Distillation:

(vol%)	Middle Oil (°F)	Gas Naphtha (°F)
IBP	185	91
5	327	117
10	354	124
20	394	135
30	421	144
40	453	154
50	487	165
60	516	180
70	549	192
80	579	216
90	-	248
Final Boiling Point	604	282
Distillate vol%	89.5	97.0
Last Runnings vol%	1.5	0.5
Residue + Loss vol%	9.0	2.5

Liquids from brown coal (semi-coke plant)

	Tar	Middle Oil
Water	6.8%	2.1%
Dust (insoluble in benzene)	21.1	0.2
Ash	2.9%	N.A.
Acid Oils	9.7%	28.8
Specific Gravity	1.16	0.95
IBP (°F)	397	257
Distillate up to 482°F	14.2 Vol%	72 Vol%
Color	N.A.	Dark brown

Middle Oil Distillation:

(vol%)	(°F)
IBP	257
4	284
9	320
15	356
27	392
58	428
66	464
78	500

(3) Char from brown coal (semi-coke plant)

Proximate Analysis, dry	(Wt%)
VM	17.0
FC	69.5
Ash	13.5
	100.0

Size - 81% in 0.1 to 3 mm range

INTENDED PRODUCT USE/MARKET

(1) Char or semi-coke:

Char - When the process is designed to maximize liquid yields (at about 1100°F), the residual VM content of the char is 6–8% and is expected to be highly reactive and suitable for boiler furnace feed (Reference 67). A large scale experiment for burning char with another coal was successfully completed. Char is expected to be marketable but is preferred to be used as an inhouse utility and export power source.

Semi-coke - When the process is designed for maximum char yields, the char (containing 15–20 wt% residual VM) is combined with a heavy tar which makes semi-coke. The semi-coke is marketable for coke-oven feedstock.

(2) Pyrolysis oil: The oil contains a high percentage of pitch and heavy tar which will require deep hydrogenation (the C/H weight ratio is 12—13) before the full tar can be marketed.

(3) High-Btu Pyrolysis Gas: The pyrolysis or carbonization gas is expected to be used for hydrogen manufacture to hydroconvert the tar from approximately -5° API to 20 - 40°API syncrude. The excess gas can be sold as SNG.

PROCESS EFFICIENCY

Yields (as % of gross calorific value of raw brown coal feed, Reference 68, Table 8):

	(%)
Coke + Tar	84.4
Middle Oil	2.2
Gas Liquor	0.3
Waste Gas	7.9
Cooling Water	4.2
Heat Losses	1.0
	100.0

Thermal Efficiency:

Pyrolysis process	94.8% (excludes fuel and power usage)

Utilities

Basis: Reference 68, Table 8 - 802-TPD semi-coke plant

Electricity	380 kWh
Cooling water	2378 gpm
Low Pressure steam	1874 lb/h
Fuel	37 MM Btu/h
Hydrogen Consumption	none
Catalyst Consumption	none

UNIQUE FEATURES OF PROCESS

- It is claimed the process can recover up to and over 200 percent of Fischer assay yield, depending on the coal feed.
- The mechanical mixer provides uniform mixing and short residence time; vapor residence time is kept to a minimum by rapid quenching to prevent gas-phase cracking.
- The high calorific pyrolysis vapors are completely segregated from the char combustion gases.
- The process can also be used to produce metallurgical grade semi-coke and recover oil from oil shale and tar sands (Reference 69).

PROCESS STATUS

Development Status:

There are four coal carbonization retorts built with a maximum capacity of 4,000 TPD. Development work is continuing for oil shale and tar sands.(69)

The process was first tested in a laboratory unit with high tar yields and confirmed in a 12-TPD pilot plant with tar yields from 137 to 189% of Fischer assay yields. The process was used in a 1600-TPD lignite plant in Lukavec, Yugoslavia that produced semi-coke for coke-oven feed as the main product. The process is believed to be ready for commercial-size operation for liquid hydrocarbon recovery from coal, shale, and tar sands. Coal liquefaction pilot work is now being done in a 0.3-TPH pilot plant in Germany.

The process had been patented in Germany but has since expired.

Location of Development Work: Essen, West Germany

History:

The Lurgi-Ruhrgas process was developed over many years to devolatilize fine granular fuels. The process as developed today was initially tested in a laboratory scale in the 1950s. Commercial-scale development work was carried out in a large-scale pilot plant operated at Dorstea in conjunction with a power station. The plant was shut down in 1960 when the economic incentive to produce town gas from coal vis-a-vis natural gas was lost. In 1963 a 1600-TPD lignite, carbonization plant was built in Lukavec, Yugoslavia. Since then, numerous large-scale plants have been built.

Problem Areas:

- The process, as in operation today, is primarily a coal or lignite carbonization process with low liquid yields; the conversion to a high liquid yield has been demonstrated on a pilot plant level but not commercial level.
- Pyrolysis vapor quenching: since it is imperative to quench the tars quickly to reduce the gas-phase cracking, much of the heat in the pyrolysis vapors will be lost, contributing to the inefficiency of the process.
- Char utilization: although the burning of char along with another coal in a furnace was successfully demonstrated, the burning of char by itself was not demonstrated.

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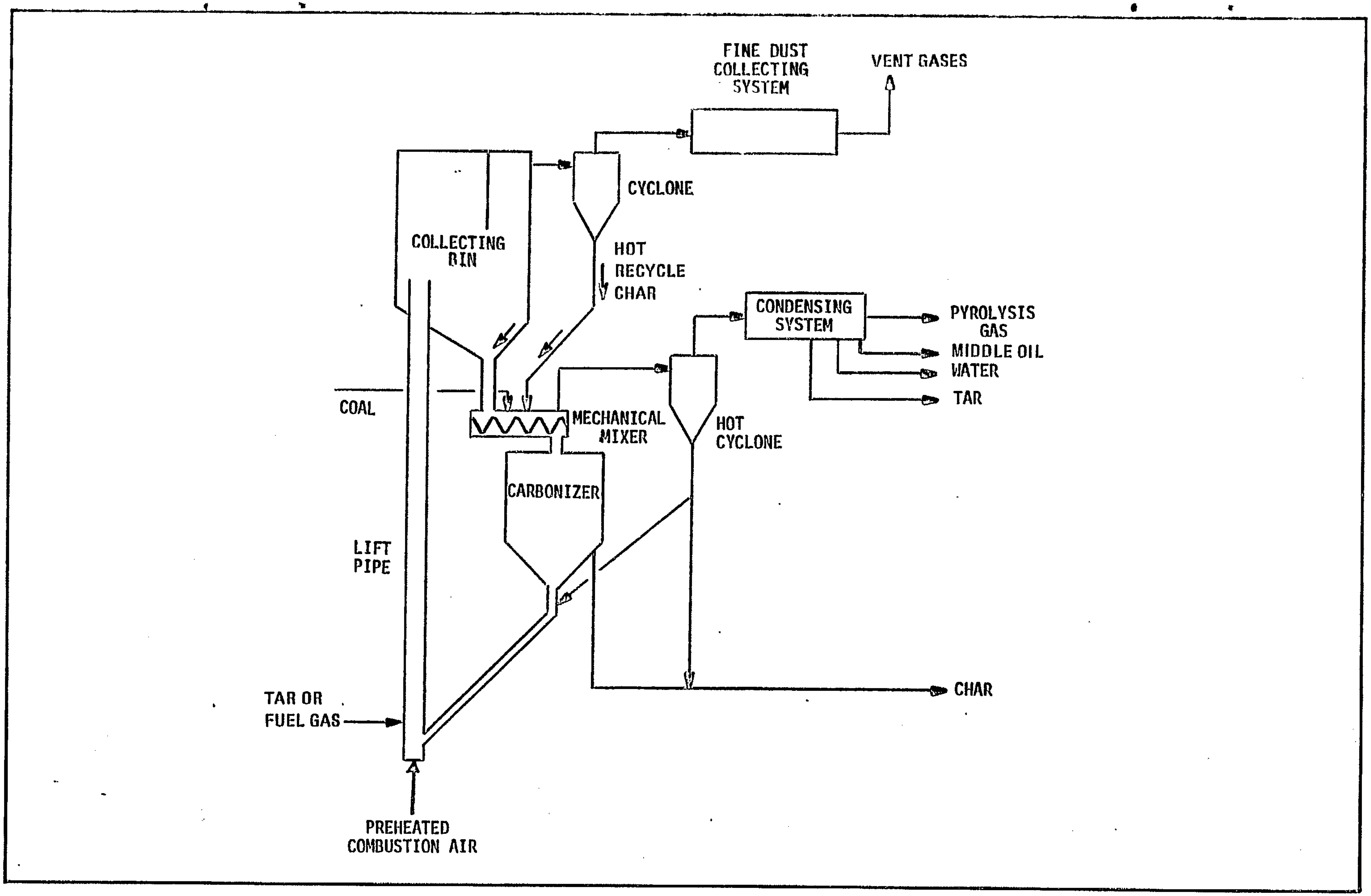

Figure 1 - Simplified Flow Diagram
Lurgi - Ruhrgas Process (69)

PROCESS INFORMATION EXTRACT

PROCESS 2.2.1 — U.S. Steel Clean Coke

Process Type: Pyrolysis, hydrocarbonization

Main Products:
metallurgical coke
tars + oils
ethylene
propylene
sulfur
ammonia
fuel gas (plant fuel)
unreacted coal + ash (plant fuel)

Development Status: Bench Scale and PDU

PROCESS DEVELOPER
U.S. Steel Corporation
U.S. Steel Research Laboratory
Monroeville, Pennsylvania

PROCESS SPONSOR: DOE

PROCESS DESCRIPTION (Refer to Figure 3)

The concept of the Clean Coke Process is to convert high-sulfur, marginal-quality coal to metallurgical coke, liquid and gaseous fuels, and chemicals. The key steps in the basic process are carbonization, coal hydrogenation, and coke production. Downstream processing steps (shown on the overall block flow diagram, Figure 3) are for separation, purification, and manufacture of commercial chemical feedstocks. PDU flow diagrams for the coal liquefaction steps, i.e., carbonization and coal hydrogenation, are also given. Description of these steps are as follows:

Carbonization (Refer to Figure 1):

The Carbonization Section, also referred to as "hydrocarbonization," consists of a two-stage fluidized-bed process. The sized coal is dried and preheated to 300°F at about 20 psi pressure, in fluidized beds before injection into the upper stage of the fluidized-bed carbonizer vessels using lock-hoppers. In the upper stage, the coal is partially devolatilized at 800° to 840°F and at 100 to 160 psig. The residence time in this stage is about 40 minutes based on output char quantities.

The partially devolatilized coal (semi-char) then flows downward to the lower (second stage) fluidized bed where the char is contacted with hot 1400°F recycle fluidizing gas. The projected residence time in the second stage is about 120 minutes. The hot char is cooled by overflowing into water quench tanks.

Heavy oil from the liquid treatment section is also carbonized in the reactors. This oil is preheated to 700°F and injected by sprays above the upper reaction bed.

The projected composition of the fluidizing gas is:

	vol%
H_2	33.3
CH_4	37.6
CO	10.7
H_2S	0.01
Other Components (NH_3, hydrocarbon gases, tars, oils, water)	18.4
	100.0

Hydrogenation (Refer to Figure 2):

This process is also referred to as coal hydroliquefaction. In this section, prepared coal is slurried with recycle oil from the liquid treatment section and hydrogenated in noncatalytic converters operating between 800° and 900°F and 5000 psia. The required hydrogen is produced by steam reforming of methane-rich gas generated in the ethylene plant and also in the carbonization section. The hydrogenated products are separated from the unreacted coal by vaporization in a hot, recycle-gas-stripping system.

The liquid products are sent to the liquid treating section and the gases go to the gas treating section. The unreacted coal and ash is disposed of as plant fuel.

OPERATING CONDITIONS

	Carbonization	Hydrogenation
Temperature:	800-840°F (1st); 1100-1400°F (2nd)	800–900°F
Pressure:	100-165 psig	3000–5000 psi
Residence time:	155 min.	5 min (slurry)
Vehicle:	Recycle gas @ 2-2.5 ft/s	Solvent
Reaction variables:	reactor temp.; res. time: H_2 partial pressure	temp., solvent ratio, etc.
Feed coal particle size:	-26 to 100 mesh	100 mesh
Solvent/coal wt. ratio:	N.A.	2.4:1
H_2 consumption:	N.A.	4 lb per 100 lb coal feed

PRODUCTS

Basis: Illinois No. 6 Seam Coal, washed and sized

Ultimate Analysis, dry wt%

C	75.11
H	5.23
N	1.36
S	1.96
O	10.69
Ash	5.65
	100.00

Moisture with feed, wet wt% - 8.50%

Yields:(70)

(1) Carbonization:

Feed:	Wt% of Dry Coal Feed
Dry Coal	100.0
Coal Moisture	9.3
Steam	0.6
Heavy Oil	37.8
	147.7%

Products:	
Char	86.0
Product Gases	21.2
Acid Gases	7.4
Oils + Tars	21.5
Sour Water	11.6
	147.7%

(2) Hydrogenation:

Feed:	
Dry Coal	100.0
Coal Moisture	9.3
Primary Slurry Oil	117.9
Secondary Slurry Oil	117.0
Hydrogen	8.7
	353.8%

Products:	
Tars	284.8
Gases	18.3

	Wt% of Dry Coal Feed
Chemical Oils	22.3
Sour Water (by difference)	28.4
	353.8%
Total Clean-Coke Process Yields:(73)	
(1) Feed:	
Dry Coal	100.0
Moisture	3.6
	103.6
(2) Products:	
Coke	39.8
Hydrogenation Residue	12.0
(3) Liquids:	
Phenol	1.2
O-cresol	0.3
M-IP-cresol	1.3
Xylenols	1.3
Pyridine	0.1
α -picoline	0.1
Aniline	0.3
Benzene	5.2
Naphthalene	2.0
	11.8
(4) Chemicals:	
Ammonia	0.6
Sulfur	0.9

	Wt% of Dry Coal Feed
Ethylene	6.4
Propylene	1.3
	9.2
(5) Tar Products:	
Creosote Blend Stock	0.3
Carbon Black Feedstock	0.3
	0.6
(6) Process Loss and Fuels Consumed:	30.2
Total	103.6% of dry coal feed

Characteristics:(70)

(1) Carbonization:

Char	Wt%
C	87.0
H	2.5
N	1.5
S	0.5
O	1.9
Ash	6.6
	100.0

Product Gases	Vol%
H_2	33
CH_4	37
CO	10
Lt. Hydrocarbons	20
	100

Acid Gases	Vol%
H_2S	25
CO_2	70
Misc.	5
	100

Oils and Tars	Wt%
Lt. Hydrocarbons	1
Lt. Oils	22
Middle Oils	19
Heavy Oils	25
Tar acids, bases, naphthalene & similar compounds	23
Heavy Residual Compounds	10
	100

Hydrogenation (Intermediate Products):

Liquids (Analyses from Reference 70)

	Chemical Oil	Middle Oil	Heavy Oil
C (wt%)	77-80	92-93	90-91
H (wt%)	8-9	6-7	5-6
N (wt%)	2-4	0.9-1.2	1.6-1.9
S (wt%)	0.03-0.2	0.1-0.4	0.4-0.5

Gases (Analyses from Reference 70)

	vol%
H_2	38
CO	2
CH_4	40

	vol%
H_2S	0.8
C_2s	12
C_3C_4	6
Tar acids, bases, other hydrocarbons	1.2
	100.0

(3) Coke Product(72)

	wt%
C	91.9
H	0.5
N	0.9
S	0.4
O	0.5
Ash	5.8
	100.0

INTENDED PRODUCT USE/MARKET (Refer to the Total Clean-Coke Process Yields):

(1) Coke: The primary product of the plant is a metallurgical coke suitable for the steel industry.(71)

(2) Byproducts (liquids, chemicals, tar products): These products are expected to be marketable.

PROCESS EFFICIENCY

Yields:

	% of HHV of Coal Feed
Coke	41%
Liquids	15%
Chemicals	13%
Tar Products	1%
	70%

Thermal Efficiency:

Sum of HHV of products = 70% of Coal Feed HHV
(electric power use excluded)

Utilities:

Basis: 17,000-TPD Clean Coke Plant

Cooling tower water	8,333 gpm
Electricity	105,000 kW
Steam (350 psig)	200,000 lb/h
Fuel Gas	120,000,000 Btu/h

Hydrogen Consumption:

Carbonization:	None
Hydrogenation:	4 lb H_2 per 100 lb coal feed

Catalyst Consumption:

Carbonization:	None
Hydrogenation:	None

UNIQUE FEATURES OF PROCESS

- The process can produce metallurgical grade coke from non-coking coals; it is also more environmentally acceptable than a conventional coke-oven process.
- The carbonizer char residence time is much lower than coke ovens but much higher than coal pyrolysis reactors (e.g. COED).
- The liquid products slate are sold as chemicals rather than fuels.

PROCESS STATUS

Development Status:

Construction of a 1/2-TPD PDU at U.S. Steel's Monroeville, Pennsylvania research laboratory was completed in 1974. Data from the PDU will be used for design of a pilot plant in the order of 100-TPD; data from bench scale apparatus is available for process yields and evaluations along with

PDU data from the coal carbonization, vapor stripper, slurry oil hydrotreating, and coke preparation sections.

U.S. Patent 3,755,136 was issued in August, 1973 for a method of separating liquid and solids in the coal hydrogenation effluent via a vaporization system (vapor-stripping solids separator).

Location of Development Work: U.S. Steel Research Laboratory
Monroeville, Pennsylvania

History:

In 1968, U.S. Steel initiated a research and development program for processes on coke making and better utilization of coal. In 1973, a three-year R&D program was awarded to U.S. Steel by the Office of Coal Research (now DOE). In 1974, the PDU facility was constructed. It is planned to complete testing of and data gathering from the bench scale unit and the PDU and to provide a design basis for a pilot plant.

Problem Areas:

- Economics: The capital investment and operating costs are high enough to require the metallurgical coke to sell for over $100/ton for 1974, substantially above current market value prices.

REFERENCES

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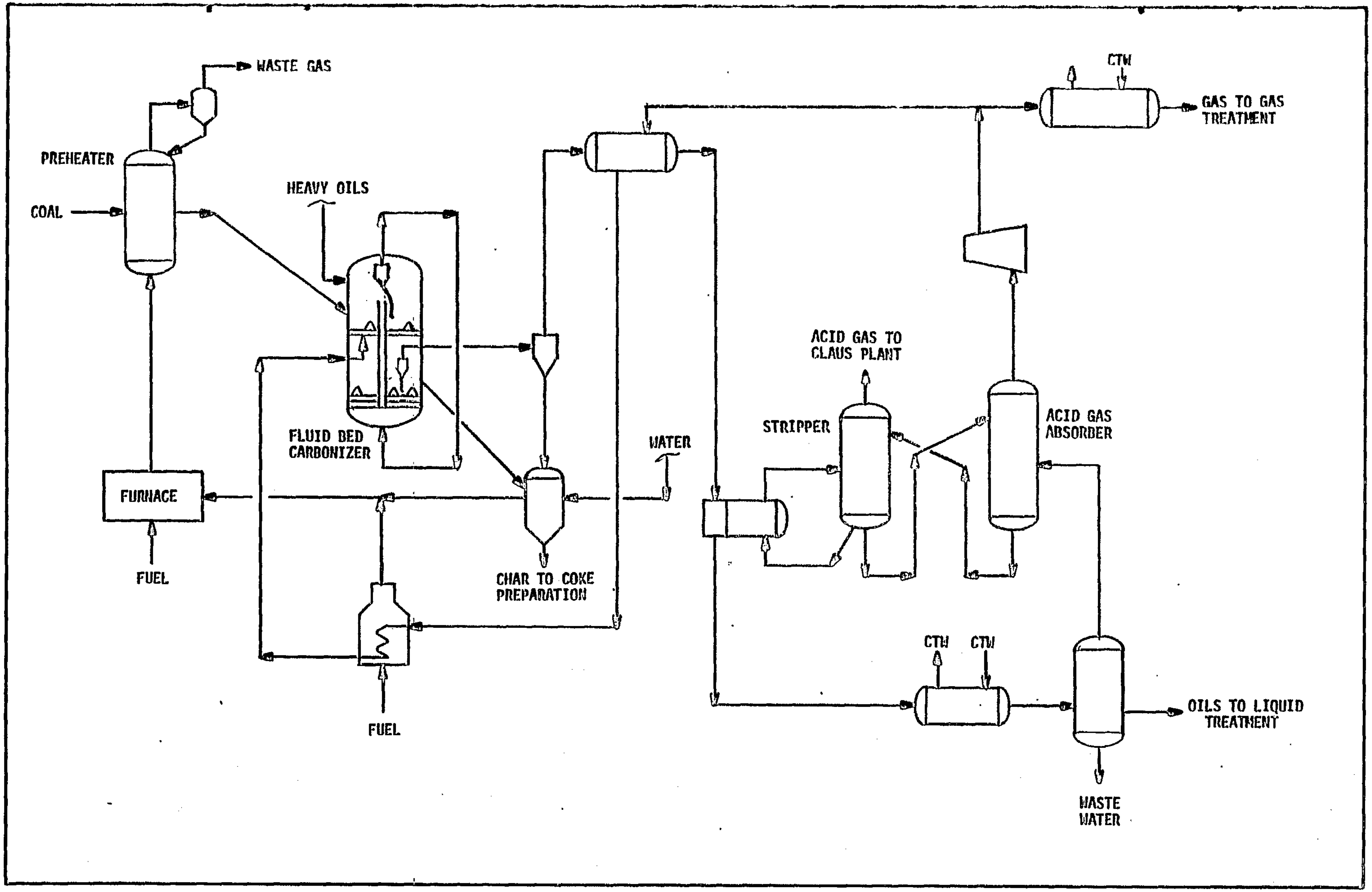

Figure 1 - Flow Diagram Clean Coke Coal Carbonization Unit (71)

