

IX. APPENDIX I

SPECIFIC COAL LIQUEFACTION PROCESSES

Coal Liquefaction Processes

Specific coal liquefaction process designs are discussed below for solvent extraction, noncatalytic hydrogenation, catalytic hydrogenation, pyrolysis, and indirect liquefaction. These designs include the Consol synthetic fuel (CSF), solvent-refined coal (SRC), H-coal, char-oil-energy development (COED), and Fischer-Tropsch processes, respectively.

Solvent Extraction

The solvent extraction process begins with a slurry of pulverized coal and a hydrogen-donor solvent. When the slurry is heated, chemical bonds in the coal structure are broken, and the donor solvent transfers hydrogen atoms to the reactive fragments that are formed. This transfer helps prevent repolymerization by decreasing free radical lifetime. Approximately 75% of the coal is liquefied due to this hydrogen transfer [2].

The CSF solvent extraction process, based upon pilot plant operations, is shown schematically in Figures IX-1 and IX-2. In this process, coal is crushed, dried, and stored under an inert gas atmosphere. The coal is then mixed with hydrogenated process solvent to form a slurry. The slurry is preheated and transferred to the stirred extraction vessel operated at about 400°C and 11-30 atm (1.1-3.0 MPa) [2].

Unreacted coal, minerals, and liquefied coal are contained in the slurry leaving the extractor vessel. The slurry passes on to the liquid-solid separation system where the unreacted coal and minerals are separated from the liquid product. The liquid product is then passed through a flash still to obtain light liquids and a heavy coal extract. Heavy coal extract is further processed in a catalytic hydrotreater (hydrogenator) where a heavy distillate product (fuel oil) and donor solvent are produced. Fractionation of the hydrotreater product stream produces light, middle (donor-solvent), and heavy distillates.

The light liquids from the flash still are fractionated and separated into light and middle distillates. The latter is used as recycle solvent and as fuel oil.

The solids-rich stream from the separation system is pyrolyzed in a fluid bed of char at about 925°F (496°C) [19] and 7 psi (48 kPa), known as the low-temperature carbonizer [1].

