Micelle (MRM) processes. In RTDS, precursors are exposed briefly to conditions of high temperature and high pressure to initiate nucleation of iron oxide and hydroxide. In MRM, high loadings of iron-bearing salts in water-in-oil microemulsions are precipitated by changing the conditions of the microemulsions. Various catalysts obtained using these methods were tested using the model compound naphthyl bibenzylmethane:



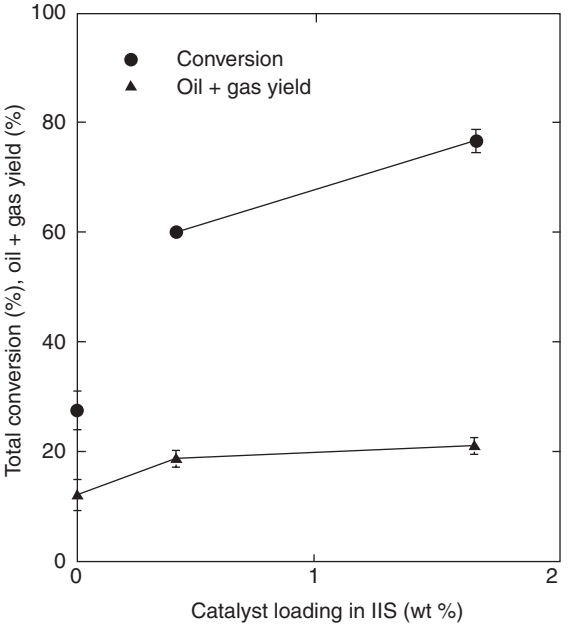


Fig. 12. Effect of loading of *in situ* impregnated ferric-sulfide-based catalyst. DECS-6 coal, 400°C, 6.9 MPa (1000 psig) hydrogen pressure (cold), 57-mL tubing-bomb reactor, vertical agitation at 5 Hz, 30 min, 3-g coal, 5-mL hexadecane. Reprinted from Ref. 39 with permission.

Here the bonds marked by arrows are analogous to those that would be cleaved in initial DCL reactions ("primary" DCL), while cleavage of the other bonds represent other, later, significant reactions in DCL. Results for some of these tests are shown in Table 7.

A good snapshot of work on iron-based catalysts in laboratories supported by USDOE as well as in other laboratories can be found in (44). However, Table 7 and Figures 11 and 12 demonstrate the difficulty in comparing catalyst performance by comparing results from different laboratories using not only different reactors, but also different solvents, coals, conditions, and even analytical techniques. To solve this problem, USDOE commissioned Sandia National Laboratories to test catalysts from different laboratories using an identical set of conditions and reagents and using a statistical design of experiments. To the authors' knowledge, the study was never completed. However, Table 8 shows results of a partial report (45).

2.2. Pyrolysis and Hydropyrolysis. The second category of DCL aimed at producing distillate materials from coal is pyrolysis and hydropyrolysis. Here a solvent is typically not used, and neither is a catalyst. Pyrolysis processes are burdened with poor liquid yield, relative to hydrogenation, and the coal-derived liquids are high in heteroatoms and in fine-particulate matter, both organic and inorganic. Pyrolysis, sometimes called destructive distillation, essentially involves heating the coal in an inert atmosphere, followed by recovery of coal-derived tars and distillates in the off-gas stream (46). Pyrolysis carried

Table 7. **Activity and Selectivity Using as Catalysts Iron Oxides and Hydroxide Made via Flow-Through Techniques**[a,b]

Catalyst sample no.	Identified phase(s)	Model compound consumed (%) (± 4%)	Selectivity[c] (%) (± 3%)
no catalyst		<5	40–60
sulfur		<20	50–70
RTDS[d] *products*			
62-79-4	hematite	23	83
54-53-5	2-line ferrihydrite	20	84
54-50-3	hematite/6-line ferrihydrite	81	96
48-20-1	6-line ferrihydrite	90	96
48-19-7	6-line ferrihydrite	<90	96
54-54-2	magnetite	<90	98
54-56-1	ferric oxyhydroxysulfate	<90	94
54-56-4	ferric oxyhydroxysulfate	<90	96
MRM[d] products			
MRM-7-2	2-line ferrihydrite	51	91
MRM-39-39	2-line ferrihydrite	41	90
MRM-7-2A	magnetite/maghemite	77	89
MRM-39-39A	maghemite	32	92
MRM-39-49	goethite/lepidocrocite	44	93

[a]Reprinted with permission from Ref. 43. Copyright © 1994 American Chemical Society.
[b]Naphthyl bibenzylmethane (NBBM), 9,10-dihydrophenanthrene (DHN), sulfur, 400°C; sealed tube, 25-mg NBBM, 10 mg S, 100 mg DHN, 10-mg catalyst precursor.
[c]Cleavage of "primary" bonds (arrows in structure above) as a percentage of total bonds cleaved.
[d]See text for acronyms.

out in a hydrogen atmosphere is termed hydropyrolysis; pyrolysis at extremely rapid heating rates is termed flash pyrolysis. These processes are not in use for producing transportation fuels because of the yield and purity disadvantages noted above.

Table 8. **Comparison of Three Iron-Based Catalysts with Pyrite as Catalyst and No Catalyst (Thermal)**[a,b]

Catalyst	THF Conv. (%)[c]	DHP (%)[d]
1wt% WVU impregnated catalyst	93.0	13.4
thermal	51.7	1.73
1wt% PNL cat. precursor + 1wt% sulfur	89.4	8.41
thermal + 1wt% sulfur	63.6	2.35
1wt% U. of Pitt. cat. precursor + 2wt% sulfur	82.3	5.35
thermal + 2wt% sulfur	63.0	2.43
1wt% pyrite	73.4	3.88
thermal	54.9	1.08

[a]From Ref. 45.
[b]DECS-17 coal, 400°C, 800 psig hydrogen (cold) pressure; 43-mL microautoclave reactor, 60 min, 1.67 g coal, 3.34 g phenanthrene, 1 wt% catalyst.
[c]THF soluble.
[d]A measure of hydrogenating ability of the catalyst.