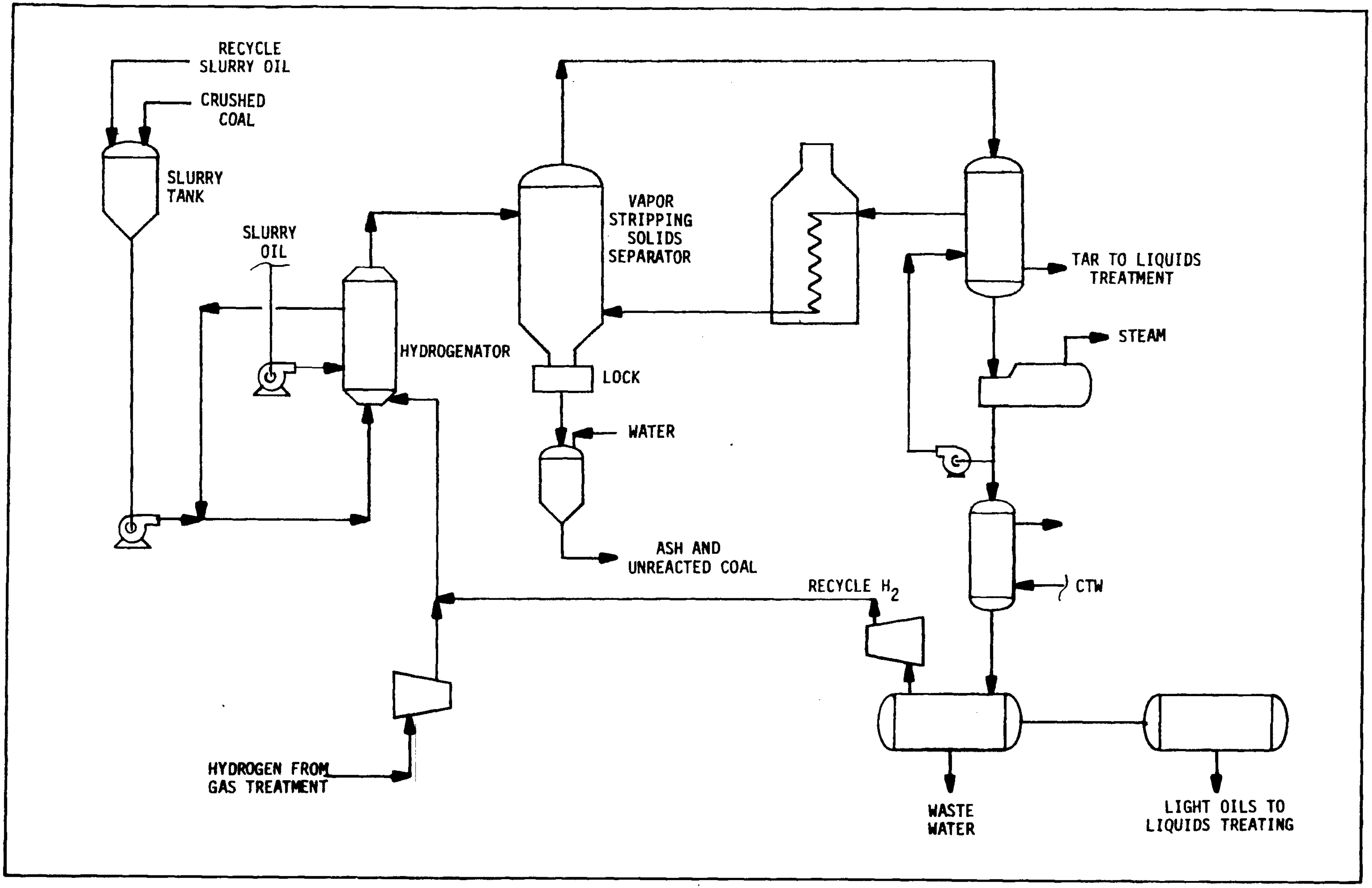

Figure 2 - Flow Diagram
Clean Coke Hydrogenaton Unit (71)

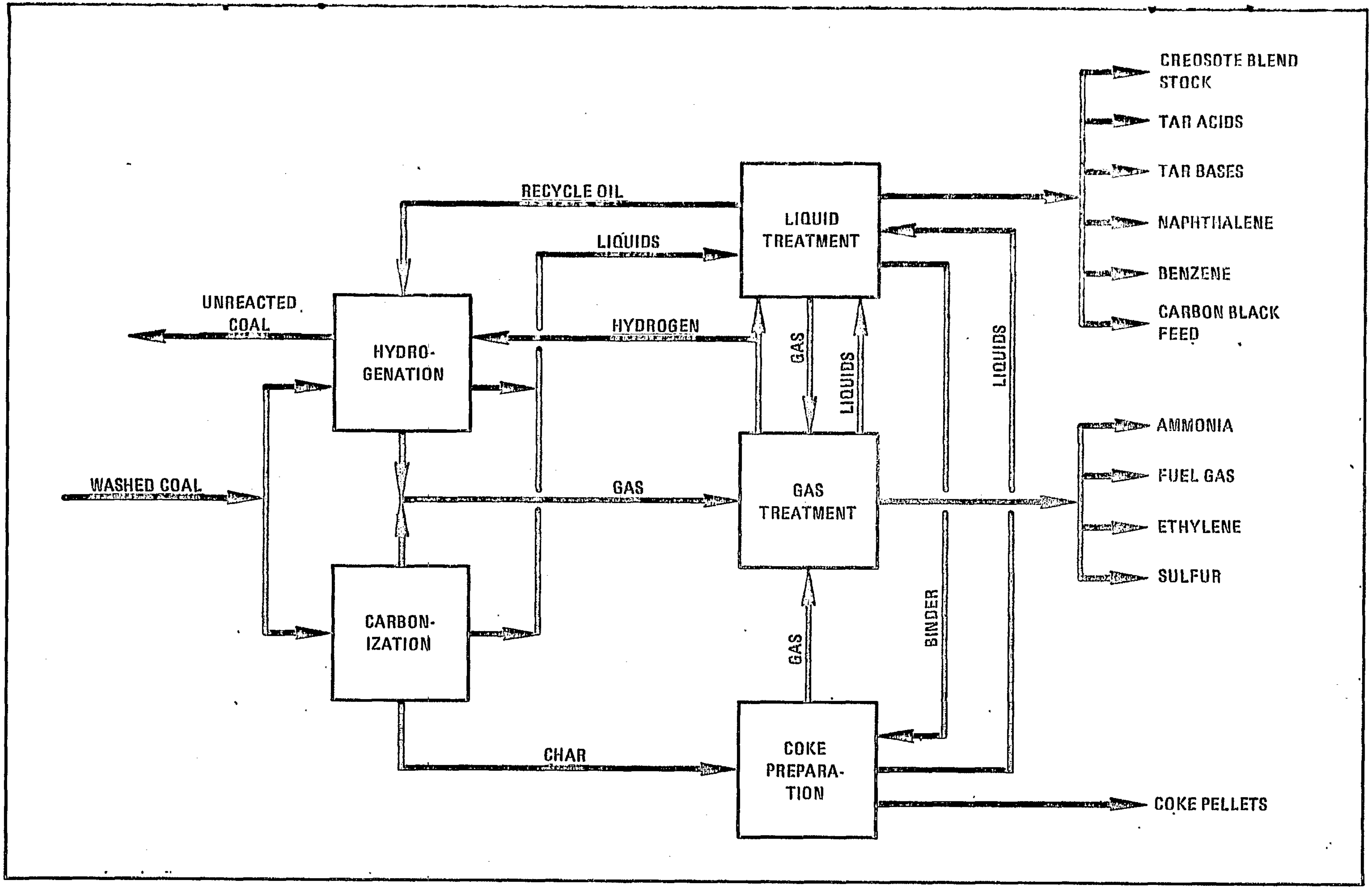

Figure 3 - Block Diagram
Clean Coke and Fuels Process

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PROCESS INFORMATION EXTRACT

PROCESS 2.2.2	Coalcon
Process Type	Pyrolysis, Hydrocarbonization
Main Products:	Char, gas, liquids
Development Status:	Pilot Plant
PROCESS DEVELOPER	Coalcon Co. (a subsidiary of Union Carbide Corp) One Penn Plaza, New York, N.Y. 10001
PROCESS SPONSOR	DOE

DESCRIPTION OF PROCESS (refer to Figure 1)

A hot flue gas is mixed with a recycle gas to heat the coal in the coal heater to 625°F without devolatilizing or caking it. The coal is disengaged from the recycle gas by cyclones and enters the coal feed lock-hopper system. The coal is pressurized using 900 psig steam and transferred to the coal holding vessel. Coal flows by gravity to the injector where a hydrogen carrier gas is used to transport the coal in a dense phase to the hydrocarbonizer. The coal is charged to each of four circulating char loops where it is mixed with ten times its weight of recirculating char. Hot hydrogen plus injector bleed gas conveys the recycle char and coal to the reactor bed. The balance of the hot hydrogen is fed to the bed to maintain fluidization and provide the desired H_2 partial pressure. Char fines are separated by an external cyclone from the recycle hydrogen and product vapors and then rejoined with the char in the surge hopper. The char is stripped of hydrocarbons by stripping steam in the bottom of the hydrocarbonizer. Agglomerated coal particles are periodically removed from the reactor and flow by gravity to the agglomerates lock hopper where it is quenched and removed from the unit as a slurry.

OPERATING CONDITIONS

Temperatures:	Hot Coal Feed 567°F Hydrocarbonizer 1040°F
Pressure:	(330 psia H_2 partial pressure)
Space velocity (lb/h dry coal feed ÷ ft^3 of hydrocarbonizer fluidized bed):	60-70
Solids Residence Time:	
heater	2-3 seconds
hydrocarbonizer	25 minutes
Superficial gas velocity in fluidized bed	1 ft/s
Reaction variables:	As reaction temperature, H_2 partial pressure, and solids residence time are increased, it was observed that liquid yields (tar) increased.(76)
Feed coal particle size:	50% through 100 mesh
Hydrogen consumption:	3.9 lb H_2/100 lb MAF Coal
Coals processed:	Lake de Smet (Western sub-bituminous)

PRODUCTS

Basis: Pittsburgh No. 8 Seam Coal

Typical analysis(74)

Ultimate Analysis, dry wt%	
Carbon	73.58
Hydrogen	5.09
Nitrogen	1.36

Oxygen	8.18
Sulfur	2.64
Chlorine	0.05
Ash	9.10
	100.00

Gross heating value (Btu/lb of as Received Coal)	11,760
Moisture with raw coal as received, wet wt%	12%
Moisture with coal to hydrocarbonizer, wet wt%	1%

Size analysis:

U.S.S. Screen Mesh	Cum. Wt%
30	99.5
35	98.0
40	95.0
60	76.0
80	42.0
100	50.0
200	22.0
325	10.0
400	8.0
30 micron	6.0
20 micron	3.5
10 micron	1.0
5 micron	0.5

Yields:

			Wt% of MAF Coal Feed (Pittsburgh No. 8)	Wt% of Dry Coal Feed (Pittsburgh No. 8)
(1)	char:	MAF	43.00	39.09
		Ash	N.A.	9.09
		subtotal char	43.0	48.18
(2)	Liquids:	C_4	0.79	0.72
		C_5s	1.27	1.15
		C_6H_6	0.52	0.47
		Toluene	1.50	1.36
		Pyridine	2.54	2.31
		P-Xylene	0.40	0.36
		propylbenzene	0.25	0.23
		mesitylene	1.01	0.92
		decane	2.80	2.55
		phenol	1.11	1.01
		o-cresol	1.58	1.44
		naphthalene	1.75	1.59
		3.5 xylenol	0.62	0.56
		1-methyl naphthalene	0.70	0.64
		Z-naphthol	1.29	1.17
		N-nonadecone	1.46	1.33
		N-pentacosane	3.63	3.30
		chrysene	8.62	7.83
		HCP	0.02	0.02
		subtotal liquid	31.86	28.96

(3) Gases:	N_2	0.01	0.01
	CH_4	10.38	9.43
	C_2H_6	5.22	4.75
	CO_2	4.17	3.79
	H_2S	1.44	1.31
	Organic Sulfur (COS, CS_2, C_4H_4S)	0.25	0.23
	NH_3	0.42	0.38
	C_3H_8	2.40	2.18
	subtotal gas	24.29	22.08
(4) Water:		5.52	5.02
	TOTAL	104.67	104.24

Characteristics:

(1) Char

Ultimate Analysis	Wt%
Carbon	72.3
Hydrogen	3.2
Nitrogen	1.3
Oxygen	1.6
Sulfur	2.7
Chlorine	0.1
Ash	18.8
	100.0%

Average char particle size = 86 microns,

Gross heating value 12,309 Btu/lb (reference 75)

(2) Liquids

	Wt%
C_4s	2.5
C_5s	4.0
Light Oils	20.3
Heavy Oils	50.3
phenolics	14.4
Thiophenes	0.6
Pyridine	7.9
	100.0%

(3) Net Gases (excluding recycle)

	Wt%
NH_3	1.8
N_2	0.0
CO_2	17.3
H_2S	6.0
C_1	43.1
C_2	21.6
C_3	10.0
COS/SC_2	0.2
	100.0

INTENDED PRODUCT USE/MARKET (refer to Figure 2)

(1) Char: The char may be gasified to produce a plant fuel gas and a synthesis gas for hydrogen manufacture. An alternate to complete gasification is char and coal burning to generate high pressure steam. The SO_2 in the flue gas may be removed in an Aqua-Claus absorber.

(2) Liquids: Liquids recovered after separation and fractionation may be marketed as a light oil and a heavy fuel oil. The light oil has a high sulfur content (2.2 wt%) but is expected to be marketable after desulfurization costs are deducted from the selling price. The fuel oil may be marketed as a utility boiler clean fuel. Its sulfur content is estimated to be lower than 1/2 wt%.

(3) Gases: Gases produced after clean-up, acid-gas removal and separation may be marketed as LPG and SNG.

(4) Miscellaneous Byproducts: Other marketable byproducts are phenols, pyridine, sulfur, and ammonia.

PROCESS EFFICIENTY

Yields (estimated): HHV yield of hydrocarbonizer products as % of coal feed HHV.

Char	44%
Liquids	36%
Gases (net)	25%
	105%

Thermal Efficiency: (products HHV ÷ feeds HHV x 100%)

(1) hydrocarbonizer (excluding utilities and heat losses)	91%
(2) Coalcon conversion plant	62.43%

Utilities:

Basis: 44,500 TPD crushed coal (1% moisture, 9% ash) to coal heating, pressurization, and carbonization)

cooling water	26,000 gpm
fuel gas	1.62×10^9 Btu/h
steam	777,000 lb/hr 900 psig S.H. Steam

Hydrogen consumption: 3.9 lb H_2/100 lb MAF Coal

Catalyst consumption: none

UNIQUE FEATURES OF PROCESS

- The distribution of sulfur in the hydrocarbonizer liquids as reported shows a high 2.2 wt% sulfur in the light oil and less than 0.5 wt% sulfur in the fuel oil.

- The process is a combination of pyrolysis and mild hydrogenation. However, unlike pyrolysis (but true to hydrogenation), the char yields decrease with increasing solids release time.(76)

- The external char circulation loops, which are used primarily to circulate char at a char to coal ratio of about 10 to 1.

- Undersirable heavy pyrolysis liquids can be recycled and converted to lower-boiling, lower sulfur liquids.

PROCESS STATUS

Developmental status:

In January 1975, Coalcon was awarded a $237 million contract to design, construct, and operate a 26,000-TPD plant to be located near New Athens, Illinois using a hydrocarbonization process to produce 3,900-BPD of 17°API liquid product and 22-MMCFD SNG. The program consists of four phases(77):

- Phase I - Conceptual design of the demonstration plant ($4 million);

- Phase II - Detailed design ($17 million);

- Phase III - Plant construction (1979);

- Phase IV - Operation of the plant for 3-1/2 years.

Phases III and IV are to be funded equally by government and industry and will cost over $200 million.

Phase I is expected to be completed in 1977; however, continuation of the project is not definite as it has been suspended pending a technical evaluation of coal-feed injection tests.(78)

Location of Development Work:

(1) Coalcon, 1 Penn Plaza, New York, N.Y.

(2) Tonawanda Mini-Test Laboratory, Tonawanda, New York

(3) South Charleston, West Virginia

(4) Buffalo Testing Laboratories, Buffalo, New York

History:(79)

The process is a development of an extensive pilot plant program by Union Carbide. In the early 1960s studies of the hydrocarbonization process had been conducted on two bench-scale levels (using Lake de Smet, Wyoming coal at 1 lb/h and 10 lb/h) and at a 1,500 lb/h level.

Problem Areas:

- Data base: At the present time, the only data available is from a 20-TPD pilot plant run in the 1960s on Lake de Smet Coal. The commercial scale designs(74),(75) were based on data extrapolated from Lake de Smet data.
- Agglomeration of the coal is a possible problem in the carbonizer and lock hopper systems.
- Coal feed injection and agglomeration.(78)
- Sulfur in the light oil is high and must be devalued as a byproduct.
- Economics(74) - the capital cost of a 50,000-TPD plant is $1.2 billion (late 1975 prices).
- Using utility financing, the required selling price of fuel oil is $14.77/bbl, still above current price for low-sulfur No. 6 fuel oil.

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74. The Dravo Corporation, *Conceptual Commercial Design and Commercial Feasibility Evaluation for Clean Boiler Feed Facility,* Vol. I, II, and III, Energy and Research Development Association Contract No. E(49-18)-1972, February 1976.

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77. Howard-Smith, I. and G.J. Warner, *Coal Conversion Technology: A Review,* May 1975.

78. Personal Communication to E.T. Coles (Coalcon) from J.F. Ferrall (The Ralph M. Parsons Company), February 17, 1977.

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79. Coles, E.T., *Coalcon's Hydrocarbonization Technology*, Paper presented at 82nd National Meeting, The American Institute of Chemical Engineers, Atlantic City, New Jersey, August, 1976.

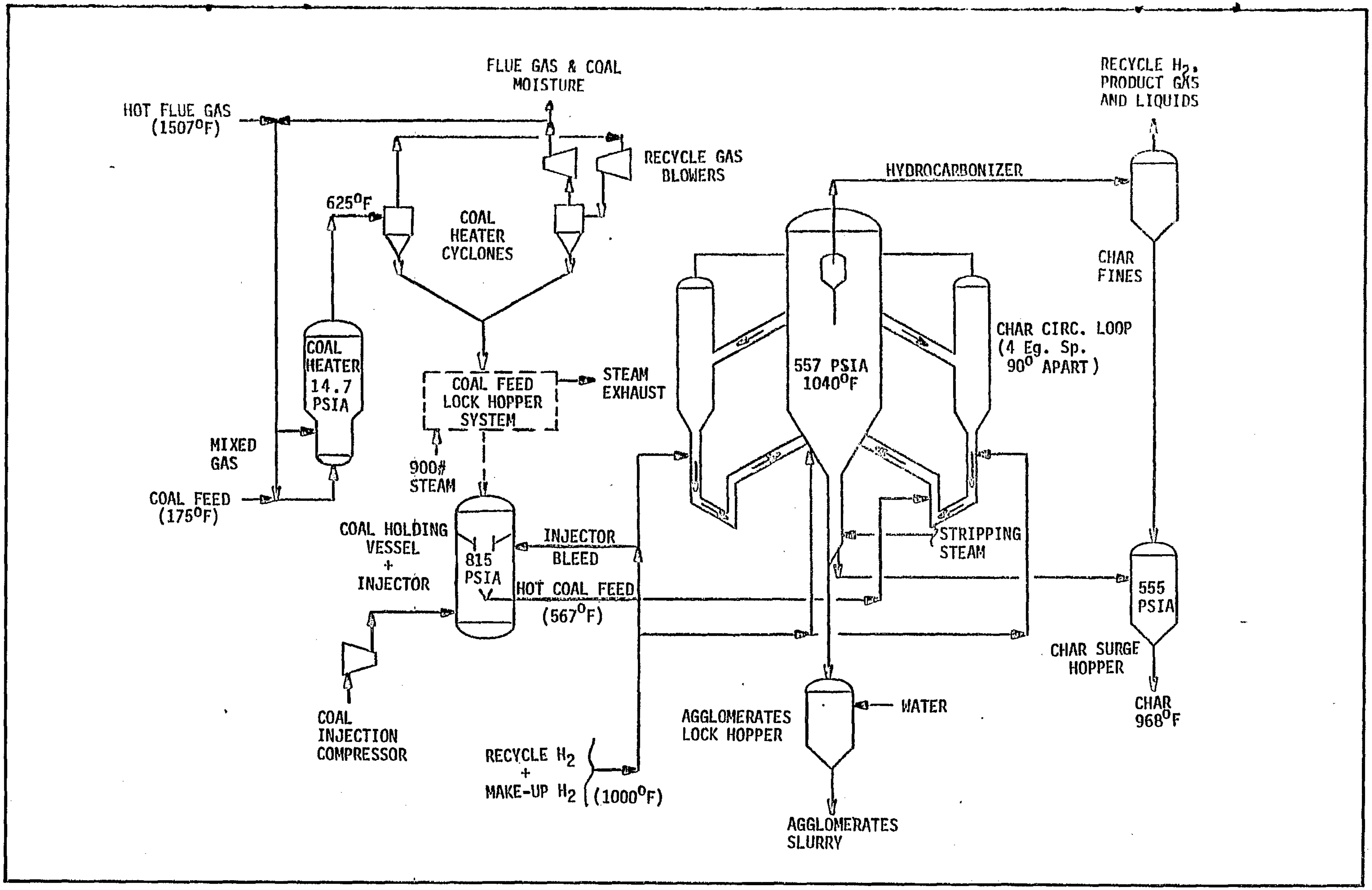

Figure 1 - Flow Diagram
The Coalcon Hydrocarbonization Process (74)

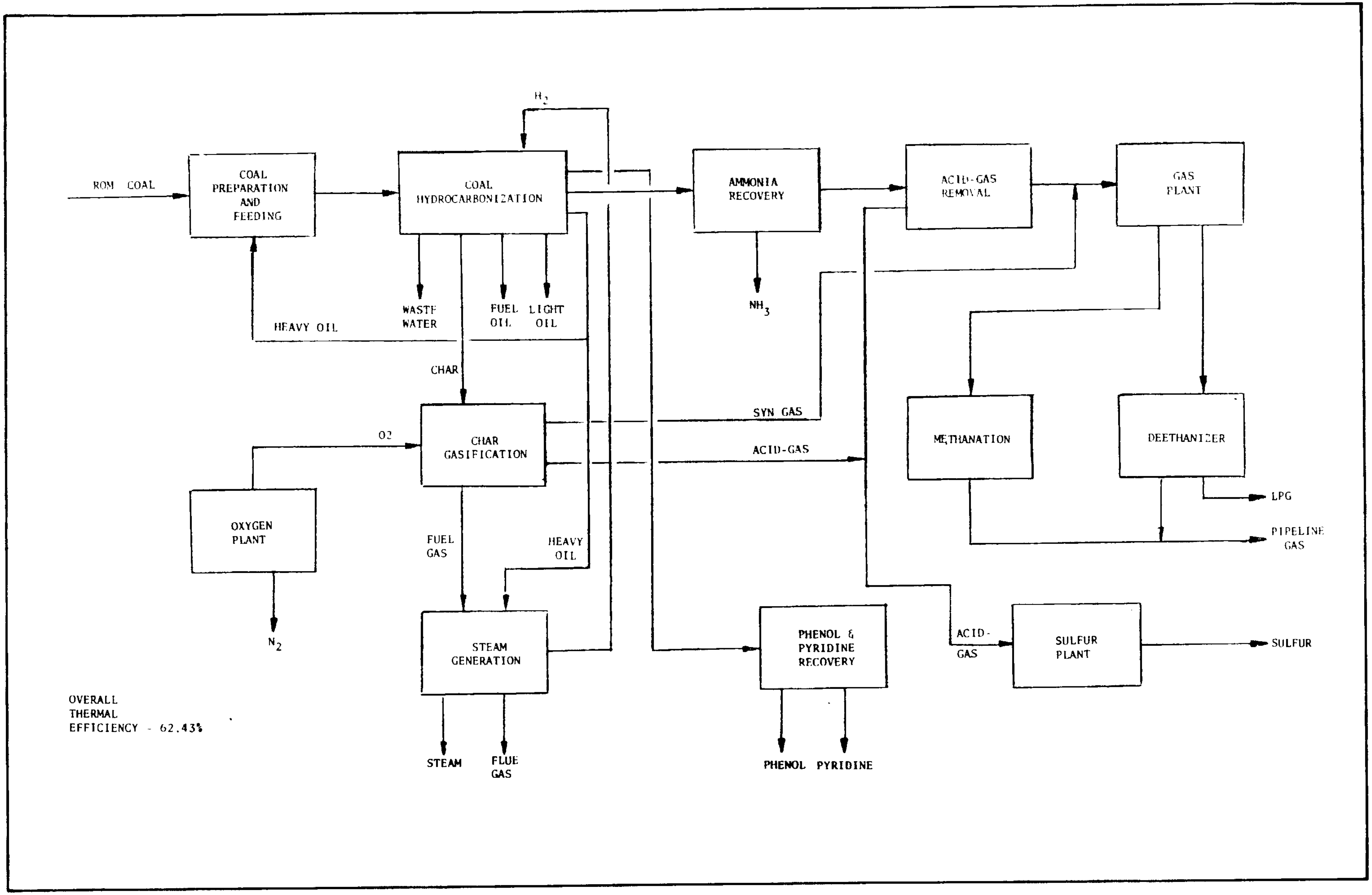

Figure 2 - Simplified Flow Diagram
Coalcon Integrated Coal Conversion Plant (74)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.1	BNL Rotating Fluidized Bed
Process Type:	Pyrolysis, Rapid Hydrogenation
Main Products:	Single ring aromatics mix
Development Status:	Conceptual
PROCESS DEVELOPER	Brookhaven National Laboratory (BNL) Upton, New York
PROCESS SPONSOR	BNL

PROCESS DESCRIPTION(80)

The BNL rotating fluidized-bed process contains three major process unit operations:

(1) Coal Hydrogenation

(2) Separation (char and ash)

(3) Hydrogen Manufacture

The integration of the units is depicted in the fluidized-bed block flow diagram (Figure 1).