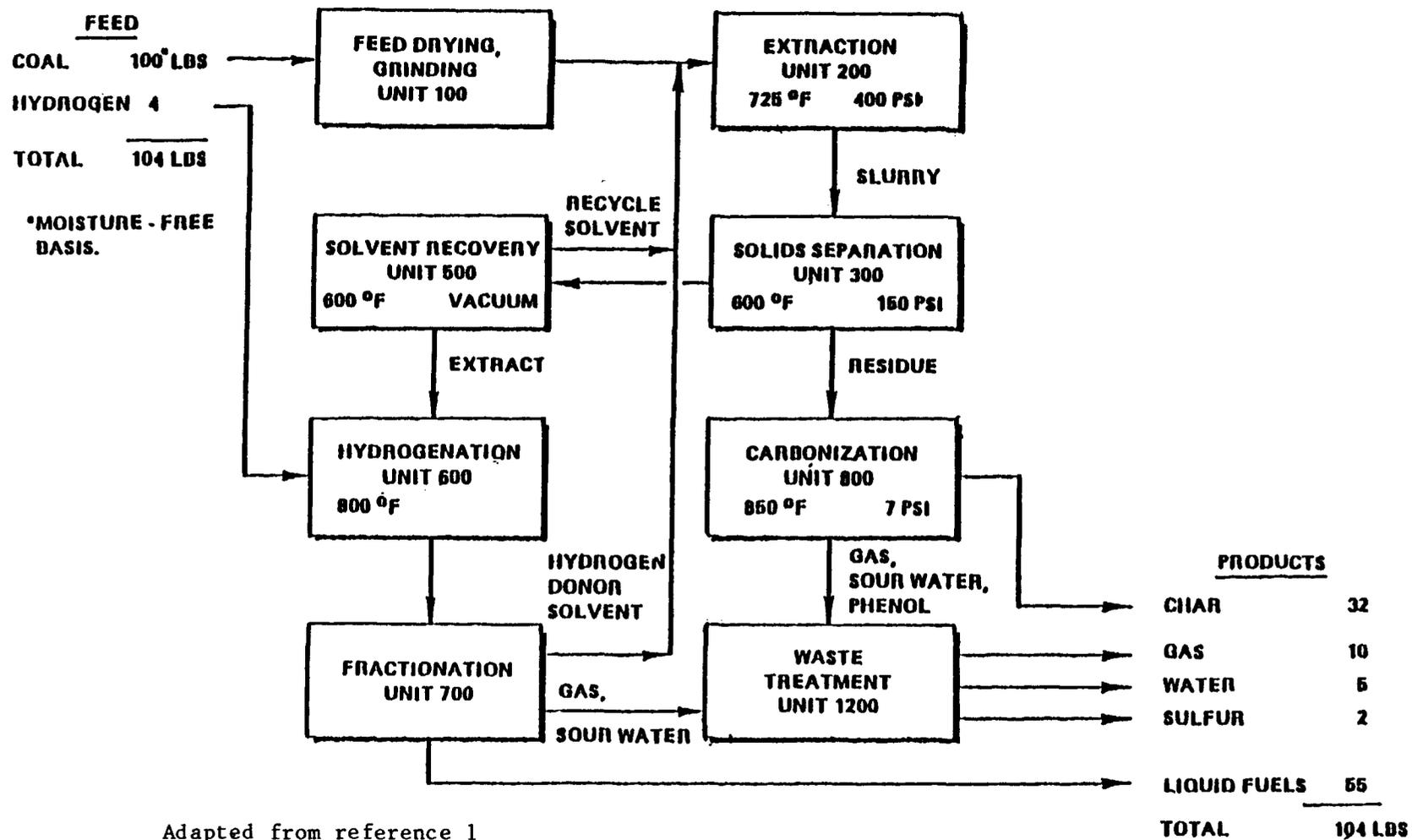


FIGURE IX-2. FLOW DIAGRAM OF THE CSF PROCESS

The vapors from the unit operations and processes are collected. Most of these vapors then pass through gas-liquid separators where sour gas, sour water, and other liquids are separated. The remaining vapors are normally sent to a desulfurization unit and then to a flare system. The sour gas and sour water are transferred to treatment facilities to remove waste materials, such as hydrogen sulfide, ammonia, and phenols.

Hydrogenation

(a) Noncatalytic Hydrogenation

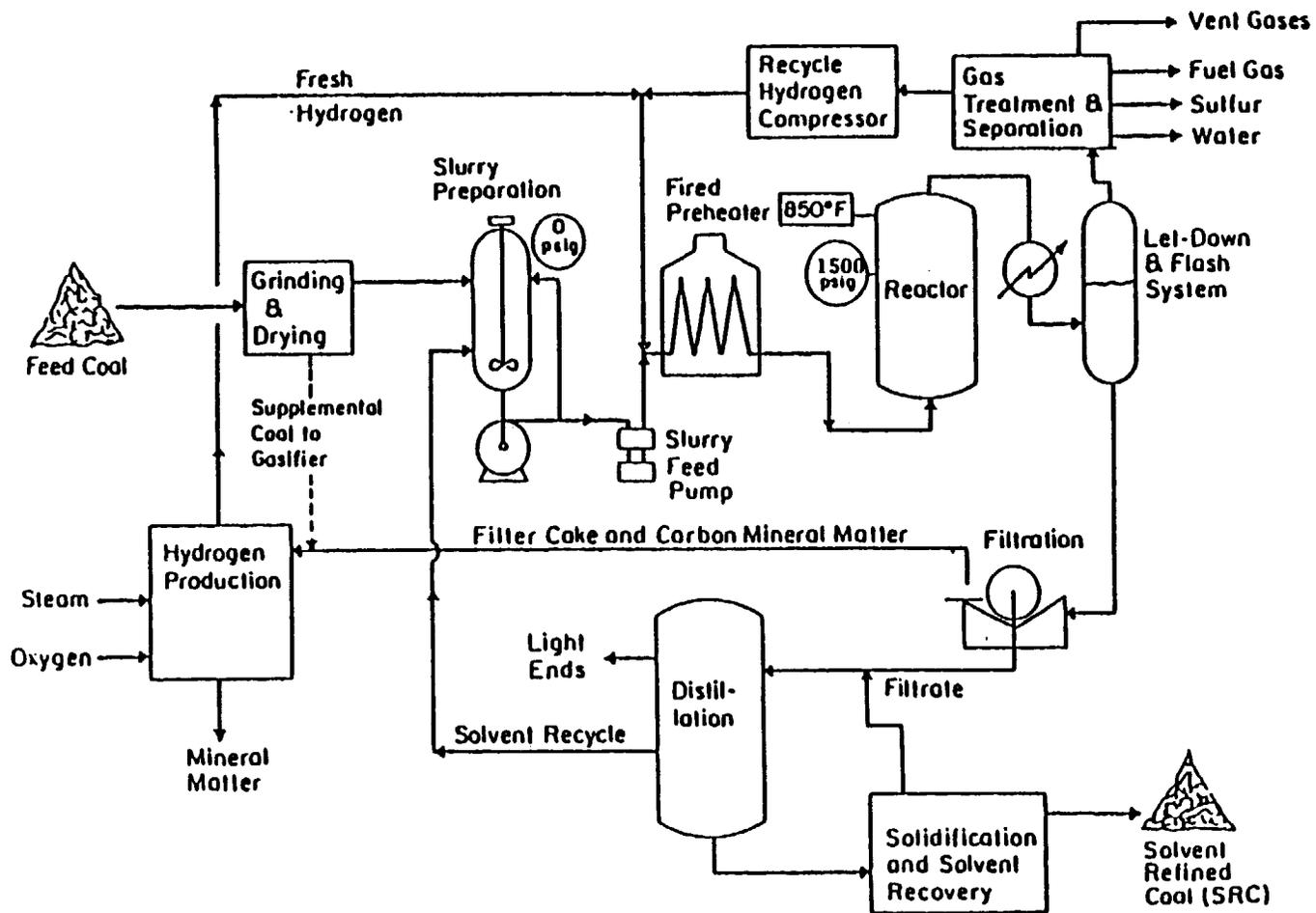
In noncatalytic hydrogenation, prepared coal, hydrogen, and a hydrogenated or nonhydrogenated solvent are combined in a pressure vessel to form hydrogenated coal products. The SRC processes, I and II, are examples of the noncatalytic hydrogenation process. However, the minerals in the recycled stream may act as a natural catalyst.