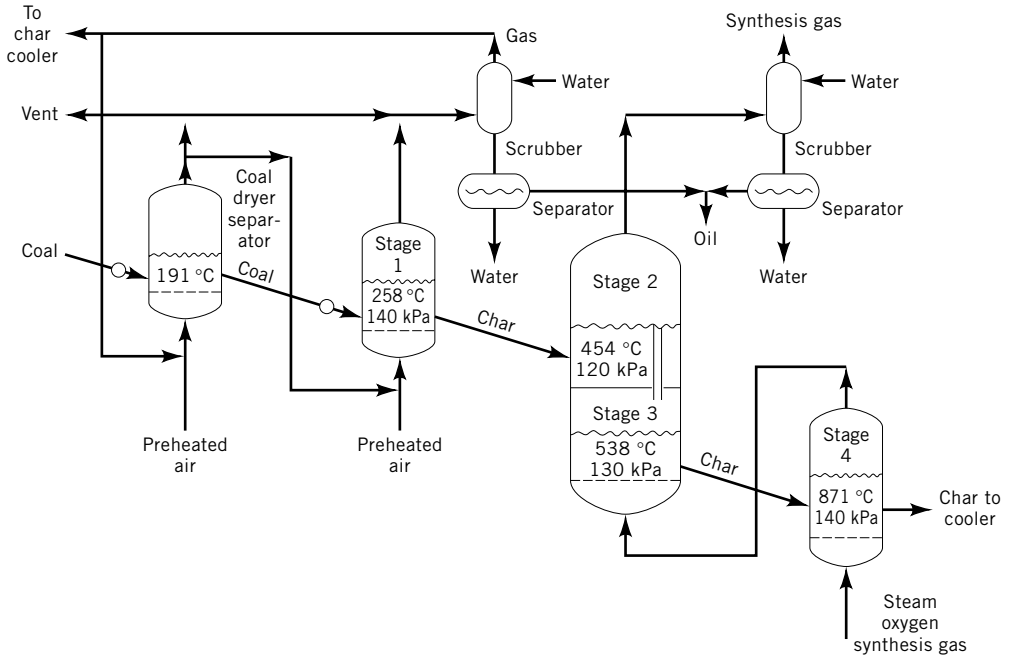


Fig. 13. COED process. To convert kPa to psi, multiply by 0.145.

Pyrolysis. Large-scale research and development on coal pyrolysis was carried out on the Char Oil Energy Development (COED) process (47). This scheme involved temperature-staged pyrolysis in a dryer–separator and three interacting fluidized beds, as shown in Figure 13, and was tested in a 36-t/day process demonstration unit during the early 1970s. Pyrolysis temperatures ranged from 191 to 871°C in the COED process, and the long residence times associated with the fluid beds mandated low yields of liquid products. Typical product yields for four different U.S. coals are shown in Table 9. The yield structure is heavily weighted toward production of char and gas. Production of coal-derived liquids ranged from 0.04 to 0.21 m^3/t of coal as compared to 0.61–0.79 m^3/t for direct hydrogenation. Further, the liquids produced were high in heteroatoms (especially nitrogen) and required extensive hydrotreating before use as a synthetic crude oil.

Table 9. **FMC/COED Process Product Distribution for Four U.S. Coals**

Coal composition, wt%	ND lignite	Utah	Illinois	West Kentucky
Yields, dry coal basis				
char	55.8	54.5	59.5	63.0
tar	5.3	21.5	19.3	17.3
gas	37.6	18.3	15.1	13.0
liquor (aq)[a]	1.3	5.7	6.1	6.7

[a]Water containing water-soluble organics produced during pyrolysis.

Process development on fluidized-bed pyrolysis was also carried out by the Consolidation Coal Co., culminating in operation of a 32-t/day pilot plant (48). The resulting CONSOL pyrolysis process incorporated a novel stirred carbonizer as the pyrolysis reactor, which made operation of the system feasible even when using strongly agglomerating Eastern-U.S. bituminous coals. This allowed the process to bypass the normal preoxidation step that is often used with caking coals, and resulted in a nearly 50% increase in tar yield. Use of a sweep gas to remove volatiles rapidly from the pyrolysis reactor gave overall tar yields of nearly 25% for a coal that had tar yields of only 15% as measured by the Fischer assay, a standardized test to measure the amount of liquids produced by pyrolysis.

Other large-scale coal pyrolysis process developments were carried out by the Tosco Corp., with its TOSCOAL process (49). Essentially a direct copy of Tosco's rotating kiln technology that was developed for pyrolysis of oil shale, this slow-heating scheme achieved tar yields at maximum temperatures of 482–521°C that were essentially identical to those obtained by a Fischer Assay.

Hydropyrolysis. Process development of the use of hydrogen as a radical quenching agent for the primary pyrolysis was conducted (50). This process was carried out in a fluidized-bed reactor at pressures of 3.7–6.9 MPa (540–1000 psi), and a temperature of 566°C. The reactor was designed to minimize vapor residence time in order to prevent cracking of coal volatiles, thus maximizing yield of tars. Average residence times for gas and solids were quoted as 25 s and 5–10 min. A typical yield structure for hydropyrolysis of a subbituminous coal at 6.9 MPa (1000 psi) total pressure was char 38.4, oil 29.0, water 19.2, and gas 16.2, on a wt% maf coal basis. Tar yields of $\sim$0.32 m^3/t were quoted. Because the scheme used hydrogen, the liquids generally exhibited lower heteroatom contents than conventional tars derived from coal pyrolysis in an inert atmosphere. Process development proceeded through a 270-t/day semiworks plant that was operated successfully on noncaking coals. Operability for caking coals was difficult, however.

Flash Pyrolysis. Development of a rapid, ie, flash, pyrolysis process was carried out in the late 1960s and early 1970s (51). The process was designed to heat coal at rates in excess of 5000 °C/s. Process development proceeded through to a 2.7-t/day process development unit (PDU) using a variety of caking and noncaking coals. The reactor section facilitated rapid heating by direct contact with hot char from the char burner. Gas residence times were brief (<2 s) and carefully controlled in order to minimize secondary cracking reactions and to maximize the yield of coal-derived liquids. Typical yield structures for pyrolysis at 580°C for two coals are shown in Table 10. Rapid heating, and hence high tar

Table 10. **Product Distribution for the Occidental Flash Pyrolysis Process for Two U.S. Coals**

Coal	Western Kentucky bituminous	Wyoming bituminous
Yield, wt%		
tar	35	27
char	56	52
gas	7	13

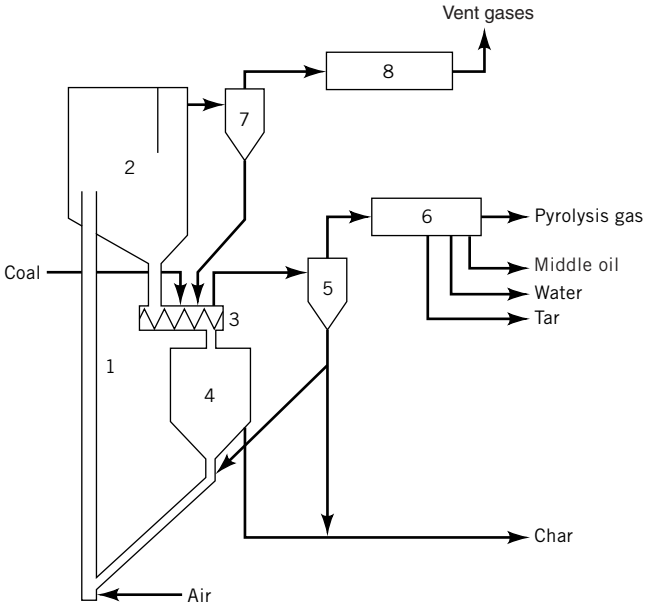


Fig. 14. Lurgi–Ruhrgas flash-pyrolysis system, where 1 is a lift pipe; 2, primary pyrolysis reactor; 3, screw feeder; 4, secondary pyrolysis reactor; 5 and 7, cyclones; and 6 and 8, product recovery and tailgas cleaning.

yields, could be obtained with this system. However, rapid quenching of reaction products proved to be a significant problem, especially as the process was scaled up from the laboratory.