A simplified flowsheet of the fluidized bed and reactor feed system is shown in Figure 2.

In the coal hydrogenation unit dry coal, crushed and pulverized to 200 - 500 micron size, is entrained into the fluidized-bed reactor with a portion of plant recycle hydrogen. The remainder of the plant hydrogen recycle and hydrogen makeup is preheated up to 1800°F maximum in a fired heater and fed to the fluidized-bed reactor where it fluidizes the coal bed. The fluidized-bed operates in a high gravitational field created by rotation of the fluidized bed at about 425 rpm. Much higher gas velocities, and short residence times, can be used compared with a 1-g bed. Heat and mass transfer coefficients are high. The coal feed is almost instantaneously raised to reaction temperature by heat exchange with the hot hydrogen, and hydrogenated in the gas phase to hydrocarbons, char, and ash.

Char and ash are separated from the hot reactor product by gravity settling and by three-stage cyclones. The hot separated char and ash are gasified, without cooling, for hydrogen manufacture.

The gaseous product is cooled by heat exchange against the plant recycle and makeup hydrogen, and then quenched to a temperature just above the gas dew point.

The gaseous products which constitute the crude aromatic mix are recovered by further gas cooling, condensation, and oil fractionation. Hydrogen-rich gases are scrubbed to remove acid gases prior to recycle to the reactor. A portion of the recycle gas is purged to prevent the accumulation of inerts in the reactor loop, and is used to hydrotreat the crude aromatic mix.

OPERATING CONDITIONS(80)

Pressure, atm	68
Temperature, °F	1,000
Hydrogen/Coal, SCF/lb	23.7
Space Velocity/Residence Time:	
Gas residence time, seconds	0.11
Coal residence time, seconds	4.60
Coal weight hourly space velocity (WHSV), $lb/h/ft^3$	23,800
Conversions:	
H_2 wt% MAF Coal	2.0
H_2, SCF/bbl oil	2,000
Catalyst:	Can be operated with or without catalyst. (Catalyst solution sprayed onto coal)

Reaction Variables:

- The BNL rotating fluidized-bed is essentially a conceptual process technique for conducting hydrocarbonization at short gas residence times, as originally proposed by Schroeder.(81)

- Schroeder obtained high yields of gas and liquids with and without catalyst by rapid heating of the coal to reaction temperature and short residence time of the gaseous and vapor products at high temperature. Yields of liquid and tar pass through a maximum as the gas residence time is increased. Coal conversion increases rapidly with residence time.(82)

- Ammonium molybdate and stannous chloride are catalysts for the reaction. Highly pulverized coal (about 200 mesh) is required to obtain high conversion with high liquid and gas yields.

- Experiments conducted at the University of Utah(83) with a high volatile bituminous coal, using 15 percent by weight of coal stannous chloride and a residence time of about 1 second, showed that:

  - The yield of liquid increased up to 959°F, but decreased at higher temperatures. Gas yield of char decreased up to 959°F, but remained almost constant at higher temperatures.

  - The liquid product increased with pressure with a corresponding decrease in the yield of char. Pressure had little effect on gas yield. Liquid yield increased slowly above 2000 psi.

Coals Processed(81), (83)

No coals have been tested in the BNL reactor. Schroeder and the University of Utah have tested bituminous coals from New Mexico and Utah in short residence time entrained-bed reactors.

PRODUCTS(80)

Yield, MAF Coal:

Hydrocarbons, wt%:	60
Char and Ash, wt%	40
Liquid yield, bbl/ton:	4.0

Characteristics:

Component	vol%
Benzene	15
Toluene	26
Xylene	30
Mixed Aromatics (C_9, H_{12})	14

Component	vol%
Ethylbenzene	5.5
Naphthalene	7.5
Methane	2.0
	100.0

INTENDED PRODUCT USE/MARKETS

Gasoline blending stock

PROCESS EFFICIENCY(80)

Thermal Efficiency:	
Product only, %	86.8
Overall, including net utilities, %	71.0
Utilities, per ton dry coal liquefied	
Steam required, lb	2091
Steam generated, lb	3648
Power, kWh	84
Fuel, MMBtu	4.8
Cooling Water, gal	8968
Hydrogen Consumption:*	
wt% MAF Coal Liquefied	7.1
SCF/bbl oil yield	6,700
Catalyst, % not recovered:	
ammonium molybdate (1 wt% coal)	100

*Including Oil Hydrotreater

UNIQUE FEATURES OF PROCESS

Main features of the process are: Coal liquefaction by centrifugal hydrogenation in a rotating fluidized bed.

PROCESS STATUS

Development Status:

The general subject of fluidized beds operating under high gravities are being studied in 5/8 in. deep beds.

Patents: U.S. patent applied for centrifugal fluidized bed reactor.

Location of development work: BNL Upton, New York

History:

Rotating fluidized bed reactor developed by BNL early 1970s.

Short residence time hydrogenation of coal proposed by Schroeder early 1960s. No further development work on the use of the fluidized-bed reactor for coal hydropyrolysis is planned.

Problem Areas:

Process is conceptual only.

REFERENCES

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81. Schroeder, W.C., *Rapid Hydrogenation of Coal,* U.S. Patent No. 3,030,297, April 17, 1972.

82. Schroeder, W.C., "Solid Phase Hydrogenation Cuts Cost," *Hydrocarbon Processing,* January 1976, pp. 131-133.

83. Qader, S.A. et al, "Coal Can Also Yield Liquid Fuels," *Hydrocarbon Processing,* September 1969, pp. 147-152.

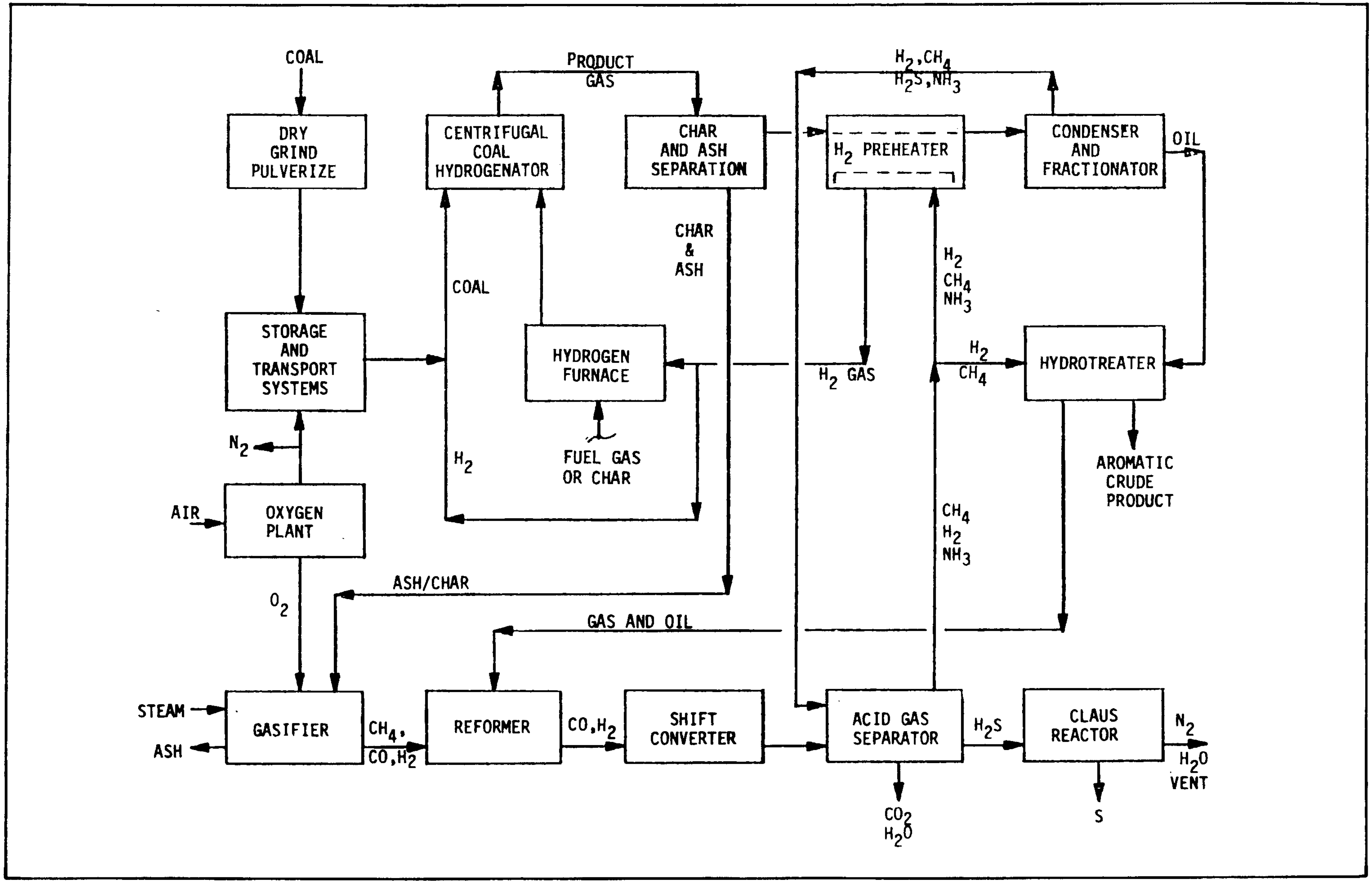

Figure 1 - Flow Diagram
Centrifugal Coal Hydrogenation Plant (80)

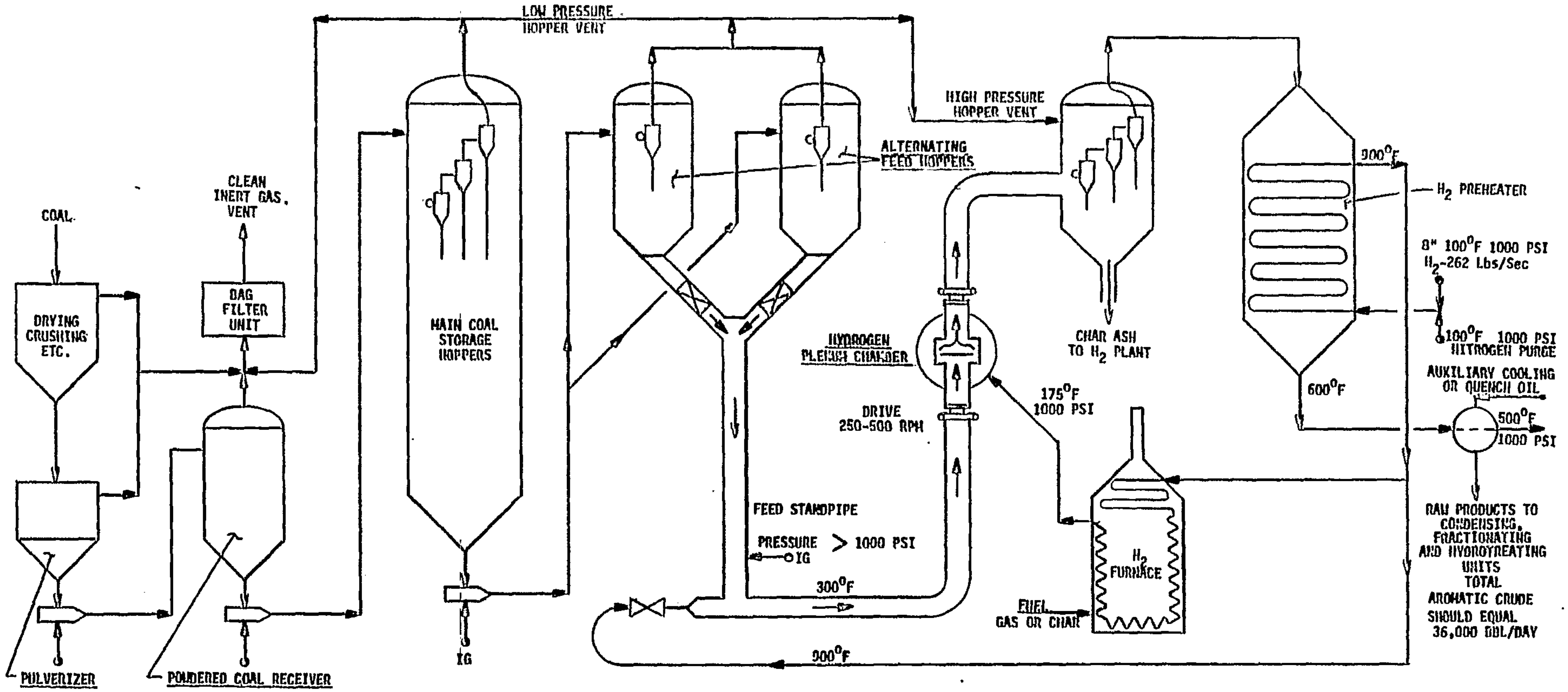

Figure 2 - Flow Diagram Centrifugal Coal Hydrogenation
Coal Feed and Fluidized-Bed Reactor (80)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.2	Short Residence Time (SRT) Coal Hydropyrolysis
Process Type:	Pyrolysis, Rapid Hydrogenation
Main Products:	High-Btu Gas, Light Aromatic Liquid, Char
Development Status:	Bench Scale Unit
PROCESS DEVELOPER	Cities Service R&D Cranbury, New Jersey
PROCESS SPONSOR	Cities Service

PROCESS DESCRIPTION(84)

The SRT process contains three major process unit operations:

(1) Coal Hydrogenation

(2) Separation (char/products)

(3) Hydrogen manufacture

The integration of these units is shown in the block flow diagram, Figure 1, for a conceptual SRT coal to oil plant. Equipment configuration for the bench scale free-fall reactor is shown in Figure 2. In the conceptual plant an entrained reactor is envisaged. In the coal hydrogenation unit dry coal, crushed to 50 to 450 microns, is fed from pressurized coal hoppers by a star-wheel feeder into the reactor where it is mixed with hot hydrogen. Heat is sufficient to reach the desired reaction temperature. A proprietary nozzle arrangement ensures that the hydrogen heats the coal very rapidly (50,000 to 150,000°F/second).

The hydrogenation reactions are quenched by the introduction of a coal quenching medium (cryogenically-cooled hydrogen in the bench scale unit). Char and ash are separated from the quenched reactor product in a solids receiver at the end of the reactor tube. The gaseous product is cooled to recover the liquid product in several fractions.

In the conceptual plant design hydrogen makeup is provided by steam reforming a portion of the methane production. Char is gasified with air to provide sufficient fuel gas to fire the reformer and to generate electrical power. In an alternative design coal and char are gasified with steam and oxygen to provide hydrogen makeup.

OPERATING CONDITIONS

Pressure, psig:	500 to 3000
Temperature, °F:	1150 to 1575
Hydrogen/coal, SCF/lb:	34 to 377
Space Velocity/Residence time:	
Vapor, seconds	0.8 to 14
Solids, seconds	0.01 to 3
Conversions:	
H_2 wt% MAF coal	**3.65 - 12.17**
H_2 SCF/bbl oil	**10,900 - 28,600**
Coal converted, wt% MAF	40 - 85
Catalyst:	None

Reaction Variables with Lignite:

- As average particle residence increases beyond 500 milliseconds, BTX is cracked to coke and hydrogen.
- Carbon selectivity to liquids passes through a maximum (approximately 43%) as carbon conversion increases through 45%. As carbon conversion increases beyond 45% the lignite is hydrogasified with methane as the principle product. These results are for 500 milliseconds residence time.
- Carbon conversion increases with reaction temperature (1200 to 1550°F) to an asymptote at about 46%. These results are for 500 milliseconds residence time and a coal heatup rate of 50,000 - 150,000°F/second.
- Carbon conversion increases with coal heatup rate.
- Above about 1200°F reactor temperature, only light aromatic liquids are produced.

Coals Processed:

North Dakota lignite, and Western Kentucky bituminous.

PRODUCTS

Coal:	North Dakota Lignite
Coal moisture, wt%:	
To unit	3.0
As received	38.8
Coal Analysis (dry):	
Proximate, wt%:	
Ash	10.0
Volatile Matter	42.0
Fixed carbon	48.0
Ultimate, wt%:	
Carbon	61.3
Hydrogen	4.1
Nitrogen	1.2
Sulfur	1.4
Oxygen	22.0
Ash	10.0
Yield: (MAF coal)	
(excluding hydrogen manufacture and utilities)	
Gas, SCF/ton coal	19,310
Liquids (BTX), bbl/ton coal	0.63

Hydrogen consumption:

wt% MAF coal	6.8
SCF/ton coal:	25,595

Characteristics:

Gas	
Methane	(70%)
Ethane	N.A.
CO (CO_2)	N.A.
C_3H_8	N.A.

Liquids	
Benzene	(94%)
Naphthalene	N.A.
Toluene	N.A.
Anthracine/Phenanthrene	N.A.

INTENDED PRODUCT USE/MARKETS

(1) Gas: High-Btu substitute natural gas.

(2) Liquids: BTX for gasoline blending or chemicals.

(3) Char: Gasified for plant fuel (or H_2) and on-site power generation.

PROCESS EFFICIENCY

Hydrogen Consumption:

wt% MAF coal liquefied:	6.8
SCF/bbl oil:	40,630
Catalyst:	None

UNIQUE FEATURES OF PROCESS

Main features of the process are: Rapid heating of the coal to reaction temperature short residence time noncatalytic coal hydropyrolysis, a light aromatics yield (essentially benzene) of 12 - 16 wt% MAF coal, and a high-Btu gas yield 34 - 68 wt% MAF coal.

PROCESS STATUS

Development Status:

1 to 2 lb/h bench scale unit operational since mid 1975.

Patents: U.S. 3,960,700

Location of Development Work:

CSR&D laboratories in Cranbury, New Jersey

History:

CSR&D began investigating SRT hydroprolysis about 1974 and constructed a bench scale unit which began operating in the summer of 1975. Most runs have been of about 4 to 5 hours duration. A detailed engineering analysis is planned.

Problem Areas:

None reported.

REFERENCES

84. Pelofsky, A.M. et al, *Short Residence Time (SRT) Coal Hydropyrolysis*, Paper presented at 172nd National Meeting, The American Chemical Society, Series 21, No. 5, August 29, 1976.

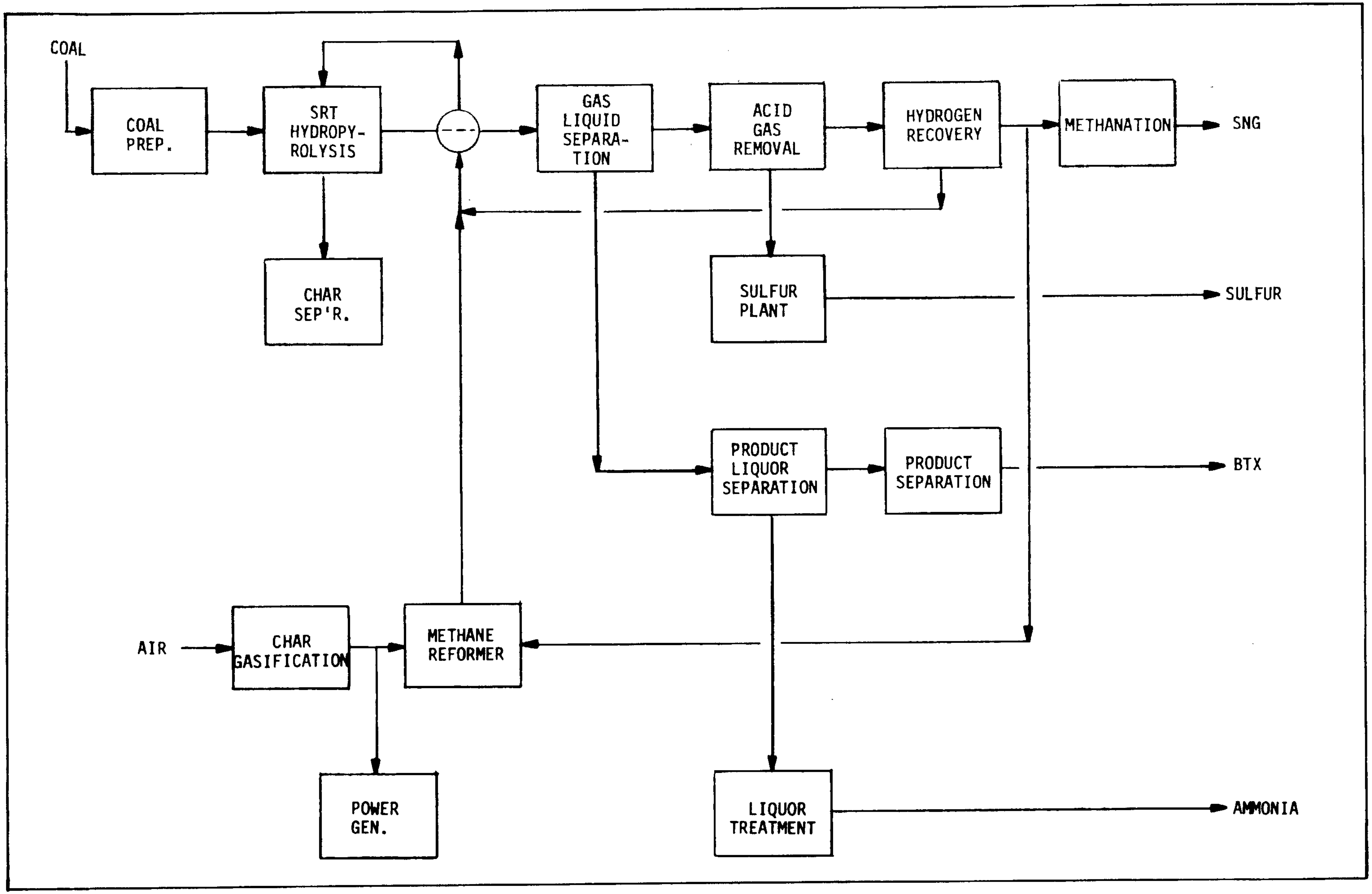

Figure 1 - Block Diagram
SRT Hydropyrolysis Process (84)

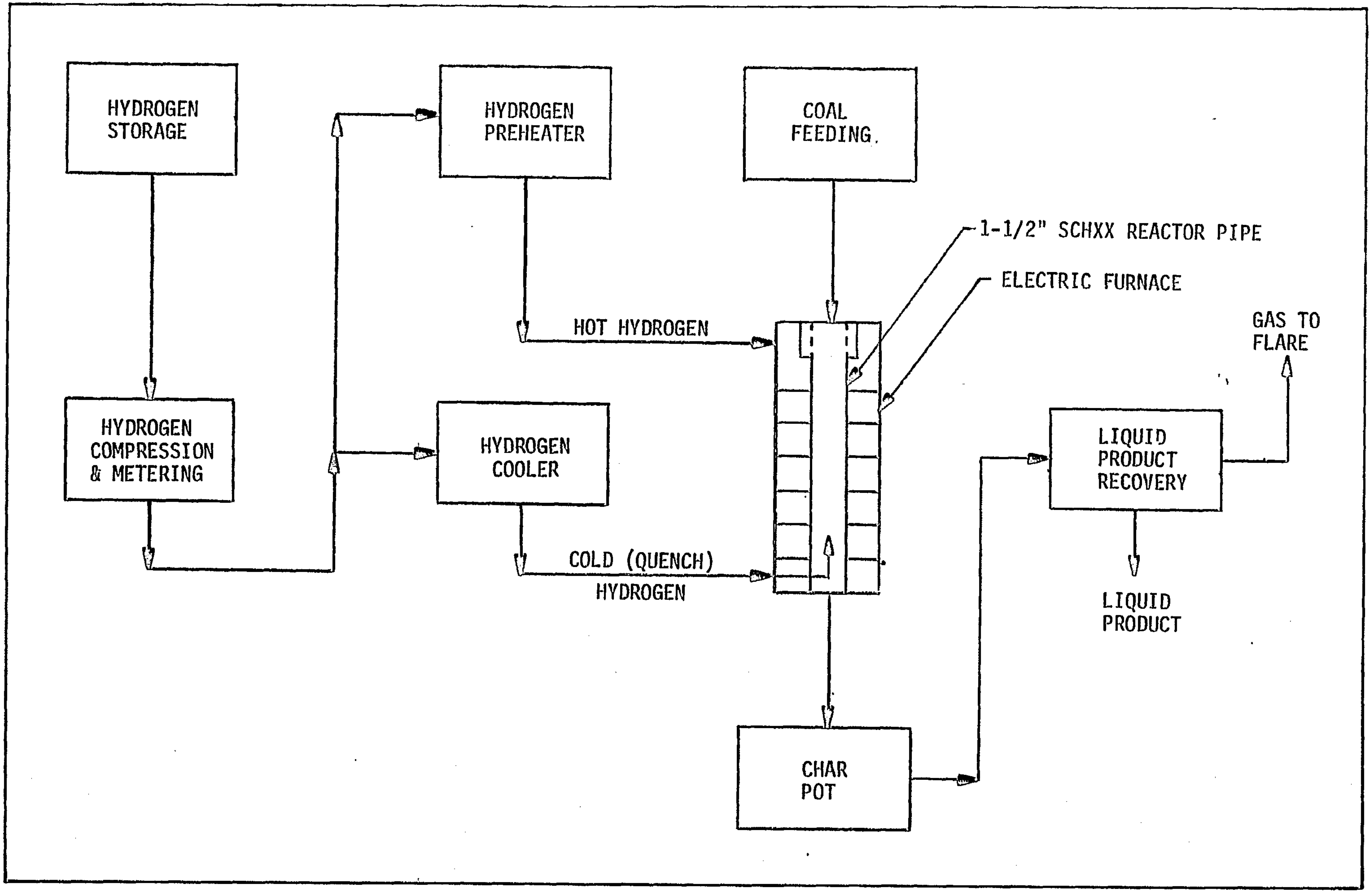

Figure 2 - Schematic of Cities Service Coal Liquefaction 2-lb/h Unit (84)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.3	Intermediate Coal Hydrogenation
Process Type:	Pyrolysis, Rapid Hydrogenation
Main Products:	Wide boiling range, low-sulfur fuel oil, high-Btu gas and residue.
Development Status:	Process Development Unit
PROCESS DEVELOPER	University of Utah Salt Lake City, Utah
PROCESS SPONSOR	DOE

DESCRIPTION OF PROCESS(85)

The Intermediate Coal Hydrogenation process contains four major process unit operations:

(1) Coal Hydrogenation

(2) Separation (char and ash)

(3) Catalyst Recovery

(4) Hydrogen Manufacture

The integration of these units is depicted in the block flow diagram for a conceptual coal refinery (Figure 1) equipment configuration for the PDU coiled tube reactor is shown in Figure 2.