(1) SRC-I Process

A schematic of the SRC-I process is shown in Figure IX-3. In the coal preparation area, raw coal is received, unloaded, crushed, and then stored in bins. The coal is sized, pulverized, and mixed with a hydrocarbon solvent having a boiling range of 550-800°F (290-430°C). Initially, a blend of petroleum-derived carbon black feedstock and a coal tar distillate is used as a startup solvent. Ultimately, coal-derived liquids replace the startup blend as the process solvent. Solvent-to-coal ratios vary from as low as 2:1 to as high as 4:1 [108].

The resulting coal-solvent slurry is pumped from the coal preparation area to the preheater. Hydrogen or synthesis gas and water are added to the slurry as it enters the preheater. The slurry and hydrogen are pumped through a natural gas-fired preheater to a reactor. The remaining undissolved material consists primarily of inorganic mineral matter and undissolved coal. The preheater and dissolver are designed to operate between 775 and 925°F (413 and 496°C) at pressures from 500 to 2,000 psi (3 to 14 MPa) [108]. The current operating temperature is 850°F (454°C) [1].

The excess hydrogen and gases, eg, hydrogen sulfide, carbon monoxide, carbon dioxide, methane, and light hydrocarbon gases, produced in the reaction are separated from the slurry. The hydrogen sulfide and carbon dioxide (acid gases) are removed using a diethanolamine (DEA) absorption system. A Stretford sulfur recovery unit is then used to convert the hydrogen sulfide to elemental sulfur. The clean hydrogen-hydrocarbon gas stream from the DEA absorber is partly vented to flare and partly recycled to the process. Such streams will probably be used for fuel gases in a demonstration and/or commercial facility [152]. Fresh hydrogen is added to the recycle stream to maintain hydrogen partial pressure in the circulating gas [108].



Adapted from reference 151

FIGURE IX-3. SCHEMATIC OF THE SRC-I PROCESS

The slurry from the gas-liquid separator goes to mineral separation where the solids may be separated from the coal solution using rotary pressure pre-coat filters. These filters consist of a rotating drum inside a pressure vessel. Diatomaceous earth is used as the filtering aid with process solvent as the precoat slurry medium. Hot inert gas is circulated through the filters and filtrate receivers to maintain filtration pressure at approximately 150 psi (1 MPa) and temperature at approximately 350-650°F (180-340°C) [108]. This process also uses solvent de-ashing separation in place of filtration [1].

Filter cake, consisting of the undissolved solids and diatomaceous earth, is dried using an indirect, natural gas-fired, rotary kiln. The drying process removes the wash solvent, which is pumped to the solvent recovery area for fractionation. The dry mineral residue from the dryer is cooled with water and stored in a silo [108].

The filtered coal solution goes to solvent recovery for solvent removal by vacuum distillation. The vacuum flash overhead is fractionated into a light oil fraction, a wash solvent fraction, and the process solvent for recycle to slurry blending in the coal preparation system [108].

The vacuum bottoms stream is the principal product of the SRC-I process. This stream is the solvent-refined coal and may be solidified using a water-cooled, stainless steel cooling belt or a prilling tower. The solidified product is then sent to product storage [108].

The SRC-I process involves reacting most of the coal in a donor solvent derived from the process, separating undissolved coal solids, obtaining original process solvent by distillation, and recovering dissolved coal as a low-ash, low-sulfur, friable, black-crystalline material with glossy fractured surfaces, known as solvent-refined coal. The SRC-II process dissolves and hydrocracks the coal into liquid and gaseous products. This process does not require the filtration or solvent de-ashing step used in SRC-I for solid-liquid separation. An ashless distillate fuel oil is produced containing substantially less sulfur than the solid solvent-refined coal [26]. The current SRC-II process is a modification of the SRC-I process.

(2) SRC-II Process

SRC-II is a coal liquefaction process in which coal is mixed with a recycled slurry and hydrocracked to form liquid and gaseous products. The primary product of the SRC-II process is a distillate fuel oil [26].

A flow diagram of the SRC-II process design is shown in Figure IX-4. In the coal preparation area, coal is pulverized, dried, and mixed with hot recycle slurry solvent from the process. The coal-recycle slurry mixture and hydrogen are pumped through a fired preheater to a hydrocracking reactor [26].

The temperature at the outlet of the preheater is about 700-750°F (370-400°C). While in the preheater, the coal begins to dissolve in the recycle slurry solvent. The heat generated by the exothermic reactions of hydrogenation and hydrocracking raises the temperature of the reactor to 820-870°F (440-470°C). Cold hydrogen is used as a quench to control the temperature in the reactor [26].

Material leaving the reactor goes to a hot, high-pressure separator. The hot overhead vapor stream from the separator is cooled to provide vapor-liquid separation by condensation. Condensed liquid from these separators is fractionated. Noncondensed gas, consisting of unreacted hydrogen, methane and other light hydrocarbons, and acid gases, is treated to remove hydrogen sulfide and carbon dioxide. A portion of the gases is passed through a naphtha absorber to remove much of the methane and other light hydrocarbons [154]. The excess gas is sent to a flare system. The recovered hydrogen is used with additional hydrogen as feed to the process [154].

The raw distillate from the vapor-liquid separation system is distilled at atmospheric pressure. A naphtha overhead stream and a bottoms stream are separated in this fractionator. The heavier slurry from the hot, high-pressure separator flashes to a lower pressure where it splits into two major streams. One stream comprises the recycle solvent for the process. Fuel oil is separated from the other stream in a vacuum flash tower. The major fuel oil product of the SRC-II process is a mixture of the atmospheric bottoms stream and the vacuum flash tower overhead [26].