Development of a flash-pyrolysis reaction system was also carried out by Lurgi–Ruhrgas (52). Between 1940 and 1960, units processing 10 t/h were operated, and a small commercial plant was built and has operated in the former Yugoslavia since 1963. As shown in Figure 14, coal is rapidly heated by mixing with hot recycled char in a screw-conveyor-type reactor. Volatiles recovery is completed at 750°C in vessel number 4. A typical product distribution for this system operating on a high volatile West Virginia bituminous coal gave a tar yield of 28 wt%, char of 58 wt%, and gas + liquor of 14 wt%, all on a basis of maf coal.

A novel high pressure flash hydropyrolysis reaction system was designed and operated by Rockwell Corp. during the mid-1970s (53). The process was operated in a 1-t/h pilot plant, where the technology was successfully demonstrated for a variety of different feed coals. The reactor was designed to mix hot high pressure hydrogen and coal in a highly turbulent zone such that extremely rapid heating rates could be obtained, >10,000 °C/s. A schematic of the reactor is shown in Figure 15(**a**). In this system, the energy required to heat coal to temperatures of 871–1038°C was generated by combustion of a portion of the hydrogen feed to the reactor. Rapid heating then was facilitated by direct contact with hot hydrogen and the combustion gases. The rapid heating, coupled with extremely fast transition through the coal's plastic regime, prevented problems associated with operation using agglomerating coals. Further, the extremely short

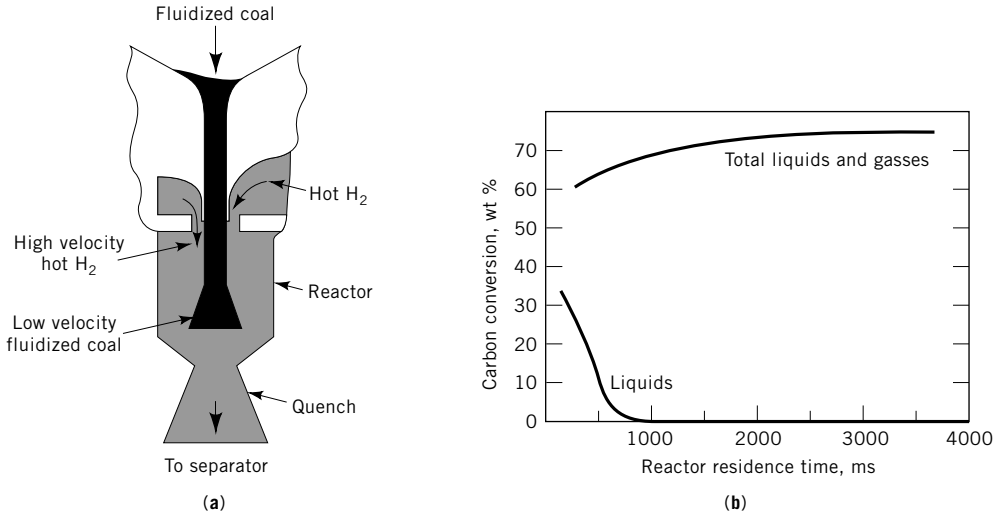


Fig. 15. (**a**) Rockwell flash-hydropyrolysis reactor; (**b**) carbon conversion as a function of reactor residence time. The reaction was run at 1038°C and 10.3 MPa (1500 psig).

residence times for coal-derived volatiles and the activity of hydrogen as a radical scavenger helped minimize secondary cracking reactions, thus permitting yields of coal-derived tars to exceed greatly that predicted by the Fischer assay. Whereas total coal conversion was relatively insensitive to reactor residence time, the yield of liquid or oil was a maximum at ~0.1s for a U.S. bituminous coal. Longer residence times favored formation of gases. Operating pressure also had an effect on coal conversion and product distribution. Higher pressures favored production of liquids.

2.3. Coprocessing. The main difference between coprocessing and hydroliquefaction is that the solvent is not simply a recycled stream from the process but is a separate feed stream, either a resid fraction (or other fraction, typically heavy) of petroleum or a waste (such as postconsumer plastic material, tire rubber or even municipal waste). The motivations for the additional feed are to reduce the severity of the liquefaction conditions compared to coal-alone hydroliquefaction, to recycle to extinction the heavy fraction, to take advantage of synergies of operation, and to take advantage of the favorable economics and/or politics in eliminating an unneeded stream.

Coal–Oil Coprocessing. Chevron, CANMET, and Ohio-Ontario Clean Fuels are among the organizations that developed strategies and technologies for coal–oil coprocessing. The two-stage coprocessing scheme of HRI (now HTI/Headwaters) illustrated in Figure 16 was used on coal ranks from lignite through high volatile bituminous and with a variety of resids. As an example of the synergistic benefits of coprocessing, resid-based organometallic Ni and V compounds (that would serve as poisons for downstream processing if present in the liquid product) were found to be included in the solid (ash) phase contributed by the coal, and thereby removable before downstream processing. Further, the conversion to the heaviest products (liquids boiling above ~225°C) is greater in coprocessing than the value expected for individual processing of the feedstocks (54).