In the coal hydrogenation unit dry coal, crushed to about 250 microns, is mixed with zinc chloride catalyst. The catalyst can be applied in the solid powder form as well as by impregnation from solution. Prepared coal, fed from fluidized lock hoppers, is entrained into a stream of recycle hydrogen. The coal/hydrogen mix passes in turbulent flow through a helical coil, part of which forms the preheater, where the mix is rapidly heated to reaction temperature, and the remainder flows through the "coiled tube reactor" where the mixture is held for a short time at reaction temperature.

Char and ash are separated from the hot reactor product in a solids receiver at the end of the reactor tubes.

The gaseous product is cooled to recover the liquid product in two or more fractions. The heavy viscous oil fraction is separated first by removal of water, and then filtered to remove char.

Separated gases are recycled to the reactor. Following the hydrogenation step the zinc is distributed about equally between the liquid and solid products. In the liquid the zinc is primarily in the water phase.

Zinc is recovered from the oil phase by water washing, and from the char by water and mineral acid washing (nitric acid). Recovered char can be used for power generation or hydrogen production.

The tar acids, sulfur, and nitrogen contents of the recovered oil can be almost completely removed by hydrorefining and hydrocracking.

OPERATING CONDITIONS(85)

Pressure, atm	136
Temperature, °F	950 - 1,000
Hydrogen/Coal, SCF/lb	194 - 321
Space Velocity/Residence Time:	
Residence time mixture, seconds:	
Preheater	1
Reactor	4 - 6
Coal weight hourly space velocity (WHSV), lb/h/ft^3:	
60% conversion	800 - 900
70% conversion	500
Catalyst to coal wt ratio, zinc metal/ MAF coal:	
hvAb or hvBb coals	0.03
hvCb or sub-bituminous coals	to 0.08

Conversions:

H_2 wt% MAF coal	5 - 12
SCF/bbl	7,337
Coal converted, wt% MAF	66.5

Analysis of MAF char is approximately the same as MAF coal and in this content is considered unconverted coal.

Catalyst:	Zinc Chloride

Stannous halides, zinc bromide, and zinc iodide are more active catalysts than zinc chloride but their use is unjustified by their high cost.

Reaction Variables:(85)

General conclusions with respect to operation of the reactor are as follows:

- Increasing temperature increases conversion. Reactor wall temperatures above 1380°F result in reactor plugging.
- Increasing hydrogen pressure increases coal conversion, but the improvement for pressures over 2000 psi is minimal.
- A catalyst to coal ratio of .03, applied by impregnation from water solution and measured in terms of zinc metal to MAF coal, is adequate for a reactive high volatile bituminous B or A coal. Higher ratios, to .08, are effective for lower rank hvCB or sub-bituminous coals.
- Decreasing catalyst concentration with this technique to ratios of .01 Zn to coal result in reactor plugging.
- Increasing the feed rate uniformly decreases the coal conversion.
- Decreasing the particle size of the coal fed decreases the coal conversion.
- The weight ratio of liquids to gases is a maximum at about 60% conversion.
- Hydrogen consumption increases uniformly with coal conversion in the range 55 to 75%.

Related observations made from the work with respect to coal preparation and product treatment are:

- The char, after a first pass through the reactor, still contains 25 - 35% volatile matter and may be further treated without adding fresh catalyst.
- When the char is subjected to a second treatment in the reactor the liquid products are generally higher boiling or heavier than those from the first pass through the reactor.

Coals Processed:

The design concept of the reactor was made to take advantage of the short residence time hydrogenation-pyrolysis for high volatile bituminous coals. Several coals from Western U.S. coal deposits have been tested in a small diameter tube reactor, and rated as follows:

Coal		Coal Characteristic		
		Feeding	Reacting	Plugging
Sidney, Montana	(Lignite)	Good	Poor	None
Big Horn, Wyoming		"	"	"
Navajo, Utah		"	"	"
Beluga River, Canada		"	"	"
Kanab, Utah		"	"	"
Alton, Utah	(hvCb)	"	"	"
River King, Illinois		Fair	Fair	Some
Last Chance, Utah		"	"	"
Kaiparowitz, Utah		"	"	"
Coalville, Utah	(hvCb)	"	"	"
Powers, Utah		"	"	"
Geneva-Somerset		Poor	Good	Some
Utah-Colo.		"	"	"
Spencer, Utah		"	"	"
Castle Valley, Utah	(hvBb)	"	"	"
Orangeville, Utah		"	"	"
Hiawatha, Utah	(hvAb)	"	"	"
Castle Gate, Utah		"	"	"

Spencer, Hiawatha, and Kaiparowitz Utah coals have been tested in the coiled PDU reactor.

PRODUCTS(85)

Coal:	Kaiparowitz, Utah
Coal Moisture, wt%:	
To Unit	0.
As received	6.65
Coal Analysis (dry)	
Proximate, wt%:	
Ash	10.80
Volatile Matter	45.82
Fixed Carbon	43.38
Ultimate, wt%:	
Carbon	65.45
Hydrogen	5.51
Nitrogen	1.70
Sulfur	0.50
Oxygen	16.04
Ash	10.80
Yield: MAF coal at 2000 psig:	
excluding hydrogen manufacture and utilities	
Gas, wt% MAF coal:	16.6
Light Oil	14.9
Heavy Oil	36.6
Char (MAF)	35.5
Water	4.4
	108.0
H_2 used	5.36

Ultimate Analysis (dry, catalyst free) wt%:

	Gas	Light Oil	Heavy Oil	Char
Carbon	71.7	84.91	87.67	47.52
Hydrogen	22.1	9.30	9.01	6.05
Nitrogen	1.65	1.30	1.90	1.65
Sulfur	1.9	0.096	0.107	0.86
Oxygen	2.65	4.384	1.103	24.12
Ash	0.0	0.01	0.21	19.80
	100.0	100.0	100.0	100.0

The hydrocarbon portion of the gases contains about 60 vol% CH_4, 20% C_2H_6, and 10% C_3H_8 as well as H_2S and NH_3. The light oil is aromatic in nature. The heavy oil contains about 27 wt% benzene insoluble residue, 20% asphaltene (cyclohexane insoluble) and a 53% cyclohexane oil soluble fraction. This soluble oil fraction contains 5 – 10% tar bases and up to 20% tar acids. The MAF char has a similar analysis to that of the MAF coal.

INTENDED PRODUCT USE/MARKETS(83)

The University of Utah has experimentally investigated coal oil hydrorefining and hydrocracking as means to further upgrade the liquid products to gasoline and diesel oil with results as follows:

(1) Hydrorefining

Pressure, psig	1500
Temperature, °F	788
Space Velocity, LHSV	1
Catalyst	Cobalt-molybdate on alumina
Yields, vol%:	
Total product	100.0
Gasoline	27.0
Diesel Oil	56.0
Solvent-refined diesel oil	48.0
Gas	2.0
Residual Oil, +360°C	12.0

Composition of gasoline, vol%:	
Saturates	58.0
Olefins	3.0
Aromatics	39.0
Research Octane number of gasoline:	78.0
Diesel Index:	
Diesel oil	43.0
Solvent-refined diesel oil	50.0

(2) Hydrocracking

Pressure, psig	2000
Temperature, °F	914
Space velocity, LHSV	1
Catalyst	nickel-sulfide-tungsten-sulfide on silica-alumina
Yields, vol%:	
Total product	100.0
Gasoline	69.0
Diesel Oil	17.0
Refined diesel oil	12.0
Gas	8.0
Solvent-residual oil, +360°C	6.0
Composition of gasoline, vol%:	
Aromatics	52.0
Isoparaffins	21.0
Olefins	2.0
Naphthenes	8.0
N-paraffins	17.0

Research octane number of gasoline	93.0
Diesel Index:	
Diesel oil	31.0
Solvent-refined diesel oil	50.0

Hydrogen consumption for these operations is 2 to 3 wt% of the oil.

PROCESS EFFICIENCY(85)

Hydrogen Consumption (including hydrorefining):	
wt% MAF coal liquefied	6.65
SCF/bbl oil yield (sp.gr.=1.0)	8508
Catalyst:	
percent zinc deposited (dry coal)	2.97
percent zinc not recovered	1 to 2

UNIQUE FEATURES OF PROCESS

Main features of the process are: Turbulent flow entrained bed reactor, short residence time coal hydrogenation pyrolysis using zinc chloride catalyst dispersed on the coal in a 3 to 8 wt% deposit, large gas recycle to prevent catalyst plugging, 98 to 99% zinc recovery by water and acid extraction of products, and hydrorefining of coal oil to gasoline and diesel oil.

PROCESS STATUS

Development Status:

Half pound per minute 1/4 inch I.D. helical coil 100-feet-long reactor operational under ERDA sponsorship up to May 1975.

Research work undertaken on hydrotreating, hydrocracking, and catalytic cracking of coal oils.

Patents: U.S. Patent applied for

Location of Development Work:

College of Mines and Mineral Industries, University of Utah, Salt Lake City, Utah.

History:

Research conducted at the University of Utah under Department of the Interior, Office of Coal Research Contract No. 14-01-0001-271 (August 25, 1962 - December 24, 1969) indicated a possibility for a short residence time conversion of coal to useful liquid and gaseous fuels in a free-fall reactor using $SnCl_2$ catalyst. Under contract no. 14-32-0001-1200 (October 1, 1969 - May 31, 1975) this concept was tested in short (6 ft) small-diameter tubes (1/8 in.-1/2 in.) at high temperatures (2000 psi hydrogen pressure and 650 to 700°C) and then extended to longer tubes at lower temperatures (1800 psi hydrogen pressure at 480-520°C). An application of 5% $ZnCl_2$ to the coal results in 70 — 75% conversion of coal matter to liquid and gaseous fuels at a coal feed rate of 1/2 pound of coal per minute in a 1/4 in. I.D. tube 100-feet-long. Tests were run for periods of up to 1 hour, as limited by the capacity of the solids receiving vessel at the reactor outlet. Process was also evaluated in a batch operated microreactor.

Problem Areas:

Plugging problems experienced in free-fall reactor overcome by use of entrained (turbulent flow) reactor. High levels of catalyst recovery are crucial to process economics.

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83. Qader, S.A. et al, "Coal Can Also Yield Liquid Fuels," *Hydrocarbon Processing*, September 1969, pp. 147-152.

85. Wiser, W.H., *Hydrogenation of Western Coal in Dilute Phase Under Medium Pressure for Production of Liquids and Gases, University of Utah Final Report (October 2, 1969 - May 31, 1975)*, Energy Research and Development Association Report No. FE-1200-1, Distribution Category No. UC-90d.

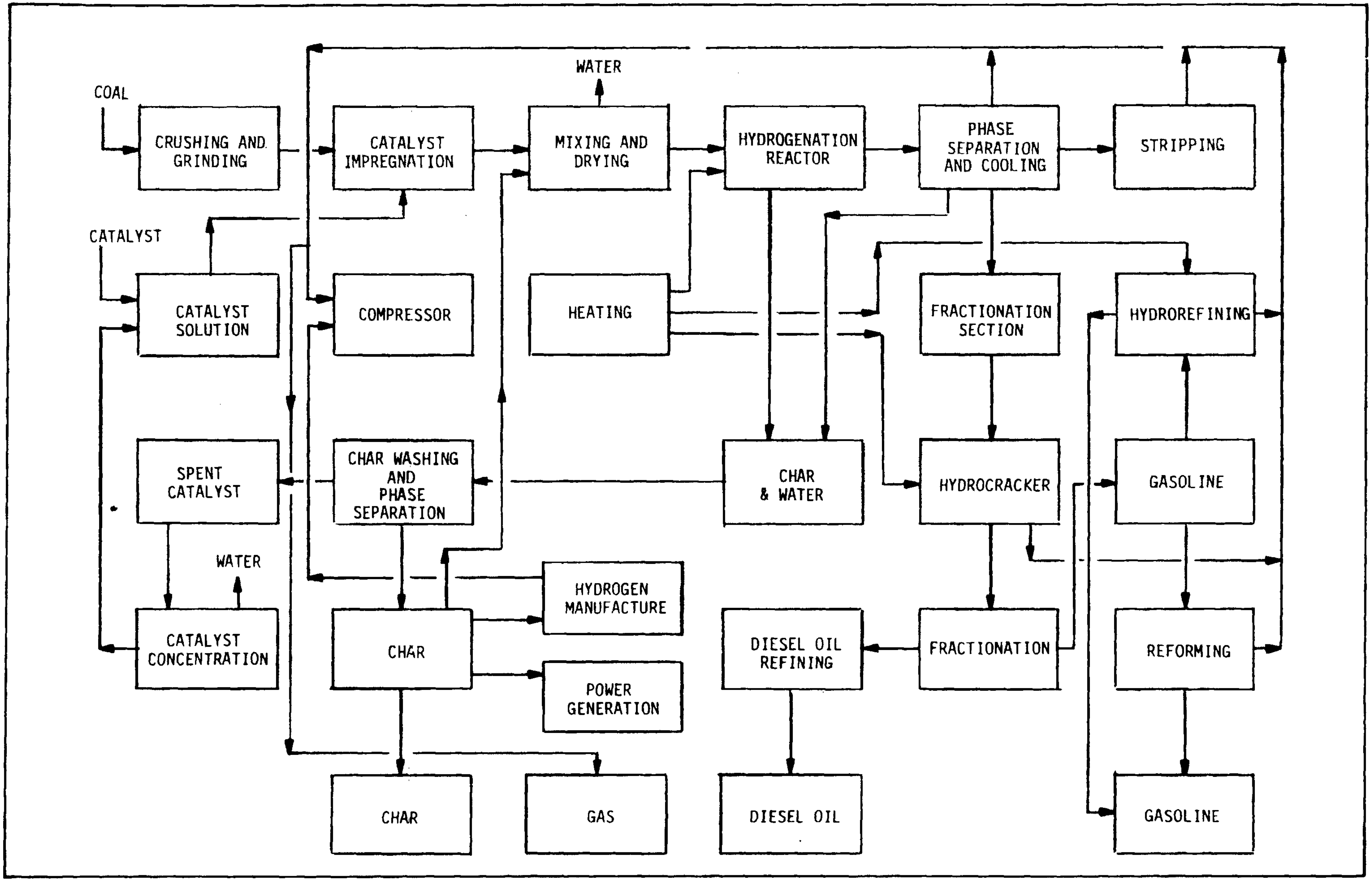

Figure 1 - Block Flow Diagram
Conceptual Coal Refinery –
Intermediate Coal Hydrogenation Process (85)

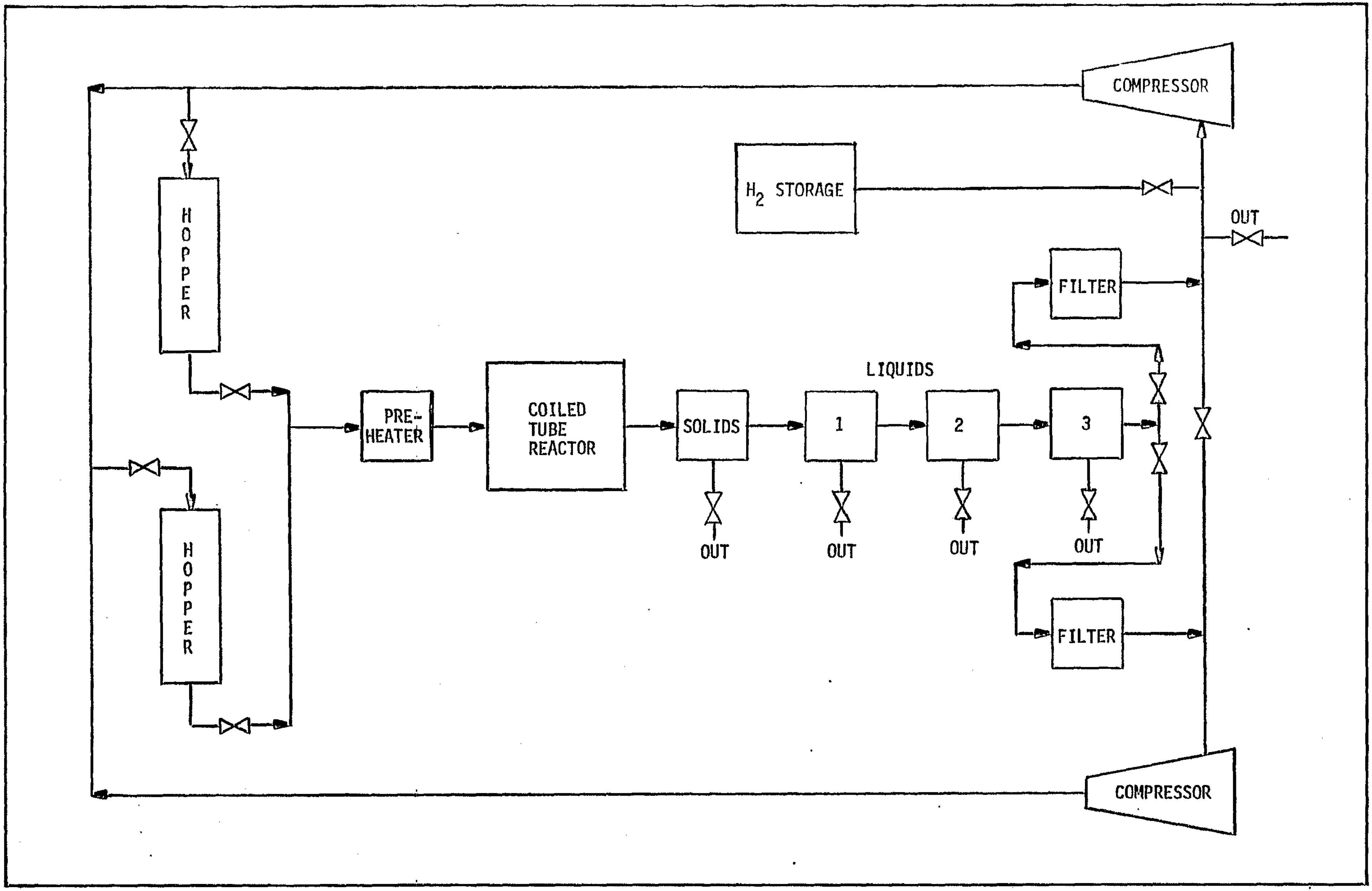

Figure 2 - Equipment Configuration
For Coiled Tube Reactor PDU —
Intermediate Coal Hydrogenation Process (83)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.4 Schroeder's Rapid Hydrogenation

Process Type: Pyrolysis, Rapid Hydrogenation

Main Products: Fuel Gas, Aromatic Distillate, Fuel Oil

Development Status: Process Development Unit

PROCESS DEVELOPER W. C. Schroeder
University of Maryland

PROCESS SPONSOR Fossil Fuels Inc.

PROCESS DESCRIPTION (82), (86), (87)

The Schroeder Rapid Hydrogenation process contains four major process unit operations:

(1) Coal hydrogenation

(2) Tar hydrogenation

(3) Separation (char and ash)

(4) Hydrogen manufacture

The integration of these units is shown in the conceptual flow sheet for a coal to syncrude plant (Figure 1). Equipment configuration for the PDU tubular reactor is shown in Figure 2.

Coal is prepared for hydrogenation by grinding to approximately 70% through 200 mesh and impregnating with hydrogenation catalyst by spraying with a solution of the catalyst (e.g. ammonium molybdate) followed by drying.

In the coal hydrogenation unit the dried catalyzed coal is fed from pressurized feeders to the hydrogenation reactor along with hot hydrogen from the reformer. Heat is sufficient to reach the desired reaction temperature.

Products from the reactor are cooled and separated tar is further hydrogenated to distillable oils and gases. Hydrogenation products are separated in a cyclone separator to remove ash and unreacted coal. Distillable oils and gases from both coal and tar hydrogenation are combined and cooled to remove oil from the pressurized system. These oils are refined to produce desired products.

Hydrogen, methane, and higher hydrocarbon gases are purified under pressure to remove CO_2, H_2S, NH_3, and impurities. Purified gases are reformed with oxygen and steam to make hydrogen.

The reformer operates at system pressure.

Reformer effluent is used to preheat reformer feed and coal to hydrogenation temperature.

Sufficient methane and higher gas is produced to furnish needed hydrogen. If additional reformer feed is needed, it can be provided from product oil. Hot reformer gases contain CO, some of which reacts with steam to produce hydrogen and carbon dioxide at hydrogenation reactor temperatures. The CO concentration in the recycle gas stream may be reduced by shift conversion prior to gas purification.