In a pilot plant, the vacuum tower bottoms are normally packaged into drums and either stored onsite or disposed of offsite. However, in a commercial plant, the vacuum tower bottoms, consisting of all of the undissolved mineral residue and the vacuum residue portion of the dissolved coal, may be used in an oxygen-blown gasifier to form synthesis gas. Synthesis gas can be converted to hydrogen and carbon dioxide using a shift converter. These product gases would then undergo an acid gas removal step to remove carbon dioxide and hydrogen sulfide. The hydrogen from the shift conversion step would comprise the principal source for the hydrogen requirements of the process. Any excess synthesis gas produced in the gasifier would be treated in an acid-gas removal unit to remove hydrogen sulfide and carbon dioxide, and burned as plant fuel. The excess synthesis gas can be separated into hydrogen and carbon monoxide, and the carbon monoxide can be used as plant fuel [26].

(b) Catalytic Hydrogenation

In catalytic hydrogenation, coal is suspended in a recycle solvent, mixed with hydrogen, and contacted with a catalyst in a reactor to form a coal-derived liquid product [2]. The catalytic hydrogenation process described in this document is the H-coal process.

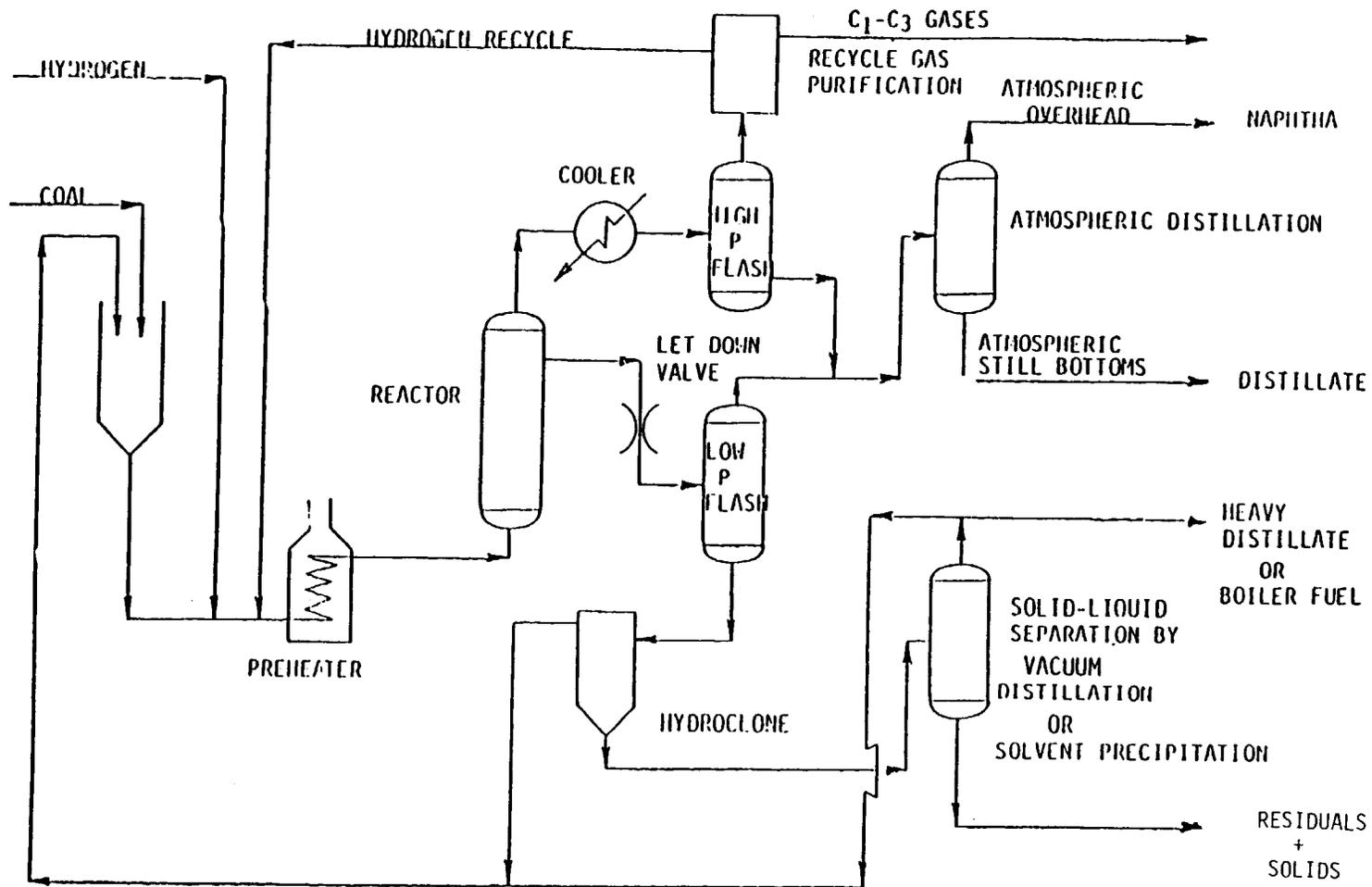
A schematic of the H-coal process development unit is shown in Figure IX-5. Pulverized coal is dried using hot nitrogen gas and then stored in a vessel under a nitrogen blanket. The prepared coal is slurried with a process-derived oil, eg, refined hydroclone products, atmospheric still bottoms, and vacuum tower overhead. Hydrogen is added to the coal slurry prior to preheating. The slurry and hydrogen mixture is then fed to a catalytic ebullated-bed reactor, which operates at an approximate temperature of 850°F (454°C) and a pressure of approximately 3,000 psig (21 MPa). Cobalt/molybdenum is the catalyst. Preheated high-pressure recycled hydrogen is also introduced into the reactor. The catalyst size is such that it remains suspended while ash particles and some unreacted coal leave the reactor in the liquid stream. Small amounts of catalyst fines may be carried over in the liquid stream, which is let down at essentially reactor temperature to atmospheric pressure. At this stage, a portion of the lighter hydrocarbon liquids is flash vaporized and fed to an atmospheric distillation tower. The products from this tower are naphtha and atmospheric still bottoms. The naphtha is sent to storage, and the bottoms are used as a slurry oil. Excess bottoms are stored in drums [1].