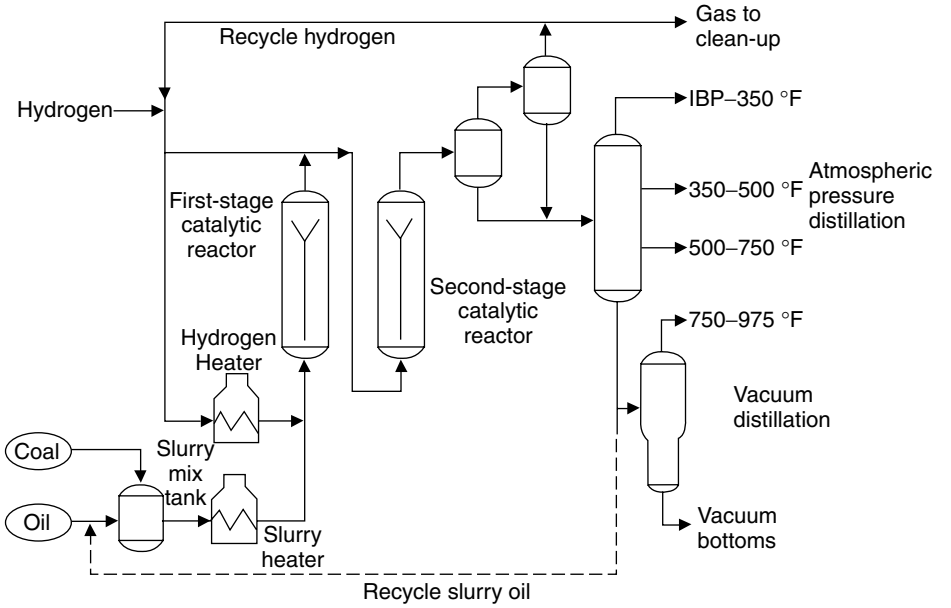


Fig. 16. Schematic of the HRI Two-Stage Coprocessing Scheme (54).

Coal–Waste Coprocessing. The use of catalysts, iron-based and others, on coal-waste coprocessing has been quantified in tests at the bench scale and larger. Bench-scale tests have been carried out on a standard commingled waste plastic developed by the American Plastics Council, as well as on pure low density polyethylene, high density polyethylene, polypropylene and poly(vinyl chloride); these were used alone, with coal, and with coal and resid (55,56). Sawdust and farm manure have also been used in bench-scale coprocessing (57). A two-stage process was suggested for coprocessing waste rubber (from tires) with coal (58)—the tire would be liquefied noncatalytically at relatively low severity conditions to obtain a tire oil and (marketable) carbon black, and the tire oil would be combined with coal containing *in situ* ferric sulfide-based catalyst at higher temperatures and pressures.

HTI used a proof-of–concept bench-scale unit to study the effect of adding waste plastics to either coal/resid feedstock, or resid alone (59). The plastics were obtained from curbside recycling in northern New Jersey, the coal was subbituminous (Wyoming Black Thunder) and the resid was Hondo-VTB. A proprietary iron catalyst was combined with Molyvan-A and used in a dispersed slurry in a first-stage reactor. An interstage separator operated at high pressure. After the second-stage reactor, the product was flashed and the light ends hydrotreated to yield a naphtha-like fraction. The addition of the waste plastics was found to increase the yield of distillate and to decrease the consumption of hydrogen, regardless of whether coal/resid or resid alone was used as the feedstock.

The Duales System Deutschland (DSD) has supported the recycling of ~300,000 t/year of waste plastic, including mechanical recycling as well as conversion to oil, chemical feedstocks or synthesis gas in Germany. In the United

States, a feasibility study for a demonstration plant for coprocessing of waste plastics, tires, and coal was carried out (60). Base-case amounts were 200 t/day of plastic and 100 t/day of tires. Under these conditions, using typical tipping fees and with oil priced at $20/barrel, the return on investment was found to range between 9 and 20%.

3. Indirect Liquefaction

The second category of coal liquefaction involves those processes that first generate synthesis gas (syngas), a mixture of CO and H_2, by steam gasification of coal:

$$C(s) + H_2O \rightarrow CO + H_2 \quad (1)$$

followed by production of solid, liquid, and gaseous hydrocarbons and oxygenates via catalytic reduction of CO in subsequent stages of the process (61). Whereas coal is usually the preferred feedstock, other carbon-containing materials such as coke, biomass, or natural gas can also be used (see FUELS FROM BIOMASS; GAS, NATURAL).

Processes whereby coal is gasified to syngas are not discussed here; these involve commercial gasifiers such as those of Lurgi, Kellogg, or Koppers-Totzek (see COAL CONVERSION PROCESSES, GASIFICATION). Processes to obtain fuels and/or chemicals from syngas are discussed below, regardless of the feedstock used for syngas. Wender (62) illustrates the principal paths for fuels and chemicals as shown in Figure 17.

In the general process, syngas from the gasifier is first cleaned to remove gasifier tars, hydrogen sulfide and organic sulfur. The composition of the gas is then adjusted in a catalytic shift converter to increase the H_2/CO ratio via the water–gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (2)$$

This clean and shifted gas is finally converted to hydrocarbons and/or other products in a series of catalytic reactors. The synthesis reaction is usually carried out using two or three reactors in series because of the highly exothermic nature of the overall reaction.

The first demonstration of catalytic conversion of synthesis gas to hydrocarbons was accomplished in 1902 using a nickel catalyst (63). The fundamental research and process development on the catalytic reduction of carbon monoxide was carried out by Fischer, Tropsch, and Pichler (64). Generalized stoichiometric relationships such as those below are often used to represent the fundamental aspects of the formation of hydrocarbons and oxygenates:

$$n\ CO + 2n\ H_2 \rightarrow (—CH_2—)_n + nH_2O \quad (3)$$

$$2n\ CO + n\ H_2 \rightarrow (—CH_2—)_n + nCO_2 \quad (4)$$

$$n\ CO + 2n\ H_2 \rightarrow H(—CH_2—)n\ OH + (n - 1)\ H_2O \quad (5)$$

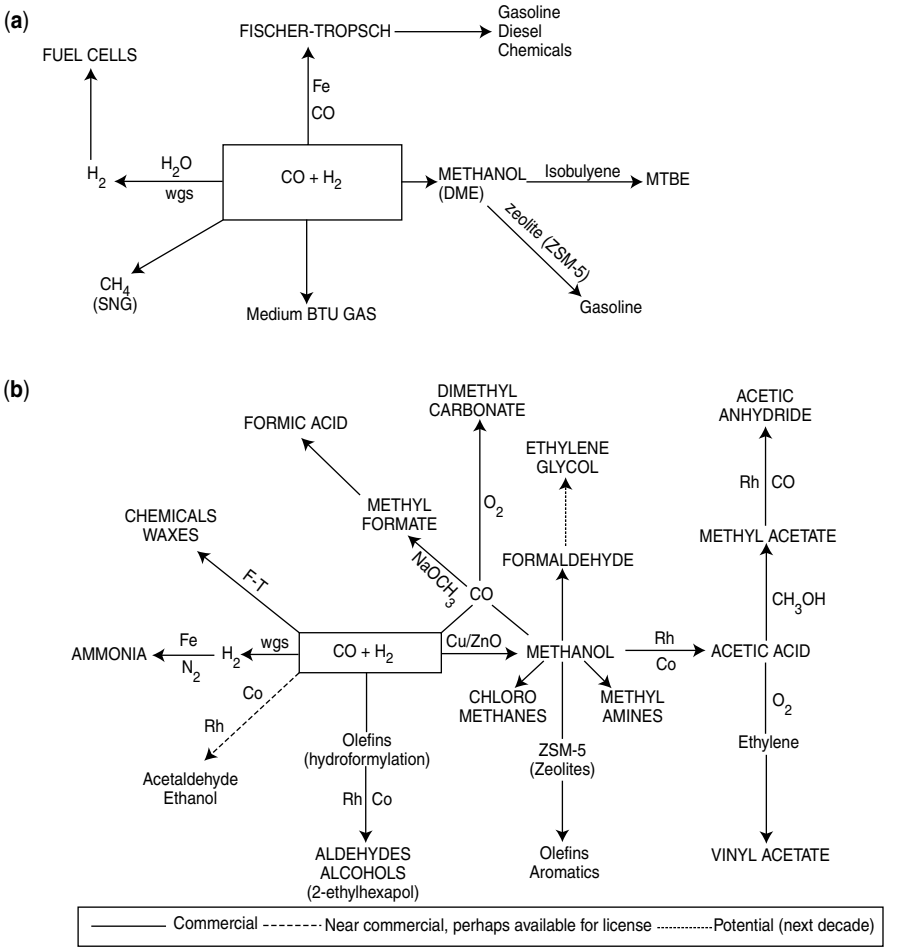


Fig. 17. Schematics for production from Syngas of (**a**) Fuels (**b**) Chemicals. Reprinted from Ref. 62 with permission from Elsevier Science.

However, the chemistry of the synthesis reactions is complex, and the formation of hydrocarbons is fundamentally different in many respects from the formation of oxygenates. For example, the side products vary, depending upon the H_2/CO ratio. Further, the formation of hydrocarbons requires a catalyst upon which CO can adsorb dissociatively, with rupture of the C–O bond, while CO may adsorb on a single site, without rupture of the bond, for oxygenate formation. By proper selection of catalyst and reaction conditions, including the H_2/CO ratio, hydrocarbons and oxygenates ranging from methane and methanol through paraffin waxes of high molecular weight (>10,000) can be synthesized, as indicated in Figure 18 (65).

3.1. Production of Hydrocarbon Fuels. By convention, only the production of hydrocarbons is termed Fischer-Tropsch (FT) synthesis. Hydrocarbons are typically used as fuels or fuel enhancers, generally diesel fuel.

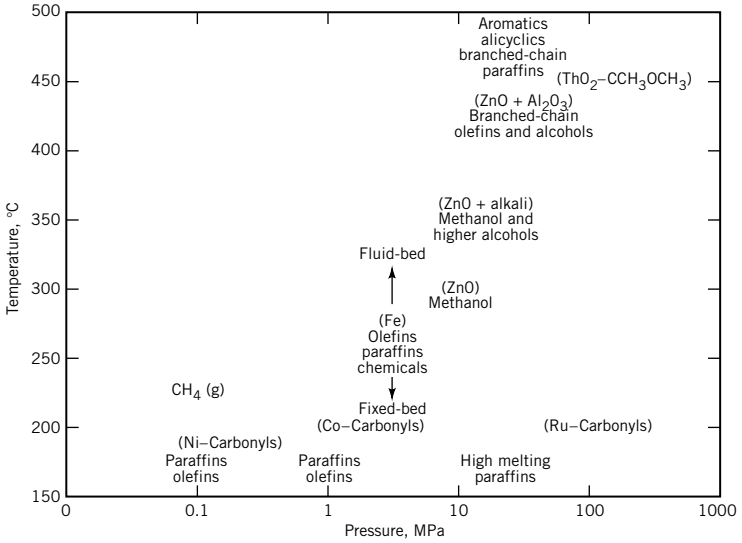


Fig. 18. Optimum pressure–temperature ranges for indirect synthesis processes showing the various catalysts in parentheses. To convert MPa to psi, multiply by 145.

Processes that operated at relatively low pressures, in the range of 100–200 kPa (1–2 atm) dominated commercial applications of FT synthesis in Germany prior to 1939 (66). Catalysts were primarily cobalt based. However, catalyst lifetimes were short and deactivation was difficult to reverse. At the other extreme, high pressure synthesis has been carried out at pressures in the range 5–100 MPa (50–1000 atm) and temperatures of 100–400°C. Supported ruthenium catalysts are used, and the products are typically straight-chain paraffin waxes (67).

The greatest successes, including the processes used by the South African Coal Oil and Gas Corporation Ltd. (SASOL), have occured at medium pressures, typically in the range 0.5–5 MPa (5–50 atm). Cobalt catalysts, similar to those used for the low pressure synthesis, were typically used at temperatures of 170–200°C. Iron catalysts, usually promoted, have also been used in the SASOL process, but at temperatures of 220–340°C. The primary differences between low and medium pressure synthesis are increased catalyst life for the medium pressure process, more diesel fuel, and a slightly higher hydrocarbon yield.

SASOL. The SASOL plants are worthy of mention as probably the only commercial facilities currently operating. They have supplied between one-third and one-half of South Africa's fuel requirements.

SASOL-I. This was the first plant, put into operation at Sasolburg, South Africa in 1955 (68). An overall flow schematic for the original setup of SASOL-I is shown in Figure 19. The product slate from this facility comprised materials ranging from FT products (hydrocarbons) to oxygenates, including alcohols and acids.

The plant utilizes iron catalysts. The catalyst is manufactured by precipitation from an iron nitrate solution using sodium carbonate. Copper and potassium