OPERATING CONDITIONS

Pressure, atm	136
Temperature, °F	932
Hydrogen/coal SCF/lb	254
Space Velocity/Residence Time	
Gas phase, s	29
Coal weight hourly space velocity (WHSV), $lb/h/ft^3$	18.5
Coal mass velocity, $lb/h/ft^2$	145
Conversions:	
Coal (basis carbon content), wt%	92.4
Catalyst:	
Ammonium molybdate, wt% MAF coal	1.0

Reaction Variables:

- The preferred temperature for producing liquid products for refining into gasoline and light oil fractions is in the range 800° – 1000°F. From 1000° – 1300°F gas production increases and liquid production decreases.

- Above 1300°F the hydrocarbon products are largely gas and any liquids are essentially all aromatics.

- As gas residence time increases tar and oil production increases rapidly, passing through a maximum after 15 to 20 seconds, and then declines and approaches an asymptotic value.

- As gas pressure increases from 2000 psig to 6000 psig, the residence time for maximum liquids production decreases from 20 to 15 seconds, 100% carbon conversion is achieved in 18 seconds rather than 25 seconds, and gas yield asymptotes after 35 seconds instead of 70 seconds.

- Ammonium molybdate has a marked catalytic effect when employed from 0.5 to 1.0 wt% MAF coal. Maximum catalytic effect obtained at 1 wt% concentration. At temperatures below 1000°F it is important to use a catalyst for high conversions and liquid yields.

- Increased coal particle size decreases the conversion of the coal to liquids and tars. Total conversion remains approximately unchanged.

- Coals from different sources show some variations in conversion percentages, but in general maximum conversions are obtained under substantially the same conditions for all coals.

Coals Processed:

Colorado, Missouri, Kansas, and New Mexico bituminous coals.

PRODUCTS(86)

Coal:	Bituminous (New Mexico)
Coal moisture, wt%	
To unit	1.5

Coal Analysis (dry):

Ultimate, wt%:

Carbon	76.1
Hydrogen	5.4
Nitrogen	1.9
Sulfur	1.8
Oxygen	14.8
Ash	9.9

Yield, wt% carbon in feed excluding hydrogen manufacture and utilities:

Hydrocarbon gas	37.3
Light oil	29.0
Heavy oil and tars	26.0
Char	7.6

Hydrogen consumption:

SCF/ton coal	20,000 (approx.)

Characteristics:

Gas (Hydrogen free basis):	vol%
Methane	50
Ethane	33
Propane	13
n-Butane	3

Light Oil:

Primarily alkyl substituted cyclohexanes, benzene, toluene, xylene, and other alkyl-substituted benzene compounds.

Tars and Heavy Oils:

Tars and heavy oils from the coal hydrogenation reactor, together with ash and unreacted coal, can be further hydrogenated to light oils and gases.

INTENDED PRODUCT USE/MARKETS

(1) Gas

Hydrocarbons are either used as fuel or reformed to hydrogen.

(2) Oil

Gross oil is an aromatic distillate, about 0.92 specific gravity. The oil may be refined to gasoline and aromatic chemicals.

PROCESS EFFICIENCY(82)

Thermal Efficiency:	
Product only, %:	75
Overall, including net utilities, %:	71
Utilities, per ton as received coal:	
Steam generated/used, lb/h	1012
Power, KWh	116
Fuel,* MM/Btu	0.87
Cooling water, gal	262

*Oil product used for steam and power generation

Catalyst:	
Ammonium molybdate, lb/ton MAF	20

UNIQUE FEATURES OF PROCESS

Main features of the process are: Rapid heating of the coal to reaction temperature; short residence time (<30 s) catalytic coal hydropyrolysis below 1000°F; separation of light oils from the ash, char, and heavy oils;

and further hydrogenation of the latter to yield more light oils and gases. This second hydrogenation permits easy separation of the heavy oils from the ash.

Oil yield: 3.44 bbl/ton coal

PROCESS STATUS

Development Status:

1 lb/h bench scale reactor operated until development work on the process was stopped in 1960 due to poor process economics.

Patents:

U.S. 3,030,297
3,152,063
3,926,775

History:

Earlier work was instigated and directed by W. C. Schroeder and sponsored by the El Paso Natural Gas Company, while the experimental work was performed by the Bureau of Mines. This was followed by individual investigations by both the El Paso Natural Gas Company and the Spencer Chemical Company. At a later date, the Spencer Chemical Company and the El Paso Natural Gas Company formally combined into an operation which was known as Fossil fuels.

Problem Areas:

None reported. Process has only tested non-caking bituminous coal. Run lengths are of insufficient duration (<10 hours) to establish process reliability and plant corrosion resistance.

REFERENCES

82. Schroeder, W.C., "Solid Phase Hydrogenation Cuts Cost," *Hydrocarbon Processing*, January 1976, pp. 131-133.

86. Schroeder, W.C. et al, *Hydrogenation of Coal*, U.S. Patent No. 3,152,063, October 6, 1964.

87. Schroeder, W.C., *Hydrogenation of Coal*, U.S. Patent No. 3,926,775, December 16, 1975.

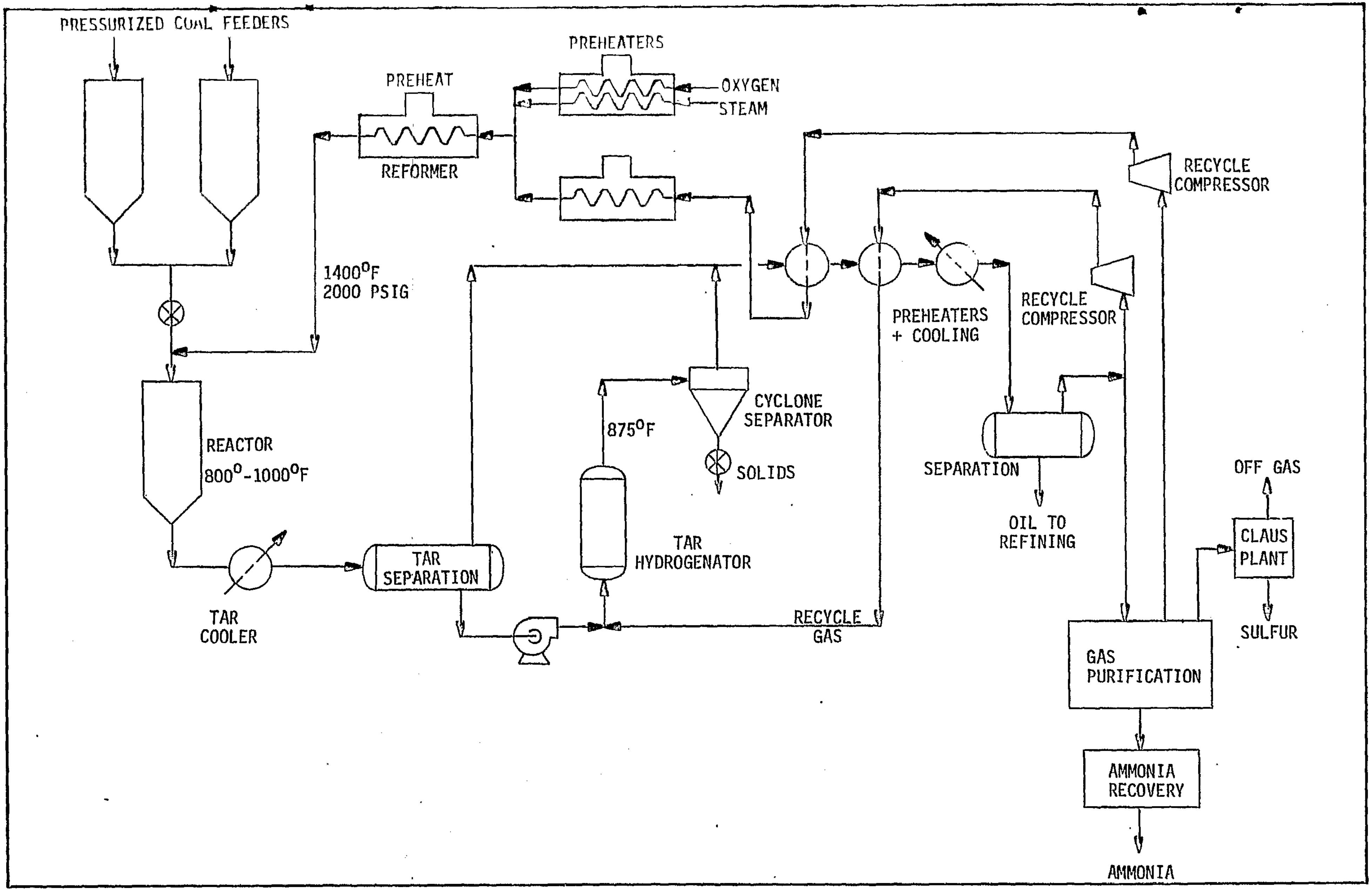

Figure 1 - Flow Diagram
Solid Phase Hydrogenation of
Coal To Syncrude (SRH) (87)

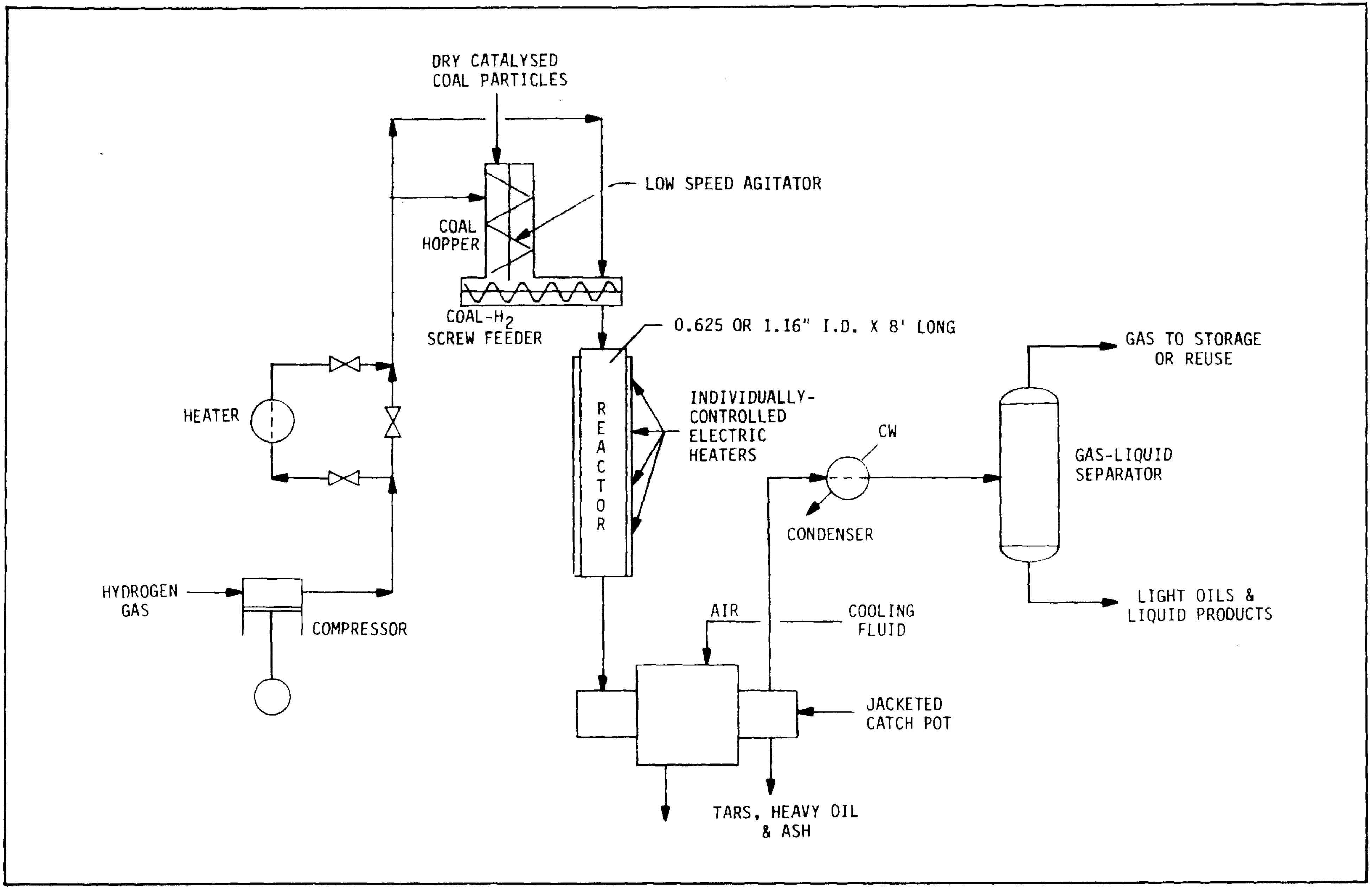

Figure 2 - Flow Diagram
Schroeder's Rapid Hydrogenation PDU (82)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.5 BNL Flash Hydropyrolysis

Process Type:	Pyrolysis, Rapid Hydrogenation
Main Products:	Light aromatics liquid, high-Btu gas
Development Status:	Bench scale unit

PROCESS DEVELOPER Brookhaven National Laboratory (BNL)
Upton, New York

PROCESS SPONSOR DOE

DESCRIPTION OF PROCESS(88),(89)

In the BNL Flash Hydropyrolysis process, coal is hydrogenated, in a non-liquid, noncatalyzed gas phase system, by rapidly heating the coal in the presence of hydrogen at elevated pressure and temperature, maintaining these conditions for 16 to 18 seconds, and then quench cooling the gaseous products to prevent free radical polymerization.

Equipment configuration for the process development unit is shown in Figure 1. Dry pulverized coal, ground to less than 150 microns, is fed from a pressurized lock hopper to the entrained downflow tubular reactor. A cold stream of hydrogen, introduced just below the coal feeder, is used to cool the line between the coal feeder and the reactor. The main flow of hydrogen to the reactor is preheated before it enters the top of the reactor.

The coal/hydrogen mix flows down through the reactor where it is raised to reaction temperature by heat supplied through the reactor walls. Char and unreacted coal are separated from the hot reactor product by a cooled solids receiver at the end of the reactor tube. The gaseous products pass through the solids trap at elevated temperature and pressure, and are cooled rapidly to recover any oil produced.

A conceptual plant design has been prepared by BNL to evaluate overall process economics (Figure 2). The conceptual plant reactor is a quasi entrained upflow fluidized reactor. Heat required to raise the coal to reaction is supplied by a preheater, where it is brought to about 500°F by hot (1800°F) recycle hydrogen to reach a final temperature of 1300°F.

Char is separated from the reaction product in multistage cyclones, and routed to a gasifier for hydrogen production. The gas stream from the cyclones is passed through an iron oxide tower for H_2S removal and rapidly cooled by transfer-line heat exchangers. A portion of the gas is recycled to the reactor, while the remainder goes to a quench tower for product recovery.

Recovered oil flows to an extractive distillation unit for benzene extraction. Raffinate is sent to a stabilizer to yield a light oil similar to No. 4 fuel oil.

Overhead hydrocarbon vapor product from the quench tower is passed through MEA and copper wash units to remove residual sulfur, CO_2, and CO. Then it is directed to a gas separation unit where methane and ethane are cryogenically separated and recovered from the hydrogen, which is recycled back to the flash hydropyrolyzer. CO recovered in the copper wash is fed to the hydrogen furnace as fuel.

OPERATING CONDITIONS (PDU)(88)

Coal:	North Dakota Lignite	New Mexico Sub-bituminous
Pressure, atm	102	102
Temperature, °F	1290	1290
Hydrogen/Coal, SCF/lb	130	107
Space Velocity/Residence Time:		
Established maximum coal residence time, seconds	18	16
Coal weight hourly space velocity (WHSV), $lb/h/ft^3$	13.3	19.4
Conversions:		
H_2, wt% MAF coal, SCF/bbl oil	6.3	N.A.
Carbon converted to gas and liquids, %	66.1	49.9

Reaction Variables:

- Lignite is not reactive at temperatures below 1200°F.
- Lower pressures tend to result in lower yields.
- As the coal particle residence time increases over the range 16-38 seconds:
    - % carbon converted decreases
    - % carbon converted to gas increases slowly
    - % carbon converted to liquid decreases rapidly
- The percent carbon converted to liquid decreases rapidly as the coal WHSV increases.
- Preheating the reactor hydrogen feed increases the overall yield. No appreciable changes in yields were observed when the hydrogen preheat was increased from 660 to 1100°F.
- The addition of 1% ammonium molybdate to the lignite produced no significant changes in the yields.

Coals Processed:

(1) Mainly a North Dakota lignite was used in these experiments.

(2) A few runs were made with a New Mexico sub-bituminous coal.

(3) A caking eastern bituminous coal was unsuccessfully tried in a few preliminary runs.

PRODUCTS(88)

Coal:	North Dakota Lignite	New Mexico Sub-bituminous
Coal Analysis (dry):		
Proximate, wt%:		
Ash	9.4	
Volatile matter	43.0	
Fixed carbon	47.6	

Ultimate, wt%		
Carbon	62.39	64.21
Hydrogen	4.29	4.86
Nitrogen	0.97	1.41
Sulfur	1.17	0.61
Oxygen	21.75	12.26
Ash	9.43	16.65
Yield, % Carbon in Coal:		
C_1-C_5 Hydrocarbons -mainly CH_4 and C_2H_6	47.0	37.0
C_6 + Hydrocarbons	19.1	12.9
CO	1.0	1.0
CO_2	5.0	5.0
Characteristics:		
Gas:		
C_1/C_2, vol/vol	2/1	
C_3, C_4, C_5	Not significant	
Liquid Hydrocarbons:		
Total oil benzene content, wt%	60	
Light oil benzene content, wt%	98	
Heavy oil (from first trap) is a low viscosity light colored oil.		
Char		
Carbon content, wt%	72	

INTENDED PRODUCT USE/MARKET

(1) Gas: High-Btu substitute natural gas, ethylene plant feedstock (C_2H_6).

(2) Liquid: Benzene, No. 4 fuel oil.

(3) Char: Char is gasified for plant fuel/hydrogen makeup.

PROCESS EFFICIENCY(89)

Thermal Efficiency, %:	
Product only:	86.8
Overall, including net utilities:	71
Utilities, per ton dry coal liquefied:	
Steam required, lb	2091
Steam generated, lb	3648
Net steam (generated), lb	1557
Power, kWh	84.0
Fuel, MMBtu	4.8
Cooling water, gal	8968
Hydrogen:	
wt% MAF coal liquefied	6.3
Catalyst	None

UNIQUE FEATURES OF PROCESS

Main features of the process are: Noncatalytic high-pressure, high-temperature, short residence time, and coal hydrogenation process. Up to 15% of the carbon in the coal is converted directly to BTX. A further 10% of the carbon is converted to light fuel oil.

PROCESS STATUS

Development Status:

1/2 lb/h bench scale unit operational since about 1974. Run times 10 - 15 minutes duration.

Patents: None applied for

Location of Development Work:

BNL, Upton, New York

History:

Rapid gas phase hydrogenation of coal at 2000 psig and temperatures up to 1110°F, with reaction times in the order of several minutes, to yield aromatic hydrocarbons and light oils, was first demonstrated in the early 1960s at the U.S. Bureau of Mines. In the 1960s other research workers obtained significant liquid yields by rapid gas phase hydrogenation of coal dusted with suitable catalysts, using residence times below 30 seconds.

BNL began experimental studies on short residence time hydrogenation chemistry with the operation of the 1/2 lb/h bench scale unit in 1973/74.

Economic evaluation of a conceptual plant was made by BNL in 1975.

Problem Areas:

Reactor design at an early stage of development. Corrosion resistance and reliability have to be demonstrated for extended run times. Most runs have been in the order of 10 to 15 minutes duration. PDU reactor cannot process caking coals.

REFERENCES

88. Steinberg, M. and P. Fallon, *Coal Liquefaction by Rapid Gas Phase Hydrogenation*, Paper presented at 169th National Meeting, The American Chemical Society, Philadelphia, Pennsylvania, April 6-11, 1975.

89. Steinberg, M. et al, *Flash Hydropyrolysis Process for Conversion of Lignite to Liquid and Gaseous Products*, Paper presented at National Meeting, The American Chemical Society, New York, New York, April 4-9, 1976.

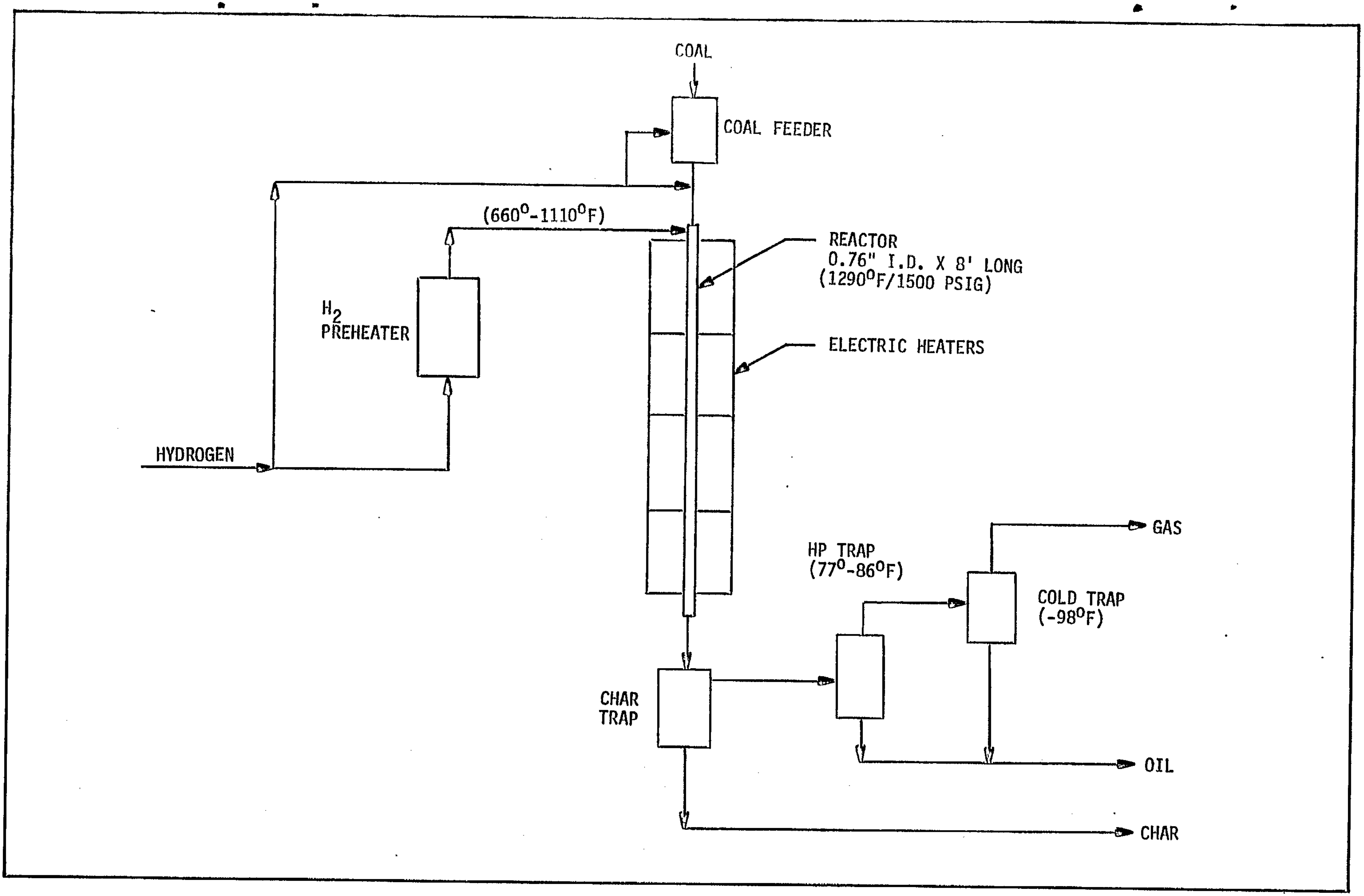

Figure 1 - Flow Diagram
BNL Rapid Gas Phase Hydrogenation
1/2 lb/h Bench Scale Unit (88)