The slurry remaining in the flash drum is fed to hydroclones for partial solid separation. The refined hydroclone product is used as a slurry oil and/or stored in drums. The hydroclone bottoms are sent to either a vacuum distillation tower (syncrude mode) or a solvent precipitation unit (fuel oil mode). In the syncrude mode, the vacuum overhead, which is a heavy distillate, may be partially recycled to the slurry mix tank. The vacuum bottoms are stored in drums as a solid. All gases are scrubbed to remove light hydrocarbons, ammonia, and hydrogen sulfide. Hydrogen gas of approximately 80% purity is recompressed and recycled to the process. The remaining off-gases are sent to a flare system [1].

Pyrolysis/Hydrocarbonization

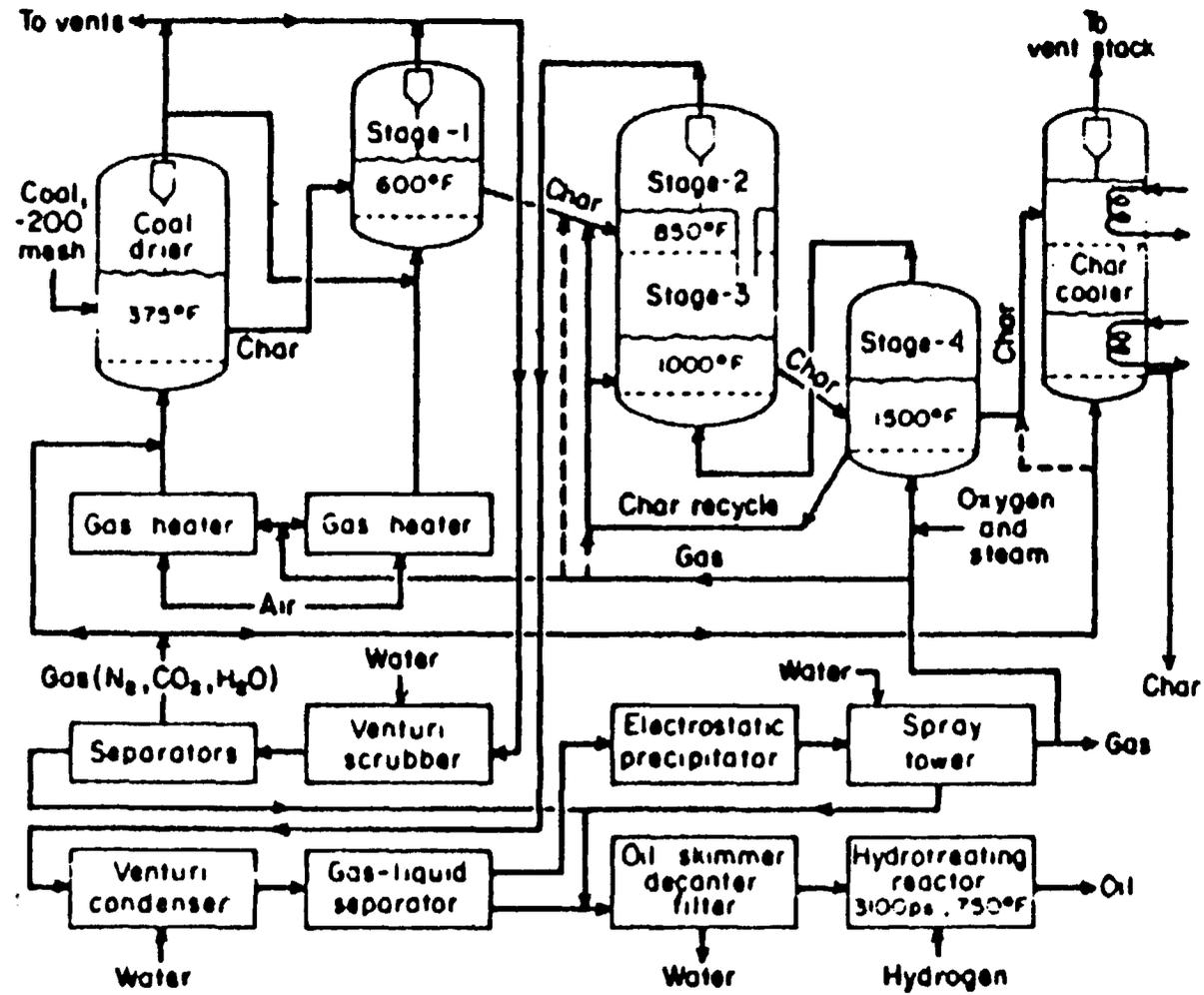
Pyrolysis is the thermal decomposition and recombination of coal with coal-derived or donor hydrogen that occurs in the absence of oxygen. If thermal decomposition occurs with added hydrogen, the process is known as hydrocarbonization. Oils, gases, and char are produced in the pyrolysis reactor. Char may be burned to produce heat needed for the endothermic pyrolysis process [19].