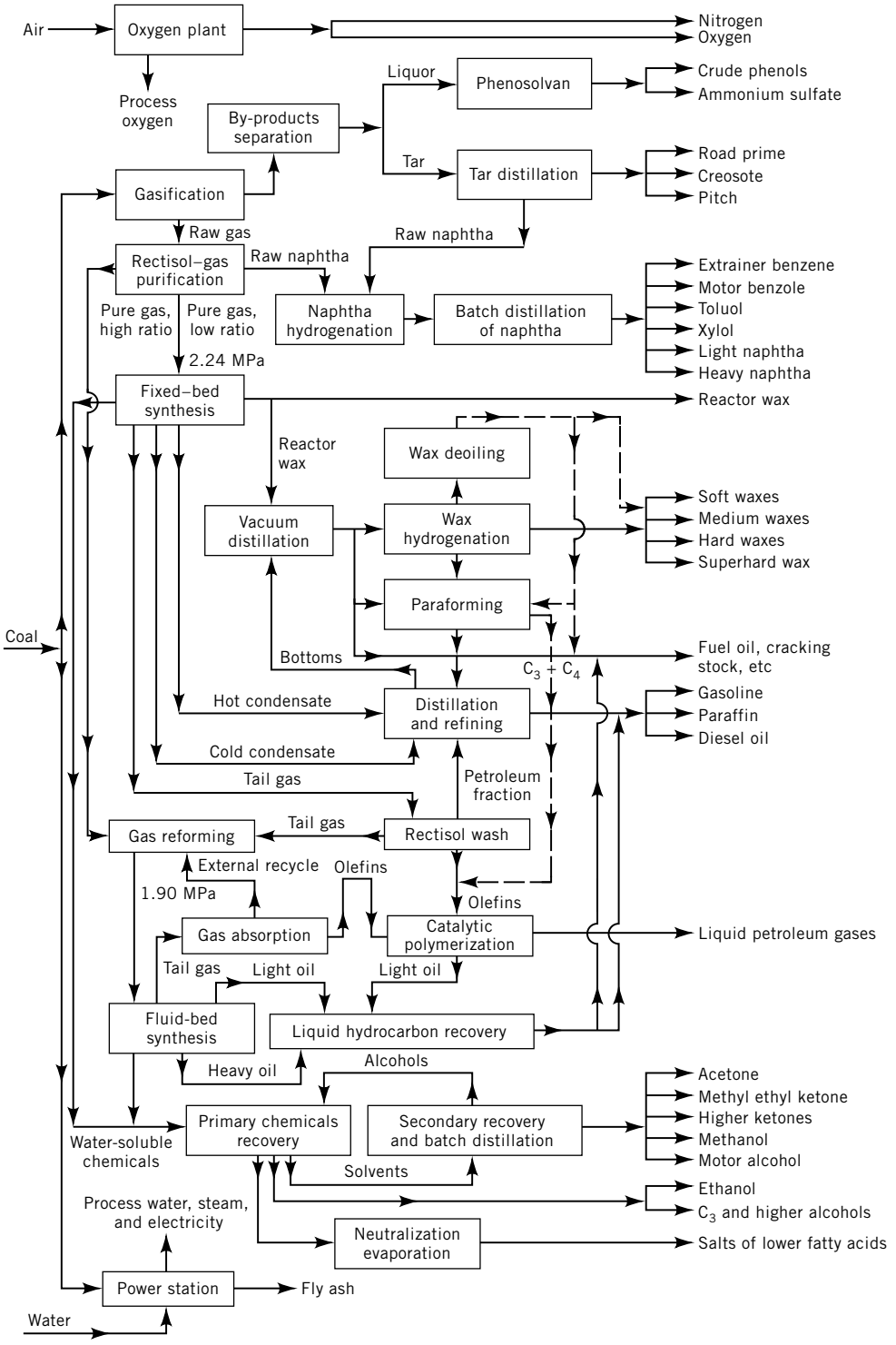


Fig. 19. Flow scheme for the SASOL-I Fischer-Tropsch process. To convert MPa to psig, multiply by 145.

are added as promoters, and the final material is pelletized and reduced with hydrogen prior to use. Catalyst life is variously reported to be 100 days to 6 months.

The overall processing scheme at SASOL-I involves steam-oxygen gasification of coal using high pressure (3 MPa, 30 atm) Lurgi gasifiers producing 22,500 m^3 each of raw gas having a H_2/CO ratio of 1.7. The feed to the plant is coal of high ash (35 wt%) and low energy content (23 MJ/kg) from mines near Sasolburg. SASOL-I consumes ~5.5 million tons per year of coal, with 60% going for gasification and synthesis and 40% for generation of onsite power. The raw gas is purified using Rectisol (chilled methanol) technology for removal of gasification tars, H_2S, CO_2, and some methane. The purified gas is then sent to the reactors.

Originally, both fixed-bed reactors (ARGE) and fluidized-bed reactors (Synthol) were used. The fixed-bed reactors, designed by Lurgi, contain approximately 40 m^3 of catalyst in over 2000 vertical tubes having diameters of 4.5 cm OD. There are six fixed-bed reactor trains in parallel, each reactor processing 30,000 m^3/day of feed at relatively low temperature (220–255°C) and medium pressure (2.5 Mpa, 25 atm), and producing 87.4 m^3 (550 barrels) of product per day (69). A flowsheet showing one fixed-bed reactor train is given in Figure 20.

In 1992, the three fluidized-bed reactors of SASOL-I were shut down and replaced by a single low temperature slurry-bed reactor. The SASOL Slurry-Bed Reactor (SSBR) is 5 m in diameter and 22 m high and has a capacity of 2400 barrels/day (70). It contains the catalyst suspended as a slurry in a FT wax or other liquid. The SSBR is cheaper to build, can be scaled up, permits

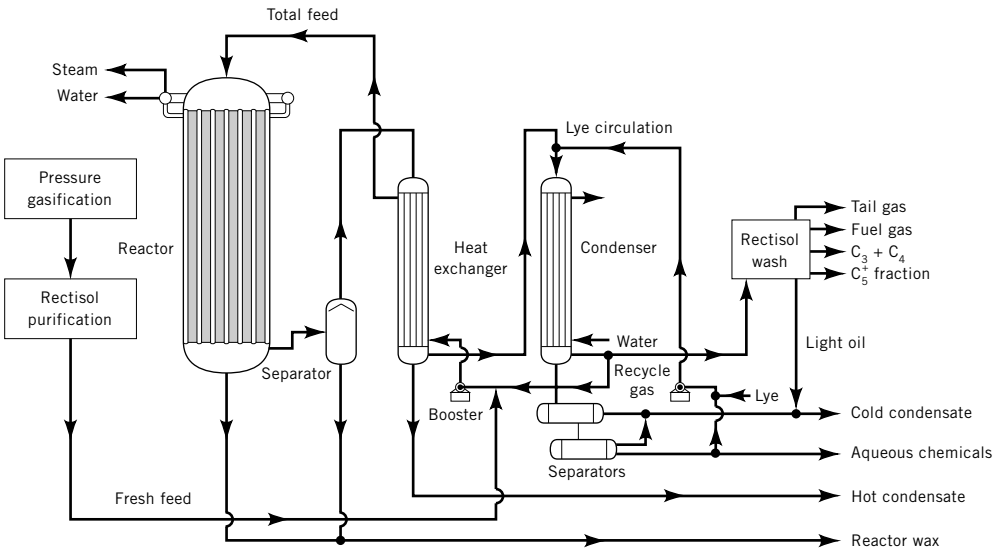


Fig. 20. Flowsheet of medium pressure synthesis, fixed-bed reactor (Lurgi-Ruhrchemie-Sasol) having process conditions for SASOL-I of an alkaline, precipitated-iron catalyst, reduction degree 20–25%; having a catalyst charge of 32–36 t, at 220–255°C and 2.48 MPa (360 psig) at a fresh feed rate of 20,000–22,000 m^3/h in the reactor.