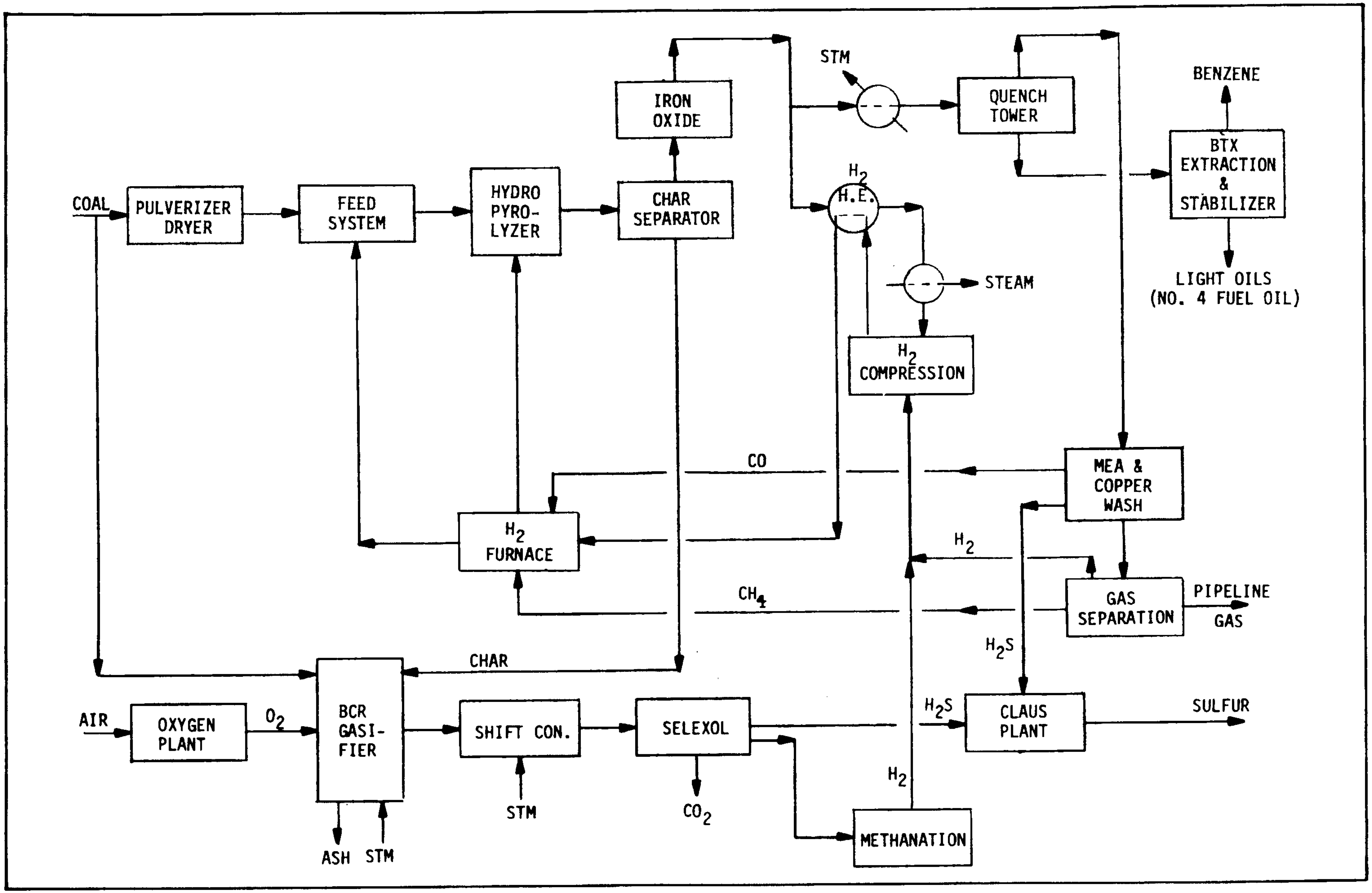

Figure 2 - Schematic Block Diagram
Flash Hydropyrolysis of Coal to
Gasoline and Motor Distillates (89)

PROCESS INFORMATION EXTRACT

PROCESS 2.3.6 Rockwell International Direct Coal Hydrogenation

Process Type: Pyrolysis, Rapid Hydrogenation

Main Products: Char, heavy and light tars, high-Btu gas

Development Status: Process Development Unit

PROCESS DEVELOPER

Rocketdyne Division
Rockwell International Corp.
Canoga Park, California

PROCESS SPONSORS

DOE
Rockwell International Corp.

PROCESS DESCRIPTION (90)

The Rockwell International Direct Hydrogenation of coal process is at a very early stage of development and only the reactor development unit will be described.

The attached diagram, Figure 1, shows the equipment configuration for the process development unit.

The basic concept of the process is to obtain high liquid yields in a non-catalytic hydropyrolysis process by rapidly heating the coal to reaction temperature with hot hydrogen, reacting for a period of less than 10 milliseconds, and quenching the coal/hydrogen mix to prevent further reaction.

Dry pulverized coal, ground to less than 150 microns, is fed from a pressurized lock hopper to the reactor injector using only the gas contained within the coal interstices as carrier gas. The reactor injector mixes the pulverized coal feed with heated hydrogen (2000°F) to ensure rapid mixing of these materials, with a mixing efficiency greater than 80%. Two types of nozzles have been tested in the injector:

- A concentric tube type nozzle wherein the pulverized coal and the hot hydrogen flow coaxially.
- A 4-on-1 type nozzle wherein four hot hydrogen jet streams impinge on a central coal stream.

The coal/hydrogen mix react for a period of 10 to 100 milliseconds in the downflow reactor before being quenched by a water spray and heat exchange.

Char and liquids are separated from the hot reactor product in a solids receiver at the end of the reactor tube and by a cyclone separator downstream of the quench system. The gaseous product is cooled to recover light tars. In the experimental unit, heavy tars are recovered from the char by solvent extraction.

Hydrogen is heated to reaction temperature by heat exchange and through partial combustion with oxygen in a preburner upstream of the reactor itself.

OPERATING CONDITIONS(90)

Pressure, psig:	1000
Temperature, °F:	1000 - 2000
Hydrogen/coal, SCF/lb:	38 - 114
Space Velocity/Residence Time:	
Residence time mixture, milliseconds	50 - 300
(particle velocity, ft/s)	10 - 30
Coal weight hourly space velocity (WHSV), $lb/h/ft^3$	23,000 - 3,800
Coal mass flux, $lb/ft^2/h$	up to 33,600
Conversions:	
Coal converted, wt% Carbon	25 - 55

Reaction Variables:(91)

- Overall carbon conversion increases with temperature up to a maximum of about 55% at 1800°F to 2000°F.
- Carbon conversion to gas increases only slowly with temperature.
- Adding oxygen directly to the reactor rather than into the hydrogen feed drastically increases gas production.
- Varying the reactor residence time from 35 to 150 milliseconds produced no significant change in yields.

Coals Processed:

High volatile bituminous coals, Western Kentucky.

PRODUCTS (90)

Coal:	(Expt. 15)
Coal moisture, wt%:	
To Unit	2.46
Coal analysis (dry):	
Proximate, wt%:	
Ash	10.19
Volatile matter	37.77
Fixed carbon	52.04
Ultimate, wt%:	
Carbon	70.32
Hydrogen	5.16
Nitrogen	1.41
Sulfur	3.98
Oxygen (Diff.)	9.19
Ash	9.94

Yield:

excluding hydrogen manufacture and utilities

	MAF Coal	Carbon
Gas, wt%	12.9	11.9
Oil, wt% (Diff.)	45.6	42.5
Char, wt%	41.5	45.6

Characteristics:

Gas - C_1/C_2: 5.65

Oil:

High pour point oil (100°F). Approximately 40% of oil boils below 1000°F. (Oil obtained by benzene extraction of collected tars and char.)

Char:

Ultimate analysis, dry wt%:

Carbon	71.32
Hydrogen	3.21
Nitrogen	1.13
Sulfur	3.34
Oxygen (Diff.)	3.97
Ash	17.03

INTENDED PRODUCT USE/MARKETS

Hydrocarbon liquids suitable for conversion to fuels or for use as chemical feedstocks.

UNIQUE FEATURES OF PROCESS

Main features of the process are: Rapid heating of the coal to reaction temperature by intimate mixing with hot hydrogen, noncatalytic coal hydropyrolysis for 10 to 1000 milliseconds, and reaction product quench. Oil yield up to 45 wt% MAF coal.

PROCESS STATUS

Development Status:

- 1/4-TPH reactor test system operated since July 1976.
- 1-TPH reacter test system to be completed late 1976.

Patents: U.S. patent applied for.

Location of Development Work:

Rocketdyne, Canoga Park, California

History:

Cold-flow-transport and mixing test began August 1975. High levels of mixing efficiency were obtained with both the 4-on-1 and concentric-tube type injectors.

1/4-TPH reactor facility preparation and testing began April 1976. Tests completed October 1976. A 1-TPH reactor facility has been commissioned. A 10-TPH reactor facility is planned.

Problem Areas:

- Reactor tube wall temperatures must be maintained above about 1300°F to avoid char adhesion to the tube walls.
- Material balance not yet closed due to suspected loss of material being carried out in the condensed phase with the product gas.
- Run lengths have been of insufficient duration (2 to 240 seconds) to establish process reliability and equipment corrosion resistance.

REFERENCES

90. Rockwell International, Rocketdyne Division, "Partial Liquefaction of Coal by Direct Hydrogenation (No. FE-2044-11)," *Annual Report for the Period August 1975 - July 1976*, January 1977.

91. Rockwell International, Rocketdyne Division, "Partial Liquefaction of Coal by Direct Hydrogenation," *Fifth Quarterly Progress Report; July - September 1976*, December 1976.

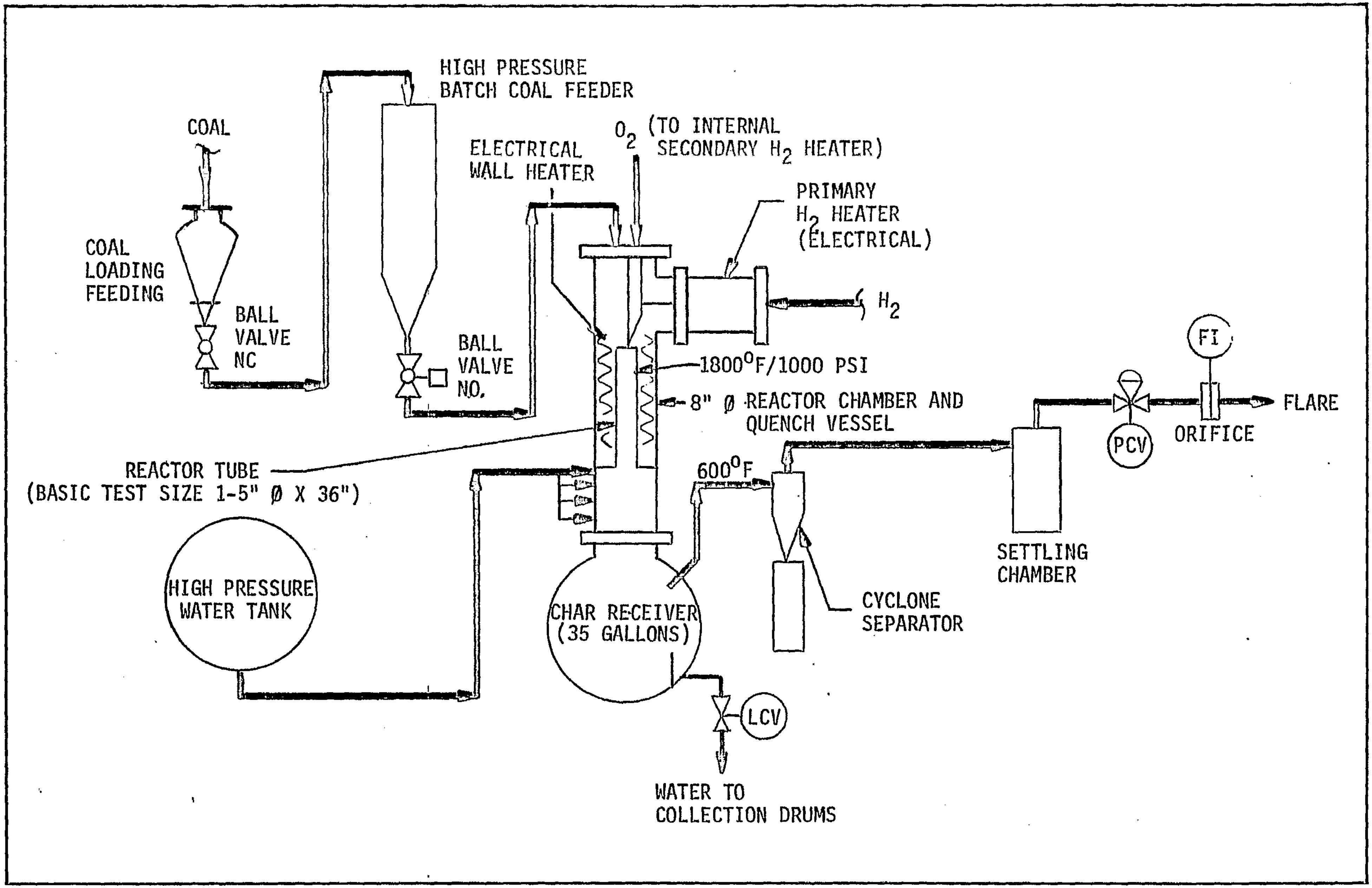

Figure 1 - Flow Diagram
Rockwell 1/4 TPH Reactor Test System (91)

PROCESS INFORMATION EXTRACT

PROCESS 3.1.1	Flame Sprayed Catalyst (FSC)
Process Type:	Indirect, Fischer-Tropsch
Main Products:	Hydrocarbons in the gasoline and diesel range
Development Status:	Conceptual/Pilot Plant
PROCESS DEVELOPERS	R.M. Parsons Company and Pittsburgh Energy Research Center (PERC)
PROCESS SPONSOR	DOE

DESCRIPTION OF PROCESS (92),(93),(94)

The Fischer-Tropsch coal liquefaction process entails two major steps:

(1) Production of synthesis gas (CO + H_2) from coal.

(2) Catalytic reaction of the synthesis gas to form hydrocarbon gases, liquids, waxes, and oxygenated compounds by Fischer-Tropsch synthesis.

In the FSC process, the synthesis takes place in a plate reactor using a flame sprayed iron catalyst. The plate reactor is a horizontal finned-tube heat exchanger, with the catalyst being flame sprayed onto the finned surface. Boiler water on the inside of the tubes removes the heat of reaction. Fresh feed gas is combined with recycled product gas. The combined gas flows across the catalyst sprayed fins and support tubes on the shell side of the reactor. The heat of reaction is used to generate 1300 psig steam in the reactor tubes. The reacted gas is passed through heat exchangers to a hot product separator where it is scrubbed with an alkaline solution to recover oxygenated compounds. Gas from this separator is then treated in a CO_2 Removal Unit to prevent a buildup of CO_2 in the recycle gas. Further gas cooling and scrubbing are used to separate product gas and liquids. Part of the gas is recycled to the reactor as described above.

OPERATING CONDITIONS(92)

Pressure, psig	400
Temperature, °F	600
Recycle/Fresh feed, v/v	1.43
Space velocity/residence time:	
Fresh feed, SCFM/SF catalyst	10
Total feed	24
Conversions:	
Overall, $(CO + H_2)$ %	79.8
H_2 %	73.7
CO %	88.7
Per pass, $(CO + H_2)$	38.7
Feed:	Syngas
Fresh feed H_2/CO molar ratio:	1.45
Catalyst:	Alkalized reduced flame sprayed Fe_3O_4

Reaction Variables:

- Pressure: Rate of reaction increases with pressure. Higher pressures favor the formation of alcohols and saturated hydrocarbons. Formation of iron carbonyl may limit application of iron catalysts to 450 psig maximum.

- Temperature: Temperature has a great influence on product selectivity and conversion per pass. Cracking reactions reduce liquid yields above 645°F.

- Feed H_2/CO ratio: Reducing feed H_2/CO ratio increases hydrocarbon olefin content.

- Residence time: Short contact times favor the formation of olefins and alcohols.

Coals Processed:

Dependent upon suitability of coal for gasification step.

PRODUCTS(92)

Yield

Lb hydrocarbons/1000 SCF ($CO + H_2$) converted	11.7

Characteristics:

Product distribution:

Component	Product	
	wt %	
C_1	11.4	
C_2	1.5	
C_2	5.7	
C_3 =	1.0	
C_3	3.4	
C_4=	2.9	
C_4	8.4	
C_5-C_{12}	47.5	20 to 30 % olefins
C_{13}-C_{18}	4.8	
C_{19}+	7.4	
Nonacid oxygenates	5.2	
Acids	0.5	
	100.0	

Diesel Oil Fraction

Centane N°	60
Pour point, °F	10

All products are sulfur, nitrogen, and ash free.

INTENDED PRODUCT USE/MARKET(92)

(1) Butanes: Mixed butane/butylene stream, containing about 83 volume percent butanes.

(2) Naphtha: Light naphtha (96 - 185°F); Heavy naphtha (186 - 300°F)

Light naphtha, consisting essentially of C_5/C_6 hydrocarbons, can be refined to gasoline blending stock.

Heavy naphtha is excellent feedstock for chemicals production.

(3) Diesel Fuel Oil: Diesel fuel cut (301–637°F) meets commercial diesel fuel and gas turbine fuel specifications.

(4) Fuel Oil: Fuel oil is a waxy, high-pour, sulfur-free product, meeting No. 4 light (ASTM D936) specifications.

PROCESS EFFICIENCY(92)

Thermal Efficiency:		
Product only %		74.5
Overall, including net utilities, % (System power requirements at 15,000 Btu/hp)		75.7
Utilities per 10^6 SCF ($CO + H_2$) converted		
Steam		
1320 psig (generated)	MMBtu	70.6
135 psig	MMBtu	15.1
50 psig	MMBtu	33.6
Power, kWh		833
Cooling water, gal		187
Hydrogen consumption ($CO + H_2$), SCF/lb C_4^+		111
Catalyst consumption:		
catalyst life, years		1
pound hydrocarbon per pound catalyst		2460

UNIQUE FEATURES OF PROCESS

Sprayed plate reactor with direct generation of 1300 psig steam in the reactor plate support tubes.

PROCESS STATUS

Development Status:

Conceptual reactor design only. Flame sprayed catalyst tested in PDU reactor.

Patents: None applied for

Location of Development:

PERC Bructon laboratories, Pennsylvania

History:

Flame sprayed iron catalyst was developed by PERC (formally the Pittsburgh Coal Research Center, Bureau of Mines) for the Hot Gas Recycle process, and first reported in 1965. Tests of the catalyst were made in a 3 in. diameter tubular reactor, removing the heat of reaction by a large gas recycle and external heat exchange. Bench scale tests with a 3/4 in. flame sprayed catalyst pipe, fitted over a 3/4 in. OD cooling tube, first reported by PERC in 1975.

Problem Areas:

Confirmation of assumed yield data required by PDU tests. Catalyst life predicted to be 1 year must be confirmed by laboratory tests. Catalyst spalling from the plate surface may reduce effective catalyst life.

REFERENCES

92. O'Hara, J.B. et al, *Fischer-Tropsch Complex, Concept Design/Economic Analysis, Oil and SNG Production, R&D Report No. 114, Interim Report No. 3 (FE-1775-7),* The Ralph M. Parsons Company Distribution Category No. UC-89.

93. Forney, A.J., *Recent Catalyst Developments in Hot Gas Recycle Process,* U.S. Department of the Interior, Bureau of Mines Report of Investigation No. 6609.

94. Forney, A.J. et al, *The Fischer-Tropsch Process: Gasoline from Coal,* Pittsburgh Energy Research Center, about 1975.

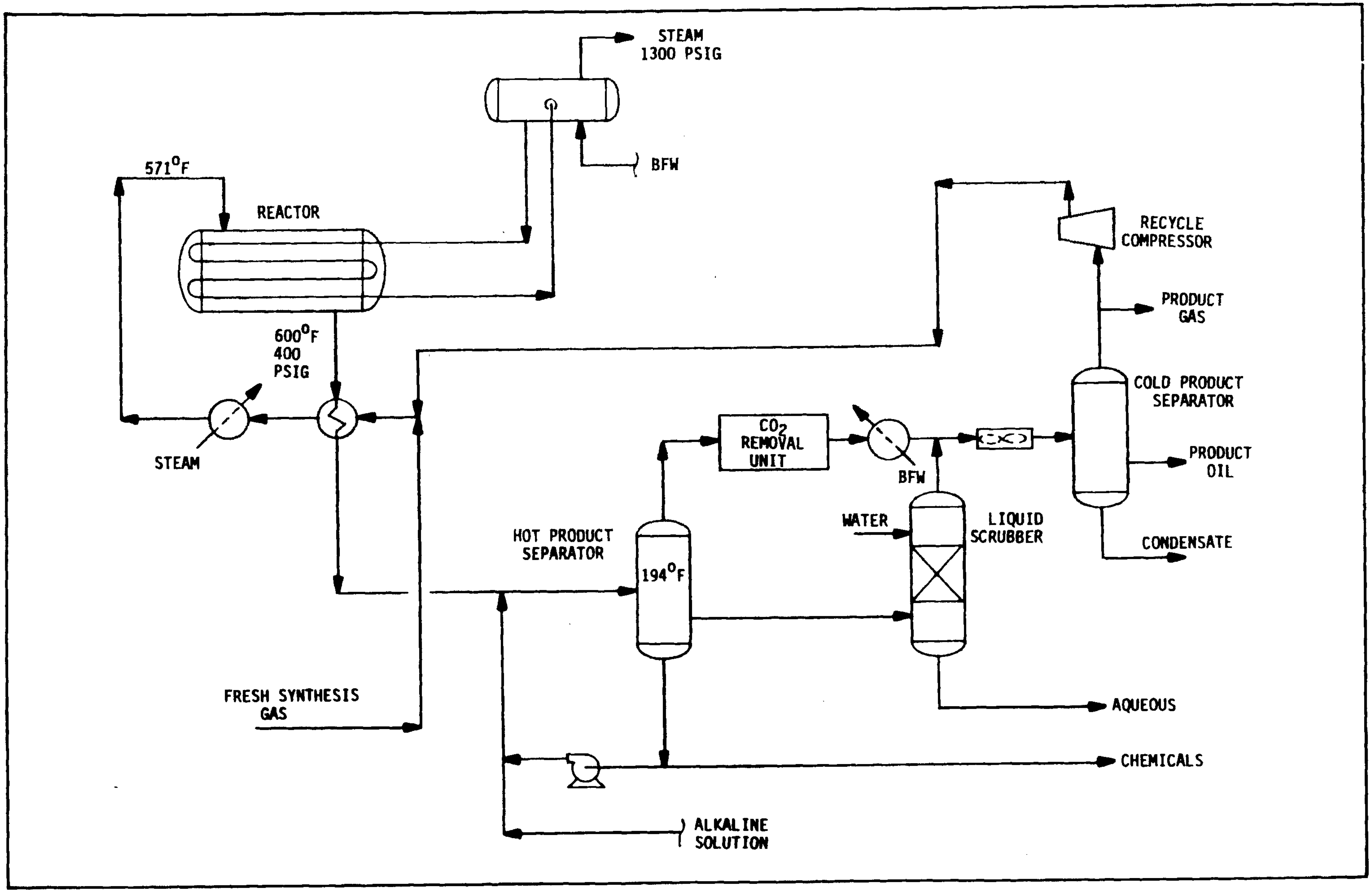

Figure 1 - Flow Diagram
Parsons FSC Fischer-Tropsch Process

PROCESS INFORMATION EXTRACT

PROCESS 3.1.2 ARGE (Arbeit Germeinschaft, Ruhrchemie/Lurgi)

Process Type: Indirect, Fischer-Tropsch

Main Products: Hydrocarbons in the diesel and wax range

Development Status: Commercial

PROCESS DEVELOPER
Ruhrchemie, Oberhausen-Holten
Lurgi, Frankfurt/Main
Federal Republic of Germany

PROCESS SPONSOR Lurgi-Ruhrchemie

PROCESS DESCRIPTION(95) (Refer to Figure 1)

The Fischer-Tropsch coal liquefaction process entails two major steps:

(1) Production of synthesis gas ($CO+H_2$) from coal.