The COED process is an example of how a coal liquefaction plant uses a pyrolysis process (Figure IX-6). In the COED process, coal is crushed, dried, and heated to successively higher temperatures (350-1,550°F or 177-843°C) in a series of fluidized-bed reactors operated at low pressures (1-2 atm or 100-200 kPa) [31,34,155]. After the coal is partially devolatilized in one reactor stage, it is heated further in the next stage. The temperature of each bed is just below the temperature at which the coal would agglomerate and plug the bed. The dryer and the four process stages typically operate at the



Adapted from reference 1

FIGURE IX-5. SCHEMATIC OF THE H-COAL PROCESS DEVELOPMENT UNIT



Adapted from reference 3
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FIGURE IX-6. COED PROCESS SCHEMATIC

following approximate temperatures, in the order of the stages through which the coal passes: 350°F (180°C), 550°F (290°C), 850°F (450°C), 1,000°F (540°C), and 1,550°F (843°C) [34,155].

The close arrangement and descending elevation of these stages permit gravity flow of the char from one stage to the next and minimize heat losses and pressure drops. In commercial plants, heat for the process may be generated using the char from the last stage. The char is burned with a steam-oxygen mixture forming hot gases and high-pressure steam. These hot gases act as the fluidizing gases and heat sources for the previous stages [31,34,155]. In pilot plants, gas heaters are used [3].

Solids are separated from the exit gases in each stage. The solids separation is accomplished by an internal particulate separation system. The volatiles stream from the second stage passes through an external particulate separation system to remove solids that would otherwise collect in and plug subsequent processing steps. The gases containing oil vapors are passed through an absorption system; hydrogen sulfide and carbon dioxide are removed, leaving a product gas [31,34,155].

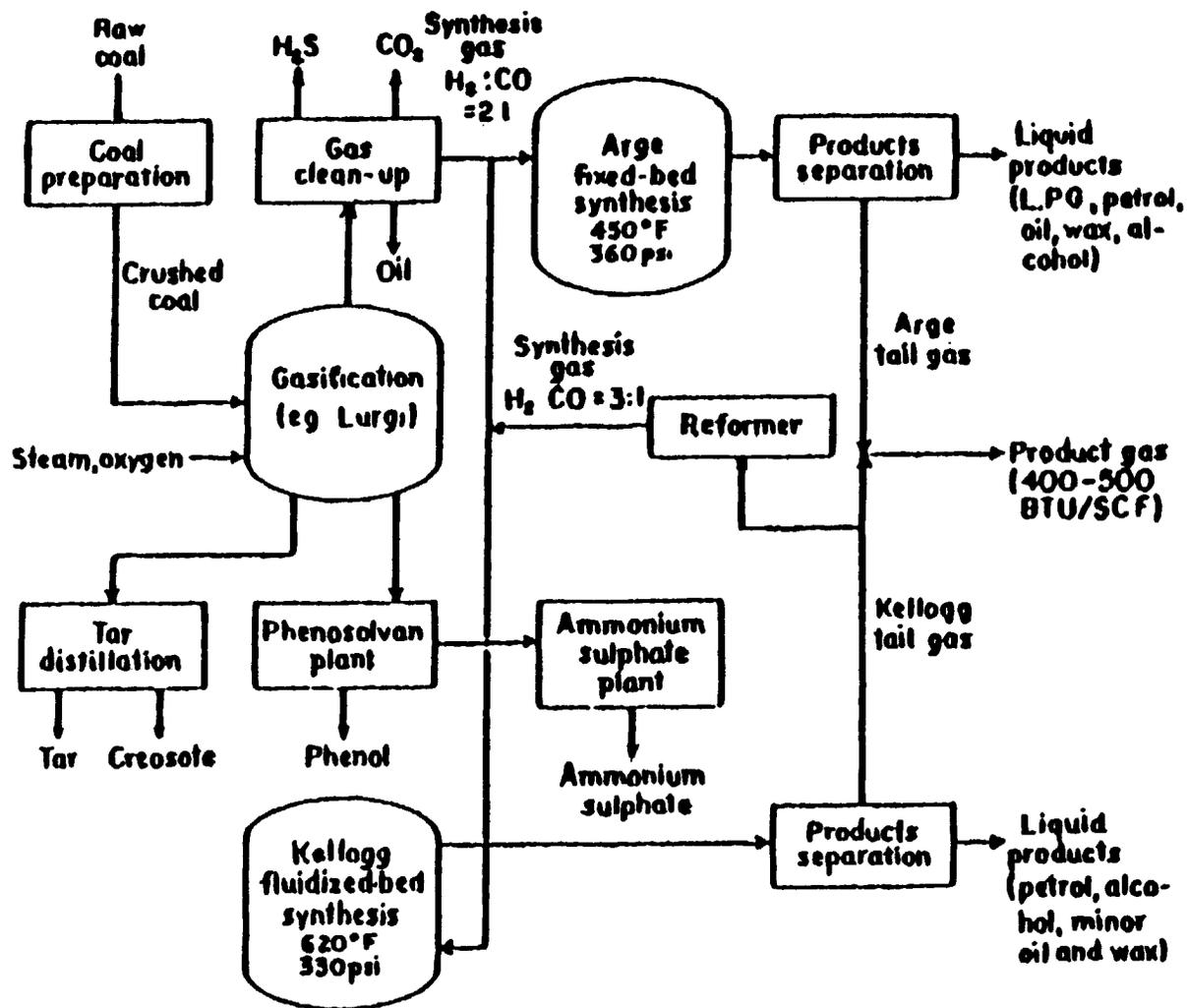
Oil and water from the pyrolysis gas/vapor stream are separated into an oil fraction heavier than water, an oil fraction lighter than water, and an aqueous fraction. The two oil fractions are dehydrated and filtered [31,34,155].