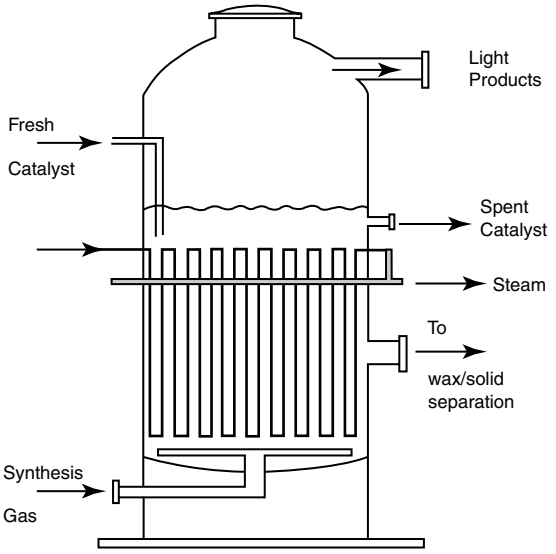


Fig. 21. Sketch of SSBR, operating at low temperatures (220–270°C) and medium pressures (2–3 MPa, 20–30 atm) for conversion of syngas to FT waxes (62).

near-isothermal behavior and results in improved catalyst economy. A sketch of the SSBR is given as Figure 21.

As a result of the revamp of the facility and the introduction of the SSBR, the primary products of SASOL-I are now waxes and waxy products. The idea is to crack the waxes to obtain diesel fuel. Oxygenates and other products are also formed.

SASOL-II and-III. Two additional plants were built near Secunda, South Africa: SASOL-II in 1980, and SASOL-III, essentially identical to SASOL-II, in 1983. A block flow diagram for the original SASOL-II and -III processes is shown in Figure 22.

The catalysts are made from millscsale from a steelworks, ground, combined with alkali and other promoters, and fused in an open-arc furnace. The consumption of coal for these two plants combined is ~35 million tons/year, and these plants together produce $\sim 1.6 \times 10^4 m^3$ (100,000 barrels) per day of transportation fuels. As can be seen in Figure 22, the original design of the SASOL-II and SASOL-III plants used only the fluid-bed Synthol reactor, and extensive secondary catalytic processing of intermediates (alkylation, polymerization, etc) maximized the production of transportation fuels. Product selectivities of the fixed-bed reactor and the Synthol reactor are given in Table 11. As shown, the fixed-bed system is more selective for middle distillates as well as heavy oils and waxes, whereas the fluidized bed system is considerably more selective for formation of C_2–C_4 olefins as well as products in the gasoline (C_5–C_{11}) boiling range.

A new design of fluidized-bed reactor has recently been coupled to the existing production facility. The SASOL Advanced Synthol (SAS) reactor is less than one-half of the size and one-half of the cost of the Synthol reactor, and eliminates

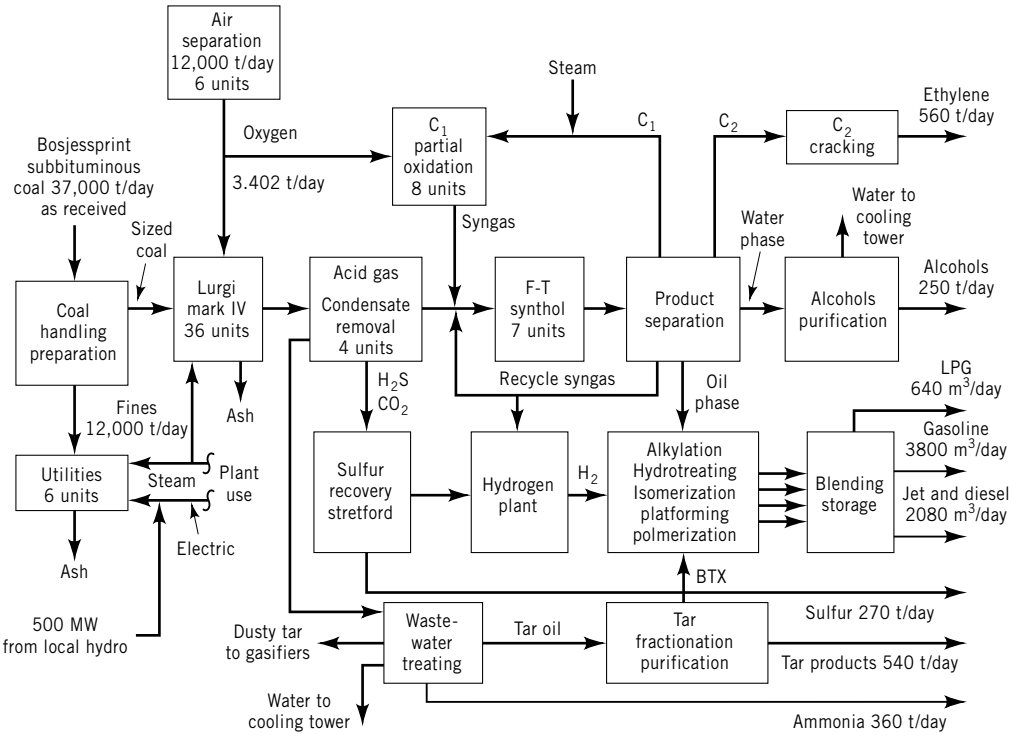


Fig. 22. Block flow diagram, SASOL-II and -III, where BTX is benzene–toluene–xylene. To convert m^3 to barrels, multiply by 6.29.

the recirculation of the catalyst. The SAS reactor results in a higher conversion and higher selectivity to oil; scale-up is also easier than for the conventional Synthol reactor (71). The Synthol reactor and the SAS reactor are shown in Figure 23. Recently the 16 Synthol reactors were replaced by eight SAS reactors, with a ninth SAS reactor under commission. Both the Synthol and SAS reactors are operated at relatively high temperatures, around 340°C. Work on the SAS reactor led to the development of the SSBR now used in SASOL-I.

Table 11. **Product Selectivities of SASOL Commercial Reactors**[a]

Product	Fixed bed	Synthol (Fluidized bed)
CH_4	4	7
C_2–C_4 olefins	4	24
C_2–C_4 paraffins	4	6
gasoline	18	36
middle distillate	19	12
heavy oils and waxes	48	9
water soluble oxygenates	3	6

[a]Reprinted with permission from Ref. 71.