(2) Catalytic reaction of the synthesis gas to form hydrocarbon gases, liquids, waxes, and oxygenated compounds by Fischer-Tropsch synthesis.

In the Arge process the synthesis takes place in a fixed-bed reactor using a precipitated iron catalyst.

The fixed-bed reactor is a vertical-tube heat exchanger with catalyst placed inside the tube and boiling water on the outside. Fresh feed gas is combined with recycled product gas. The combined gas feed flows downward through the catalyst tubes, and the heat of reaction used to generate steam up to 250 psig in the reactor shell. The reacted gas passes through a wax separator, heat exchangers, and condensers. The reactor wax is withdrawn from the reactor bottom and the wax separator. A caustic solution is added to the reactor gas after it passes through the heat exchangers to recover oxygenated compounds. Further gas cooling and separation are used to recover product gas and liquids. Part of the gas is recycled to the reactor as described above.

OPERATING CONDITIONS(95),(96)

Pressure, psig	300	
Temperature, °F	430-490	
Recycle/Fresh feed, v/v	2.2-2.5	
Space Velocity		
Fresh feed, h^{-1}	500-550	
Total feed, h^{-1}	1600-1900	
Feed	Syngas	
*Fresh feed H_2/CO molar ratio =	1.8667	
Catalyst		
Alkaline, precipitated iron catalyst, 20 - 25% reduced.		
Conversions	(96)	(97)
Overall*, $(CO+H_2)$ %	61.0	67.6
H_2	59.5	66.1
CO	63.8	70.4

Reaction Variables:

- Pressure: Rate of reaction increases with pressure. High pressures favor the formation of alcohols and saturated hydrocarbons. Formation of iron carbonyl may limit application of iron carbonyls to 450 psi-maximum.
- Temperature: Temperature has a great influence on product selectivity and conversion per pass. Cracking reactions reduce liquid yields above about 645°F.
- Feed H_2/CO ratio: Reducing H_2/CO ratio increases hydrocarbon olefin content.
- Residence time: Short contact times favor the formation of olefins and alcohols.

Coals Processed: Dependent upon suitability of coal for gasification step.

PRODUCTS

Yield:(97)

lb C_3^+ Hydrocarbons/1000 SCF fresh feed	5.1
lb C_1^+ Hydrocarbons and oxygenates/1000 SCF ($CO+H_2$) converted	11.3

Characteristics:

Product distribution(99)

Component	Product % wt	Olefin % wt	Degree of Branching Tertiary C Atoms per 1000 C Atoms
Methane	8.6		
C_2 hydrocarbons	3.3	20	
C_3 hydrocarbons	5.9	62	
C_4 hydrocarbons	4.8	51	10
C_5-C_{11} hydrocarbons	23.8	50	12
Light oil	14.7	40	5
Heavy oil + slack wax	9.1		
Paraffin wax	26.4		5

Fraction Analysis, vol%(95),(98)

	C_5-C_{12}	C_{13}-C_{18}
Paraffin	53	65
Olefin	40	28
Aromatics	0	0
Alcohols	6	6
Carbonyls	1	1
	100	100
% n Paraffins	95	93

Solid hydrocarbons are predominantly those of the crystalline paraffin type.

Gasoline fraction leaded RON	85
Diesel oil:	
Cetane No.	90
Pour point, °F	23
Ignition point, °F	180

All products are sulfur, nitrogen, and ash free.

INTENDED PRODUCT USE/MARKET(95),(96)

(1) Propane/Butane
Liquid petroleum gas

(2) Propylene/Butylene
Polymerized or alkylated to gasoline

(3) Gasoline blending stock
Primary gasoline leaded RON is about 85

(4) C_{11}-C_{15} n Olefins: Linear olefins are excellent feedstock for the oxo synthesis, and for the production of biologically soft detergents, and a wide range of high viscosity stable lubricating oils.

(5) Light furnace oil

(6) Waxy oil/cracking stock

(7) Waxes: Wax fractionation, thermal cracking, and solvent cracking enable a wide range of wax products to be obtained, varying from soft waxes to emulsifiable hard waxes.

(8) Oxygenates: Methanol, ethanol, propanol, acetone, MEK, and higher alcohols fraction.

PROCESS EFFICIENCY

Thermal Efficiency	
Product only, %	~77

Hydrogen consumption	
(CO+H_2), SCF/lb C_4^+	108
Catalyst consumption*	
Catalyst life,(95) months	6
Pound hydrocarbon per pound Catalyst,(95),(97)	275

UNIQUE FEATURES OF PROCESS

Packed tube reactor, with direct generation of 250 psig steam in the reactor shell. Pelletized precipitated iron catalyst, with promotors.

PROCESS STATUS

Development Status:

Five 550-BPSD hydrocarbon units have been commercially operated for 20 years by SASOL.

History:

Fischer-Tropsch synthesis over iron catalysts first reported 1923. Fischer-Tropsch plants operating in Germany 1938-1944 produced about 16,000-BPSD oil products using cobalt catalysts. About 25% of this was produced by the medium pressure processes. The Arge process developed from the Ruhrchemie medium pressure Fischer-Tropsch synthesis used during this period. Arge process put into commercial operation by SASOL in 1955 using a precipitated iron catalyst.

Problem Areas:

No problems have been reported. SASOL plants started up with only minor problems.

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*Catalyst life may be doubled by use of daily catalyst diesel washes.(100)

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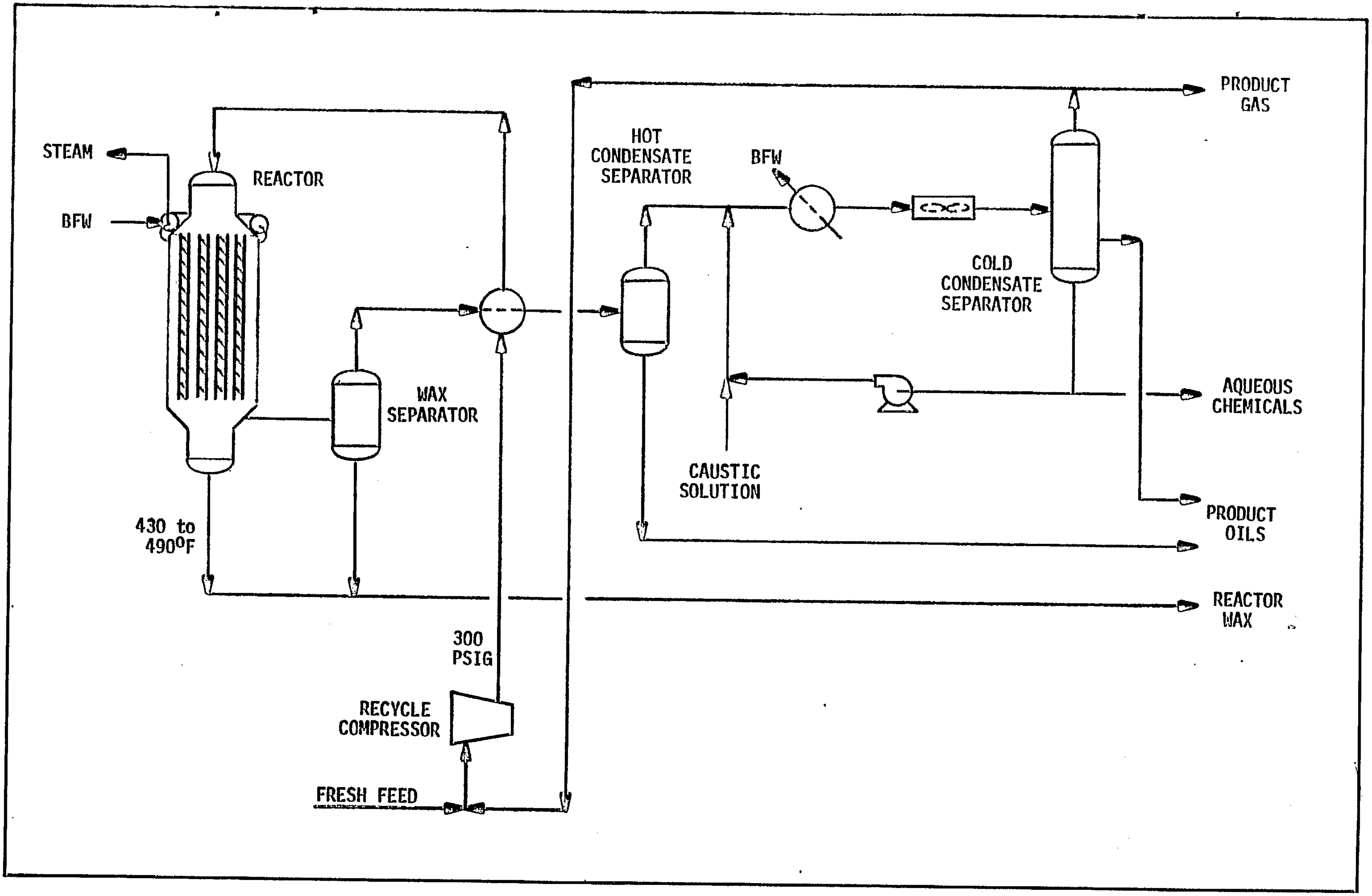

Figure 1 - Flow Diagram
ARGE Fischer-Tropsch Process

PROCESS INFORMATION EXTRACT

PROCESS 3.1.3 SYNTHOL

Process Type: Indirect, Fischer-Tropsch.

Main Products: Hydrocarbons in the gasoline and diesel range.

Development Status: Commercial

PROCESS DEVELOPER African Coal, Oil and Gas Corporation Ltd. (SASOL), Republic of South Africa.

PROCESS SPONSOR SASOL, Sasolburg, South Africa
Government of South Africa

DESCRIPTION OF PROCESS(95),(97),(101),(102)

The Fischer-Tropsch and liquefaction process entails two major steps;

(1) Production of synthesis gas (CO + H_2) from coal, coke, etc.

(2) Catalytic reaction of this synthesis gas to form hydrocarbon gases, liquids, waxes, and oxygenated compounds by Fischer-Tropsch synthesis.

In the Synthol process (Figure 1) the synthesis takes place in an entrained fluid-bed reactor using an iron catalyst. Fresh feed gas is combined with recycled product gas. Catalyst from the settling hopper is entrained into the combined gas stream as it enters the reactor. The gas/catalyst mixture flows upward through the reactor. Oil passing through cooling coils inside the reactor removes part of the heat of reaction. The circulating oil stream is used to generate steam up to 450 psig pressure in a waste heat boiler. Catalyst is separated in the catalyst settling hopper by gravity settling and by cyclones. The reacted gas is scrubbed by a circulating oil stream to remove catalyst fines, which are returned as an oil slurry to the reactor, and to cool the gas. Further gas cooling and scrubbing are used to separate product gas and liquids. Part of the gas is recycled to the reactor as described above.

OPERATING CONDITIONS(95),(96),(97)

Pressure, psig	300	
Temperature, °F	600	
Recycle/Fresh feed v/v	2	
Space Velocity/Residence time:		
Fresh feed, kg catalyst/Nm^3	100	
Feed	Syngas	Syngas
*Fresh feed H_2/CO molar ratio =	2.40	2.40
Conversions	(95)	(96)
Overall* ($CO + H_2$) %	78.3	79.1
H_2 %	70.4	71.8
CO %	97.2	97.0
($CO + CO_2$) %	N.A.	83.8

Catalyst:

Alkalized reduced metallic iron prepared from mill-scale, 75% <150 microns, 25% <49 microns

Reaction Variables:

- Pressure: Rate of reaction increases with pressure. Higher pressures favor the formation of alcohols and saturated hydrocarbons. Formation of iron carbonyl may limit application of iron catalysts to 450 psig maximum.
- Temperature: Temperature has a great influence on product selectivity and conversion per pass. Cracking reactions reduce liquid yields above about 645°F.
- Feed H_2/CO ratio: Reducing feed H_2/CO ratio increases hydrocarbon olefin content.
- Residence time: Short contact times favors the formation of olefins and alcohols.

- Coals Processed: Dependent upon suitability of coal for gasification step.

PRODUCTS

Yield(97)

lbC_3^+ hydrocarbons/1,000 SCF fresh feed	6.5
lbC_1^+ hydrocarbons/1,000 SCF (CO + H_2) converted and oxygenates	12.6

Characteristics:

Product distribution(99)

Component	Product % wt	Olefin % wt	Degree of Branching Tertiary C atoms per 1000 C atoms
Methane	13.8		
C_2 hydrocarbons	9.8	42	
C_3 hydrocarbons	15.1	78	
C_4 hydrocarbons	12.4	75	27
C_5-C_{11} hydrocarbons	31.9	70	55
Light Oil	2.5	60	50
Heavy oil & slack wax	2.5		
Paraffin wax	-		

Fraction Analysis, vol %(95),(98)

	C_5 - C_{10}	C_{11} - C_{14}
Paraffin	13	15
Olefin	70	60
Aromatics	5	15
Alcohols	6	5
Carbonyls	6	5
	100	100

%n Paraffins	55	60

Solid hydrocarbons contain up to 35% aromatics.

Gasoline fraction (86 to 428°F) RON = 55

All products are sulfur, nitrogen and ash free.

INTENDED PRODUCT USE/MARKET(95),(96)

(1) Propane/Butane
Liquid petroleum gas

(2) Propylene/Butylene
Polymerized or alkylated to gasoline.

(3) Gasoline blending stock: Primary gasoline (boiling range 86-428°F) has a RON of 55, which after refining on alumina rilicate can be increased to about 75 RON.

(4) Light furnace oil

(5) Heavy oil/cracking stock

(6) Oxygenates: Methanol, ethanol, propanol, butanol, pentanol, acetone, MEK, and higher alcohols fraction

PROCESS EFFICIENCY

Thermal Efficiency		
Product only, (Reference 101)	%	79.3
Hydrogen consumption		
$(CO + H_2)$, SCF/#C_4^+		130
Catalyst consumption:		
catalyst life	days(97)	50
pound hydrocarbon per pound catalyst,(96), (97)		110

UNIQUE FEATURES OF PROCESS

Entrained fluid-bed reactor, with hot oil cooling coils located in entrained bed. Steam up to 450-psig generated from reactor cooling circuit. Large catalyst use requires installation of catalyst manufacturing facilities at plant.

PROCESS STATUS

Development Status:

Twenty years of commercial operation by SASOL with three plants, each of 2000-BPSD hydrocarbon capacity.

History:

Entrained fluid-bed process originally developed by Pullman Kellog (then located in Jersey City, USA). Rights to the American variation of the Fischer-Tropsch process procured by Anglo Vaal of South Africa in 1943, and subsequently by the South African government in 1950.

Development since 1950 has been by the South African Coal, Oil and Gas Corporation Ltd. (SASOL) who first put the process into commercial operation in 1955. Engineering is currently underway (1976) by SASOL for the construction of a second Fischer-Tropsch complex using ten Synthol reactors with a total capacity of 50,000-BPSD.

Problem Areas:

No problems have been reported after initial process and mechanical development problems were solved by SASOL in 1950s.

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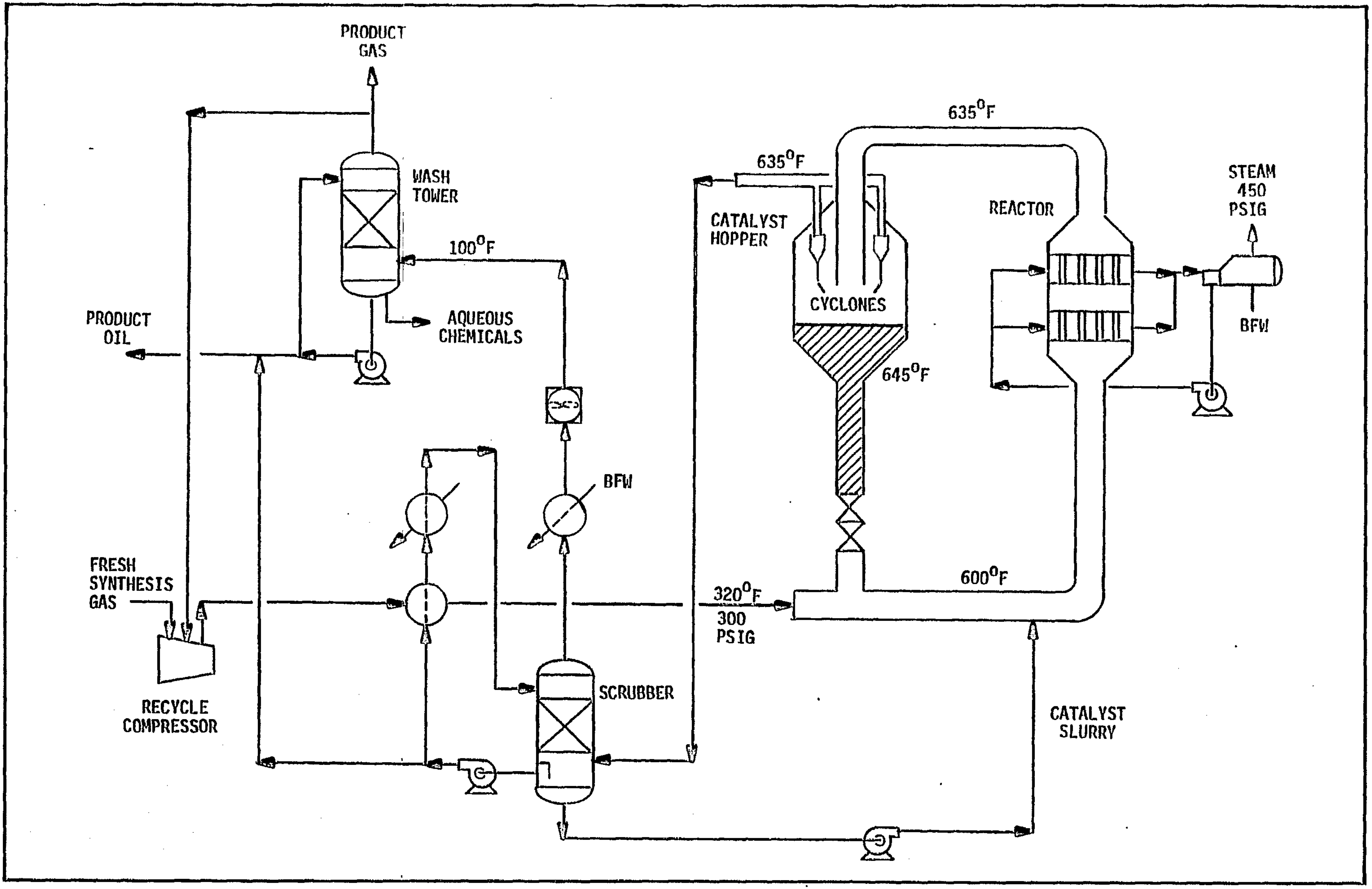

Figure 1 - Flow Diagram
SYNTHOL Fischer-Tropsch Process

PROCESS INFORMATION EXTRACT

PROCESS 3.2.1	High Pressure Methanol Process
Process Type:	Indirect, synthesis to methanol
Main Products:	Methanol
Development Status:	Commercial

PROCESS DEVELOPER

*

PROCESS SPONSOR

*

*The following is typical of the H. P. Methanol Processes offered by numerous developers. See Process Status.

PROCESS DESCRIPTION (103), (104), (105)

The methanol coal liquefaction process entails two major steps.

(1) Production of ($CO+H_2$) synthesis gas from coal.

(2) Conversion of synthesis gas to methanol. (Figure 1)

There are various types of HP Methanol reactors available:
TVA type reactor with heat exchanger tubes in the catalyst bed, or multiple adiabatic beds with quench gas mixing between beds. Some other designs use combinations of adiabatic and non-adiabatic beds, or use adiabatic beds with external cooling of the reaction mixture between beds.

The quench reactor uses four or five beds of catalyst with cooling between beds being achieved by the injection of cold synthesis gas. Quench gas is also used to prevent hot CO-rich gas from contacting the walls of the reactor pressure vessel. Fresh synthesis gas, after removal of iron carbonyl in an activated carbon adsorber, is combined with recycle gas. Part of the combined feed is preheated to reaction temperature by exchange against the reactor effluent. The unheated portion of the feed is fed as a quench gas to the reactor. The reactor effluent is cooled first by heat exchange against the reactor feed and then with air or water. The condensed crude methanol is separated from the gas, the gas being recycled to the reactor. Inerts are removed by a continuous purge of recycle gas.

The crude methanol contains water and low and high boiling impurities.

OPERATING CONDITIONS(103), (104), (105)

Pressure, atm:	300 - 375
Temperature, °F:	625 - 735
Recycle/Fresh Feed:	about 6.5
Space Velocity/Residence Time:	
Fresh feed, h^{-1}	4,000
Total feed, h^{-1}	30,000
Feed	
Fresh Feed $\frac{(H_2 - CO_2)}{(CO + CO_2)}$ Molar Ratio	Syngas ≥ 2
Conversions:	
Overall, $(CO + CO_2)$ %	95–96
Per pass, $(CO + CO_2)$ %	29–30

Catalyst:

High temperature/high pressure active zinc oxide-chromic oxide formulation.

None

Reaction Variables(103), (105)

- Pressure: The equilibrium yield of methanol increases with pressure to the second power.

- H_2/CO ratio: Highest methanol equilibrium content is obtained for a stoichiometric H_2/CO mixture. However, increased H_2/CO ratio increases equilibrium CO conversion and reaction rate. Reactor combined feed contains up to twice the stoichiometric ratio.

- CO/CO_2: Maximum molar ratio about 10:1.

Coal Processed:

Dependent upon suitability of coal for gasification step.

PRODUCTS(106), (107)

Yield:

Water-free crude methanol/1000 SCF ($CO + H_2$) converted = 28.1

Characteristics:

Crude methanol is sulfur, nitrogen, and ash free. Water content of crude methanol is 2.5 to 14% wt (typical) depending on synthesis gas composition. High CO_2 feeds result in high water content crude methanol mixes.

Organic impurities in crude methanol:

Impurity(108)	ppm
Dimethylether	10,000 w/v
Methyl	1,300 v/v
Ketones	450 v/v
Ethanol	3,000 v/v
Higher alcohols	11,000 v/v

Methanol Properties (dry)	
Specific gravity, 20/4	0.792
Higher Heating Value	
(Btu/lb)	9,760
(Btu/gal)	64,810
Latent heat of vaporization at bp, Btu/lb	502

Octane Rating	
RON	106
MON	92
Boiling point, °F	148
Freezing point, °F	-144
Flash point, °F	52

Toxicity:

Fatal dose	1 to 4 oz
Fatal vapor concentration	50,000 ppm for 1 to 2 h

Atmospheric concentrations should not exceed 200 ppm.

INTENDED PRODUCT USE/MARKETS(106),(107)

(1) Boiler Fuel: Methanol can be burned as a clean boiler fuel with only slight modification to existing boilers. Lower (NO_X) emissions are claimed.