Oil from the product recovery system contains some char particles that are removed by filtration. Hot filter cake consisting of char, oil, and a filter aid is discharged from filtration to char storage. The filtered oil contains small amounts of impurities such as sulfur, nitrogen, and oxygen. In the hydrotreating area, a catalytic (nickel-molybdenum) reactor operates at 750°F (400°C) and 2,000 psi (14 MPa) [155,156] to convert the oil impurities into hydrogen sulfide, ammonia, and water; these are then separated from the product oil to improve oil quality [31,34,155].

Indirect Liquefaction

In indirect liquefaction, coal is converted into a synthesis gas by the use of a gasifier. This gas, containing carbon monoxide and hydrogen, is then passed over a catalyst to form liquid products [19]. The Fisher-Tropsch synthesis process is an example of an indirect liquefaction process. Considerable experience has been obtained using this process. The South African Coal, Oil, and Gas Corporation, Ltd (SASOL) plant in Sasolburg, South Africa, uses the Fischer-Tropsch synthesis process to produce liquid products, such as motor fuels, on a commercial scale [19,31,34].

A schematic of the Fischer-Tropsch synthesis process used at SASOL is shown in Figure IX-7. Coal is crushed, ground, and then mixed with steam and



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FIGURE IX-7. FISCHER-TROPSCH SYNTHESIS SCHEMATIC

oxygen in the gasifier. Synthesis gas is produced in a Lurgi gasifier by burning coal in the presence of steam and oxygen. The operating pressure and temperature of a Lurgi gasification reactor are 350-450 psi (2.4-3.1 MPa) and 1,140-1,400°F (616-760°C), respectively [3]. Synthesis gas from the reactor contains impurities such as ammonia, phenols, carbon dioxide, hydrogen sulfide, naphtha, water, cyanide, and various tar and oil components [31]. These impurities are removed by using gas-purification units, such as a quenching system, or by methanol scrubbing. The cleaned synthesis gas is then passed to an Arge fixed-bed synthesis reactor and a Kellogg fluidized-bed synthesis reactor parallel with one another, where a mixture of gases, vapors, and liquids are formed. Each of these reactors contains a catalyst needed for the synthesis step. The catalysts are iron/cobalt and iron, respectively [3]. The liquids produced are sent to refinery operations for separation into products such as fuel gas, propane, butane, gasoline, light furnace oil, waxy oil, methanol, ethanol, propanol, acetone, naphtha, diesel oil, creosote, ammonium sulfate, butanol, pentanol, benzol, and toluol [31].

X. APPENDIX II

SUMMARY OF COAL LIQUEFACTION PROCESSES UNDER DEVELOPMENT IN THE UNITED STATES

Category	Process	Developer	Coal	Reactor Type	Reaction Temp ^a °F (°C)	Reaction Pressure ^a atm abs (MPa)	Status of Development ^b
Pyrolysis and hydrocarbon-ization processes	Char-oil-energy development (COED)	FMC Corp	Illinois No. 6	Multiple fluidized beds	550-1,500 (290-820)	1.4-1.7 (.14-.17)	Operated 36 ton/d (33 Mg/d) pilot plant
	Occidental coal pyrolysis	Occidental	Western Kentucky	Entrained flow	1,100 (579)	1 (.1)	Results based upon 1-in (2.54-cm) diameter reactor; process to be tested in an available 3.6 ton/d (3.3 Mg/d) pilot plant
	Toscoal	The Oil Shale Corporation (Tosco)	Subbituminous and bituminous	Kiln-type retort vessel	797-1,000 (425-540)	1 (.1)	25 ton/d (23 Mg/d) coal test; operated 1,000 ton/d (900 Mg/d) plant for oil shale
	Clean coke	US Steel Corp	Illinois No. 6	Fluidized bed	1,200-1,400 (650-750)	6.5-11 (.66-1.1)	A 0.25-0.5 ton/d (0.230-0.450 Mg/d) process development unit under development; 100 ton/d (90 Mg/d) pilot plant under design
	Union Carbide Corp	Union Carbide Corp	Lake de Smet	"	1,050 (566)	69 (7)	Successfully operated 18 ton/d (16 Mg/d) pilot plant on noncaking coals
	Flash hydro-pyrolysis process (FHP) ^c	Brookhaven National Laboratory	Lignite	Entrained tubular flow	1,382-1,472 (750-800)	136-170 (13.79-17.24)	2 lb/hr (908 g/hr) experimental unit operated

APPENDIX II (CONTINUED)