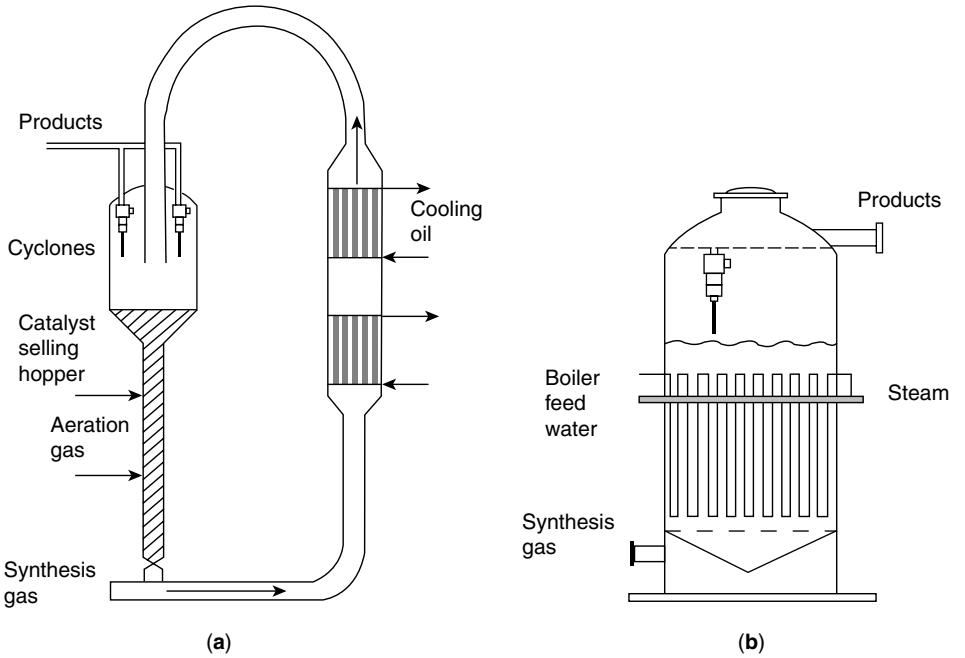


Fig. 23. Synthol reactor (**a**) and SAS reactor used in SASOL-II and-III (62).

Indirect Liquefaction from Natural Gas. These are mentioned here for completeness. The SASOL Slurry-Phase Distillate (SSPD) process has recently been developed. The idea here is to convert natural gas (rather than coal) to syngas and hence to naphtha and diesel fuel. A cobalt-based catalyst is used in the slurry-phase FT reactor. The methanol-to-gasoline (MTG) process developed by Mobil (now ExxonMobil) was used in New Zealand to convert natural gas to methanol and hence to gasoline, using a ZSM-5 zeolite catalyst. Currently, however, the process stops at methanol production. The Shell Middle-Distillate Synthesis (SMDS) process produces fuel from natural gas. Proprietary catalysts are used to convert the syngas to long-chain paraffins, which are then hydrocracked to give the required middle distillates. Conditions can be altered to maximize diesel fuel or kerosene.

3.2. Production of Alcohols and Other Oxygenates. Methanol is used as a fuel in its own right, as an octane extender for gasoline, and as a feed stock for the production of polymers and other chemicals. Methanol has been obtained from syngas since the Bayer patent in 1923. The original process operated at high temperatures and pressures (350–450°C, 25–35MPa) using a zinc oxide/chromium catalyst. Current ICI plants operate at low temperatures and pressures (220–280°C, 5–10 MPa) using a $Cu/ZnO/Al_2O_3$ catalyst in a multiquench reactor. Lurgi plants operate under similar conditions except in a multitubular reactor. In both cases, naphtha or natural gas is preferred to coal as a feed material for the syngas. Space–time yields of 1 kg methanol/Ltr of catalyst per hour are typical.

Table 12. **Composition of Some Fuel Alcohols from Syngas**[a]

Alcohol (%)	C_1	C_2	C_3	C_4	C_5	Catalyst
MAS (SEHT)	69	3	4	13	9	K/Zn/Cr
Substifuel (IFP)	64	25	6	2	2.5	K/Cu/Co/Al
Octamix (Lurgi)[b]	62	7	4	8	19	alkali/Cu/Zn/Cr
HAS (Dow)[c]	26[d]	48	14	3.5	0.5	$CoS/MoS_2/K$

[a]See Ref. 72.
[b]Isobutanol is 70% of C_4 alcohols.
[c]Straight-chain alcohols.
[d]Methanol can be recycled to extinction, increasing the amount of ethanol.

Higher molecular weight alcohols ("higher alcohols," HAs) are preferred as fuel additives because of their lower vapor pressure. The compositions of various mixed alcohols from syngas using various processes are given in Table 12.

3.3. Production of Other Chemicals. Many of the chemicals attributed to the indirect liquefaction of coal are formed from methanol; see Figure 17(**b**). However, it is worth noting the hydroformylation (oxo) reaction. Here aldehydes are produced by reacting olefins with CO using complexes of groups 8–10 (Group VIII) metals such as Co or Rh as a homogeneous catalyst. Hydroformylation is the fourth-largest use of synthesis gas, after the production of hydrogen, methanol synthesis and FT synthesis (62). As an example of hydroformylation, propylene can be converted to *n*-butyraldehyde:

$$CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO + CH_3CH(CH_3)CHO \qquad (6)$$

used in the synthesis of 2-ethyl-hexanol, a plasticizer. This is a multimillion t/year operation. More details on the hydroformylation reaction can be found in, eg, Ref. 73.

3.4. Developments in Indirect Liquefaction. Much of the research and process development on indirect liquefaction after the 1990s is aimed at matching the synthesis conditions with modern, efficient coal gasifiers such as those developed by Texaco, Dow, and Shell (see COAL CONVERSION PROCESSES, GASIFICATION). Whereas the newer gasifiers are considerably more efficient, the gas produced has a much lower H_2/CO ratio. The slurry reactor has been shown to be capable of using this type of feedstock, under the right conditions. Optimization of the performance of the slurry-bed reactor requires work on improved catalysts and on the separation of catalyst and wax in the product stream (74).

In the production of oxygenates and chemicals from syngas, the Alternate Fuels Development Unit in LaPorte, Texas has been used by Air Products and Chemicals Inc. to test several strategies for the USDOE. This includes development of the slurry-phase methanol reactor and the formation of dimethyl ether. A slurry bubble-column reactor is also used. In bench-scale tests, molybdenum- or nickel-based catalysts have been used for the production of high molecular weight alcohols. A promising development is the introduction of a high boiling inert solvent, such as tetraglyme, in concurrent flow with the syngas in a

fixed-bed reactor (75). The solvent absorbs methanol as it is produced, and shifts the chemical equilibrium to the "right" so that more methanol is produced.

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