Category	Process	Developer	Coal	Reactor Type	Reaction Temp ^a °F (°C)	Reaction Pressure ^a atm abs (MPa)	Status of Development ^b
Solvent extraction and noncatalytic hydrogenation processes	Consol synthetic fuel (CSF)	Conoco Coal Development Co	Lignite and sub-bituminous	Stirred-tank extractor; ebullated-bed catalytic hydrotreater	750 (400)	10-30 extractor; (1-3); 205 hydro-treater (21)	20 ton/d (18 Mg/d) plant operated at Cresap, WV, until 1970; revamped plant in operation
Solvent extraction and noncatalytic hydrogenation processes	Solvent-refined coal (SRC)	Pittsburg and Midway Coal Mining Co	Subbituminous and bituminous	Vertical tubular plug flow	840 (450)	69-103 (7-10)	6 ton/d (5 Mg/d) plant operating at Wilsonville, AL; 50 ton/d (45 Mg/d) plant at Fort Lewis, WA
	Solvent-refined lignite (SRL)	Univ of North Dakota	Lignite	Tubular plug flow	700-900 (370-480)	69-205 (7-21)	0.5 ton/d (0.45 Mg/d) pilot plant in startup stage
	Costeam	US BOM	Lignite and sub-bituminous	Stirred tank	707-840 (375-450)	137-275 (13.9-27.9)	Bench-scale continuous flow unit
	Exxon donor-solvent (EDS)	Exxon Research and Engineering Co	Subbituminous and bituminous	Tubular plug flow	797-900 (425-480)	100-140 (10-14)	Operated 1 ton/d (0.910 Mg/d) automated pilot plant; 250 ton/d (230 Mg/d) plant designed
Catalytic hydrogenation processes	H-Coal ^a	Hydrocarbon Research	Lignite, subbituminous, and bituminous	Ebullated bed	840 (450)	150-205 (15.2-20.8)	Successfully tested in 3 ton/d (3 Mg/d) plant, Kentucky site construction of 600 ton/d (500 Mg/d) demonstration plant

APPENDIX II (CONTINUED)

Category	Process	Developer	Coal	Reactor Type	Reaction Temp ^a °F (°C)	Reaction Pressure ^a atm abs (MPa)	Status of Development ^b
	Synthoil ^d	ERDA-- Pittsburgh Energy Research Center	"	Fixed bed	840 (450)	135-275 (13.7-27.9)	1/4 ton/d (0.23 Mg/d) pilot plant with 1.0 bbl/d (.2 m ³ /d) oil output in operation, 8 ton/d (7 Mg/d) pilot plant is in design and engineering stages
	Catalytic coal liquefaction (CCL)	Gulf Oil Corp	Lignite and subbituminous and bituminous	Fixed bed	>750 (>400)	135+ (13.7)	1 ton/d (0.91 Mg/d) pilot unit started up January 1975
	Clean fuel from coal (CFFC)	CE Lummus	Lignite and subbituminous	Expanded bed	750-810 (400-430)	68+ (6.9)	Small pilot plant scale tests, Lummus holds patents on solvent separation technique
Catalytic hydrogenation processes	Liquid-phase zinc chloride	Continental Oil Company	Bituminous and sub-bituminous	--	680-752 (360-400)	100-240 (10.1-24.3)	Small bench-scale unit; a 1.2 ton/d (1.1 Mg/d) unit to be built; funding by Conoco, Shell Development Corporation, and ERDA

NOTE: It is difficult to compare results of the processes because of the various conditions and different coals used.

^a Exact operating conditions will depend on the coal processed and the products desired.

^b Status as of December 1977

^c Taken from reference 152 [1977], status as of June 1979

^d Synthoil yields include gas and liquids obtained from pyrolysis of solids residue for Western Kentucky coal.

Adapted from reference 2

XI. APPENDIX III

SUMMARY OF SYSTEMS APPLICABILITY TO VARIOUS COAL LIQUEFACTION TECHNOLOGIES

Specific Process	System/Unit Operation/Unit Process									
	Coal Preparation	Hydrogenation	Pyrolysis/ Hydrocar- bonization	Hydro- treating	Catalytic Synthesis	Phase Separation	Fraction- ation	Gas Cleaning	Hydrogen/ Synthesis Gas Generation	Auxiliaries
Synthoil	+	+	-	-	+	+	-	+	+	+
H-coal	+	+	-	-	+	+	+	+	+	+
Bergius	+	+	-	-	+	+	+	+	+	+
SRC-I	+	+	-	-	-	+	+	+	+	+
SRC-II	+	+	-	-	-	+	+	+	+	+
Costeam	+	+	-	-	-	+	-	+	+	+
COED	+	-	+	+	-	+	+	+	+	+
Super- critical Gas Extrac- tion (SGE)	+	-	-	+	-	+	+	+	-	+
Coalcon	+	-	+	-	-	+	+	+	+	+
Clean coke	+	+	+	+	-	+	+	+	+	+
Toscoal	+	-	+	-	-	+	-	+	-	+
Occidental Research Corporation (ORC)	+	-	+	+	-	+	-	+	-	+
Fischer- Tropsch synthesis	+	+	-	-	+	+	+	+	+	+

APPENDIX III (CONTINUED)

Specific Process	System/Unit Operation/Unit Process									
	Coal Preparation	Hydro-generation	Pyrolysis/ Hydrocar-bonization	Hydro-treating	Catalytic Synthesis	Phase Separation	Fraction-ation	Gas Cleaning	Hydrogen/ Synthesis Gas Generation	Auxiliaries
Donor solvent	+	+	-	+	-	+	+	+	+	+
Methanol synthesis	+	+	-	-	+	+	+	+	+	+

+ Module or process is in the system.

- Module or process is not in the system.

Adapted from reference 12