(2) Internal Combustion Engine Fuel: Existing gasoline fueled internal combustion engines can be converted to use pure methanol by decreasing the air-to-fuel ratio, recycling more heat from the exhaust to the carburetor, and providing for cold starts. Methanol gives 5 to 10% more power than gasoline, but twice as much is consumed.

(3) Gasoline Extender: Methanol can be blended up to 15% by volume in gasoline. Blended fuels have cold start problems and some engine throttle response problems due to lean carburetion requirements of the blend. Methanol-gasoline blends undergo phase separation in the presence of very small concentrations of water causing fuel stability problems. Engines using methanol fuel blends have lower (NO_X) emissions than when using gasoline.

(4) Industrial Gas Turbine Fuel: In turbine engine combustion methanol generates lower levels of (NO_X) since both peak temperatures and durations are below those experienced with kerosine.

Blade maintenance is estimated to be one-third of that required when methane is burned.

PROCESS EFFICIENCY(109)

Thermal Efficiency:	
Product only including purge gas %	86.2
Overall, including net utilities, %	64.3
Utilities, per ton methanol:	
Heat recovered, MMBtu	1.09
Power, kWh:	
Compressor (feed @ 275 psig)	425
Recycle portion	39
Miscellaneous	8
Cooling Water (30°F rise) gal:	2500
Hydrogen Consumption	
($CO + H_2$), SCF/lb C_1OH:	35.5
Catalyst Consumption:	
Catalyst life, year	3

UNIQUE FEATURES OF PROCESS

High temperature zinc/chrome oxide catalyst, and cold wall reactor design.

PROCESS STATUS

Development Status:

Commercial plants up to 2000 tons per day capacity installed.

Patents: Numerous

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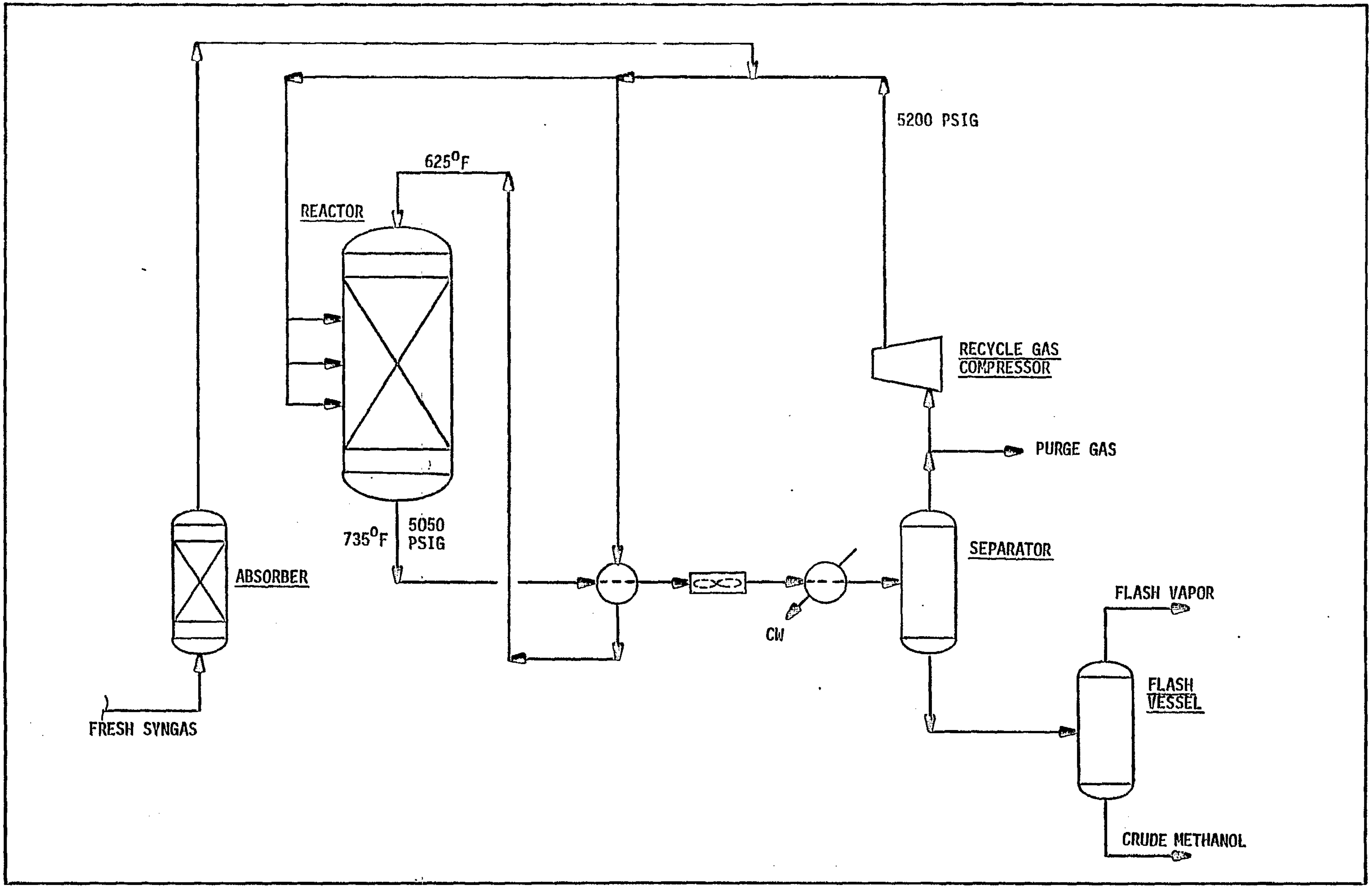

Figure 1 - Flow Diagram
HP Methanol Process

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PROCESS INFORMATION EXTRACT

PROCESS 3.2.2	ICI LP/LT Methanol
Process Type:	Indirect, synthesis to methanol
Main Products:	Methanol
Development Status:	Commercial
PROCESS DEVELOPER	Imperial Chemical Industries, Ltd. (ICI) Billingham, Teeside, UK
PROCESS SPONSOR	Imperial Chemical Industries, Ltd.

PROCESS DESCRIPTION(108),(109),(111),(113)

The methanol coal liquefaction process entails two major steps.

(1) Production of $(CO+H_2)$ synthesis gas from coal.

(2) Conversion of synthesis gas to methanol.

In the ICI low pressure process, conversion is carried out in a fixed-bed reactor using cold gas injection at several levels for temperature control (Figure 1).

Fresh feed gas is combined with recycled tail gas. Part of the combined feed is preheated to reaction temperature by exchange against the reactor effluent and flows downward through the catalyst bed. The unheated portion of the feed is fed as quench gas to the reactor. The reactor effluent is cooled by heat exchange against the reactor feed and boiler feed water. Further gas cooling and separation are used to recover unconverted gas from the crude methanol. Part of the unconverted gas is purged to prevent the accumulation of inerts in the synthesis loop, the remainder recycled to the reactor as previously described. The crude methanol contains water and low and high boiling impurities.

OPERATING CONDITIONS(111)

Pressure, atm:	50	100
Temperature, °F:	480-520	480-520
Recycle/Fresh feed, v/v:	7.8	5.1
Space Velocity/Residence Time:		
Fresh feed, h^{-1}	275	1000
Total feed, h^{-1}	2500	6000
Feed	Syngas	
Fresh Feed $\frac{(H_2 - CO_2)}{(CO + CO_2)}$ Molar Ratio	≥ 2	
Conversions*:		
Overall, $(CO+H_2)$ %	82	95

*dependent on inerts content

Catalyst:

Low temperature/low pressure active copper-zinc formulation

Reaction Variables:(103)

- Pressure: The equilibrium yield of methanol increases with pressure to the second power. Reaction rate increases with increased pressure. Maximum operating pressure for copper based catalyst is 150 atm.
- Temperature: The equilibrium yield of methanol decreases with increasing temperature. Maximum catalyst operating temperature is 570°F.
- H_2/CO Ratio: Highest methanol equilibrium content is obtained for a stoichiometric H_2/CO mixture. However, increased H_2/CO ratio increases equilibrium CO conversion. Reactor combined feed contains up to twice the stoichiometric H_2/CO ratio.
- CO/CO_2: Molar ratio may be varied in a wide range of 20:1 to 1:2. Preferred ratio is in the range of 3:2 to 4:3.(103)

Coals Processed:

Dependent upon suitability of coal for gasification step.

PRODUCTS

Yield:

lb water-free crude methanol/1000 SCF ($CO+H_2$) converted = 28.1

Characteristics:

Crude methanol is sulfur, nitrogen, and ash fee. Water content of crude methanol is 2.5 to 14% wt (typical) depending on synthesis gas composition. High CO_2 feeds result in high water content crude methanol mixes.

Organic impurities in crude methanol:

Impurity(108)	ppm
Dimethylether	150 w/v
Methyl formate	600 V/v
Ketones	80 V/v
Ethanol	625 V/v
Higher alcohols	500 V/v

Methanol properties (dry):

Specific gravity, 20/4	0.792
Higher Heating Value,	
(Btu/lb)	9,760
(Btu/gal)	64,810
Latent heat of vaporization: at bp, Btu/lb	502
Octane rating:	
RON	106
MON	92
Boiling point, °F	148
Freezing point, °F	-144
Flash point, °F	52

Toxicity:

Fatal dose	1 to 4 oz.
Fatal vapor concentration	50,000 ppm for 1 to 2 h

Atmospheric concentrations should not exceed 200 ppm.

INTENDED PRODUCT USE/MARKET(106),(107)

(1) Boiler Fuel: Methanol can be burned as a clean, boiler fuel with only slight modification to existing boilers. Lower (NO_x) emissions are claimed.

(2) Internal Combustion Engine Fuel: Existing gasoline-fueled internal combustion engines can be converted to use pure methanol by decreasing the air to fuel ratio, recycling more heat from the exhaust to the carburetor, and providing for cold starts. Methanol gives 5 to 10% more power than gasoline, but twice as much is consumed.

(3) Gasoline Extender: Methanol can be blended up to 15% by volume in gasoline. Blended fuels have cold start problems and some engine throttle response problems due to lean carburetion requirements of the blend. Methanol-gasoline blends undergo phase separation in the presence of very small concentrations of water causing fuel stability problems. Engines using methanol fuel blends have lower NO_x emissions than when using gasoline.

(4) Industrial Gas Turbine Fuel: In turbine engine combustion methanol generates lower levels of NO_x since both peak temperatures and durations are below those experienced with kerosine. Blade maintenance is estimated to be one-third of that required when methane is burned.

PROCESS EFFICIENCY(111),(112)

	Pressure (atm)	
Thermal Efficiency:	50	100
Product only including purge gas, %	88.1	86.2
Overall, including net utilities	74.6	70.5

	Pressure (atm)	
	50	100
Utilities, per ton methanol (dry basis):		
Recovered heat as preheated BFW, MMBtu	1.17	1.17
Power, kWh:		
Compressor	187.6	270.6
Circulator	115.6	65.5
Miscellaneous	7.7	7.7
Cooling Water (30°F Rise), gal	2500	2500
Hydrogen Consumption		
(CO + H_2), SCF/lb C_1OH	35.5	35.5
Catalyst Consumption		
Catalyst life, yrs.	3	2

UNIQUE FEATURES OF PROCESS

Main features of the process are: the low temperature active copper-based methanol catalyst, special reactor design, and recovery of synthesis reaction heat as boiler feed water preheat.

The reactor is of a novel design consisting of a hot wall pressure containing a single bed of catalyst. Quench gas is introduced into the bed at three levels through specially designed spargers. The catalyst can flow between these spargers for discharge from the base of the reactor.

PROCESS STATUS

Development Status:

Commercial operations first started in 1966. The capacity of ICI LP/LT plants in operation range from 150 to 1800 TPD. Over twenty plants have been constructed.

ICI Patents

U.S. 3,326,956
3,923,694
3,950,369

Process widely licensed.

History:

ICI LP/LT methanol catalyst development work started about 1959. First plant using new catalyst started up late 1966. U.S. Patent granted 1967. ICI LP/LT Methanol Process made available to manufacturing companies by first process licensees November 1967.

Original version of process operated at 50 atm pressure. A variant of the low-pressure copper catalyst, that is more resistant of deactivation, permits operation at 100 atm. This revised version put into commercial operation, August 1972.

Problem Areas:(109)

First ICI plant commissioned in one day. Several plants operating with no problems reported.

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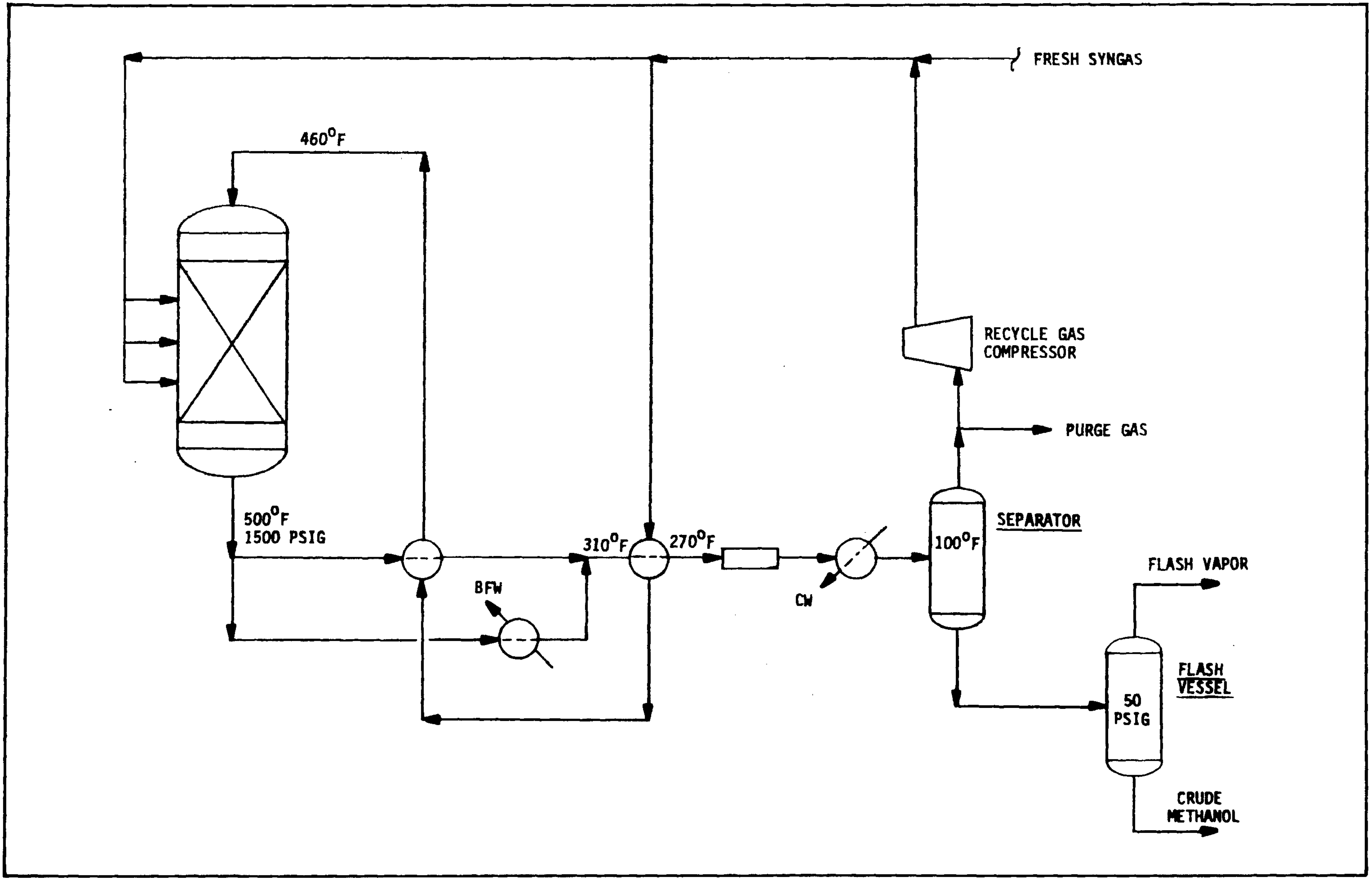

Figure 1 - Flow Diagram
ICI LP/LT Methanol Process

PROCESS INFORMATION EXTRACT

PROCESS 3.2.3 Lurgi LP/LT Methanol

Process Type:	Indirect, Methanol
Main Products:	Methanol
Development Status:	Commercial

PROCESS DEVELOPER Lurgi
Frankfurt/Main, Federal Republic of Germany

PROCESS SPONSOR Lurgi

DESCRIPTION OF PROCESS(104),(113),(114),(115)

The methanol coal liquefaction process entails two major steps.

(1) Production of synthesis $(CO+H_2)$ gas from coal.

(2) Conversion of synthesis gas to methanol.

In the Lurgi low pressure process (Figure 1), conversion is carried out in a tubular reactor whereby the heat of reaction is recovered as medium pressure steam.

Fresh feed gas is combined with recycled tail gas and the combined feed preheated to reaction temperature by exchange against the reactor effluent. The fixed-bed reactor is a vertical-tube heat exchanger with the catalyst placed inside the tube and boiling water on the outside. The combined gas feed flows downward through the catalyst tubes, and the heat of reaction used to generate steam up to 550 psig in the reactor shell. The reactor effluent is cooled by heat exchange against the combined feed, and then with air or water. The condensed crude methanol is separated from the gas and the gas is recycled to the reactor. Inerts are removed by a continuous purge of recycle gas. The crude methanol contains water and low and high boiling impurities.

OPERATING CONDITIONS(104),(114),(115),(116)

Pressure, atm.	48	77
Temperature, °F	455-490	455-490
Recycle/Fresh feed	5	3.5
Feed	Syngas	Syngas
Fresh Feed $\frac{(H_2 - CO_2)}{(CO + CO_2)}$ Molar Ratio	≥ 2	≥ 2
Conversion*:		
Overall, % CO	99	99.35
% CO_2	N.A.	90.0

*dependent on inerts content

Catalyst:

Low temperature, low pressure active copper formulation

Reaction Variables:

- Pressure: The equilibrium yield of methanol increases with pressure to the second power. Reaction rate increases with increased pressure.
- Temperature: The equilibrium yield of methanol decreases with increasing temperature.
- H_2/CO Ratio: Highest methanol equilibrium content is obtained for a stoichiometric H_2/CO mixture. However, increased H_2/CO ratio increases equilibrium CO conversion.
- CO/CO_2(113): Maximum molar ratio about 5/1

Coals Processed: Dependent upon suitability of coal for gasification step.

PRODUCTS(106),(107)

Yield:

lb water-free crude methanol/1000 SCF ($CO+H_2$) converted = 28.1

Characteristics:

Crude methanol is sulfur, nitrogen, and ash free. Water content of crude methanol is 2.5 to 14% wt (typical) depending on synthesis gas composition. High CO_2 feeds result in high water content crude methanol mixes.

Organic impurities in crude methanol:

Impurity(104)	ppm
Dimethylether	100-500
Higher alcohols	200

Methanol Properties (dry)	
Specific gravity, 20/4	0.792
Higher Heating Value,	
(Btu/lb)	9,760
(Btu/gal)	64,810
Latent heat of vaporization at bp, Btu/lb	502
Octane Rating	
RON	106
MON	92
Boiling point, °F	148
Freezing point, °F	-144
Flash point, °F	52

Toxicity:

Fatal dose	1 to 4 oz.
Fatal vapor concentration	50,000 ppm for 1 to 2 hrs.

Atmospheric concentrations should not exceed 200 ppm.

INTENDED PRODUCT USE/MARKET (106), (107)

(1) Boiler Fuel: Methanol can be burned as a clean boiler fuel with only slight modification to existing boilers. Lower (NO_x) emissions are claimed.

(2) Internal Combustion Engine Fuel: Existing gasoline fueled internal combustion engines can be converted to use pure methanol by decreasing the air to fuel ratio, recycling more heat from the exhaust to the carburetor, and providing for cold starts. Methanol gives 5 to 10 percent more power than gasoline, but twice as much is consumed.

(3) Gasoline Extender: Methanol can be blended up to 15% by volume in gasoline. Blended fuels have cold start problems and some engine throttle response problems due to lean carburetion requirements of the blend. Methanol-gasoline blends undergo phase separation in the presence of very small concentrations of water causing fuel stability problems. Engines using methanol fuel blends have lower (NO_x) emissions than when using gasoline.

(4) Industrial Gas Turbine Fuel: In turbine engine combustion methanol generates lower levels of NO_x since both peak temperatures and durations are below those experienced with kerosene.

Blade maintenance is estimated to be one-third of that required when methane is burned.

PROCESS EFFICIENCY

	Pressure (atm)	
	48	77
Thermal Efficiency		
Product only, including purge gas %	N.A.	83.0
Overall, including net utilities, %	N.A.	76.5
Utilities, per ton methanol (dry basis)		
550 psig steam (generated), MMBtu	2.35	2.35
Power, kWh		
Compressor (feed at 275 psig)	235	310
Circulator Miscellaneous	80	35
	315	345

	Pressure (atm)	
	48	77
Cooling Water (30°F rise), gal	-	7,250
Hydrogen Consumption ($CO+H_2$), SCF/lb C_1 OH	35.5	35.5
Catalyst Consumption		
Catalyst life, yrs.	2-3	

UNIQUE FEATURES OF PROCESS

Main features of the process are: the low temperature active copper-based methanol catalyst, special reactor design, and recovery of synthesis reaction heat as medium pressure steam.

PROCESS STATUS

Development Status:

Commercial operations first started late 1972. The capacity of Lurgi LP/LT plants in operation or under construction range from 130 to 1000 tons per day. Six plants have been constructed.

Patent Status:

Lurgi have existing patents and have applied for additional patents on the reactor design and the catalysts employed.

History:

Current Lurgi LP/LT methanol catalyst development work started in 1964. 4,000-TPY pilot plant started up April 1970. First commercial plant started up late 1972.

Commercial plants built operate at about 50 atm. For plants greater than 5,000-TPD capacity, optimum pressure is believed to be 80 atm.

Problem Areas: No problems reported. Several plants operating.

History:

Conventional high pressure methanol synthesis was discovered by Mittasch and Schneider of BASF, Germany, in 1923. From 1923 to 1966, HP synthesis with chrome oxide/zinc oxide catalyst was used for the commercial production of methanol from hydrogen and carbon monoxide. The first plant using LT/LP copper catalyst started up late 1966. Since 1970 about 85% of new installed methanol plant capacity has been by the low pressure process.

Problem Areas:(110)

Reliability of feed gas compression train due to high compression ratios involved.

REFERENCES

103.	Strelzoff, S., "Methanol: Its Technology and Economics," *Chemical Engineering Progress*, Symposium Series No. 98, Vol. 66, The American Institute of Chemical Engineers, 1970, pp. 54-58.
104.	Hiller, H. and F. Marschner, "Lurgi Makes Low-Pressure Methanol," *Hydrocarbon Processing*, September 1970, pp. 281-285.
105.	Shah, M.J. and R.E. Stillman, "Computer Control and Optimization of a Large Methanol Plant," *Ind. Eng. Chem.*, Vol. 62, No. 12, December 1970, pp. 59-75.
106.	Wigg, E.E., "Methanol as a Gasoline Extender: A Critique," *Science*, Vol. 186, No. 4166, November 29, 1974, pp. 785-790.
107.	Bryson, F.E., "Methanol: Old Help for a New Crisis," *Machine Design*, March 21, 1974, pp. 20-26.
108.	*Davey Powergas and the ICI Low Pressure Methanol Process*, Davy Powergas Publication No. 4-14274.
109	Rogerson, P.L., "Imperial Chemical Industries Low Pressure Methanol Plant," *Chemical Engineering Progress*, Symposium Series No. 98, Vol. 66, The American Institute of Chemical Engineers, pp. 28-34.
110.	Hedley, H. et al, "Methanol: How, Where, Who -- Future," *Hydrocarbon Processing*, September 1970, pp. 275-280.

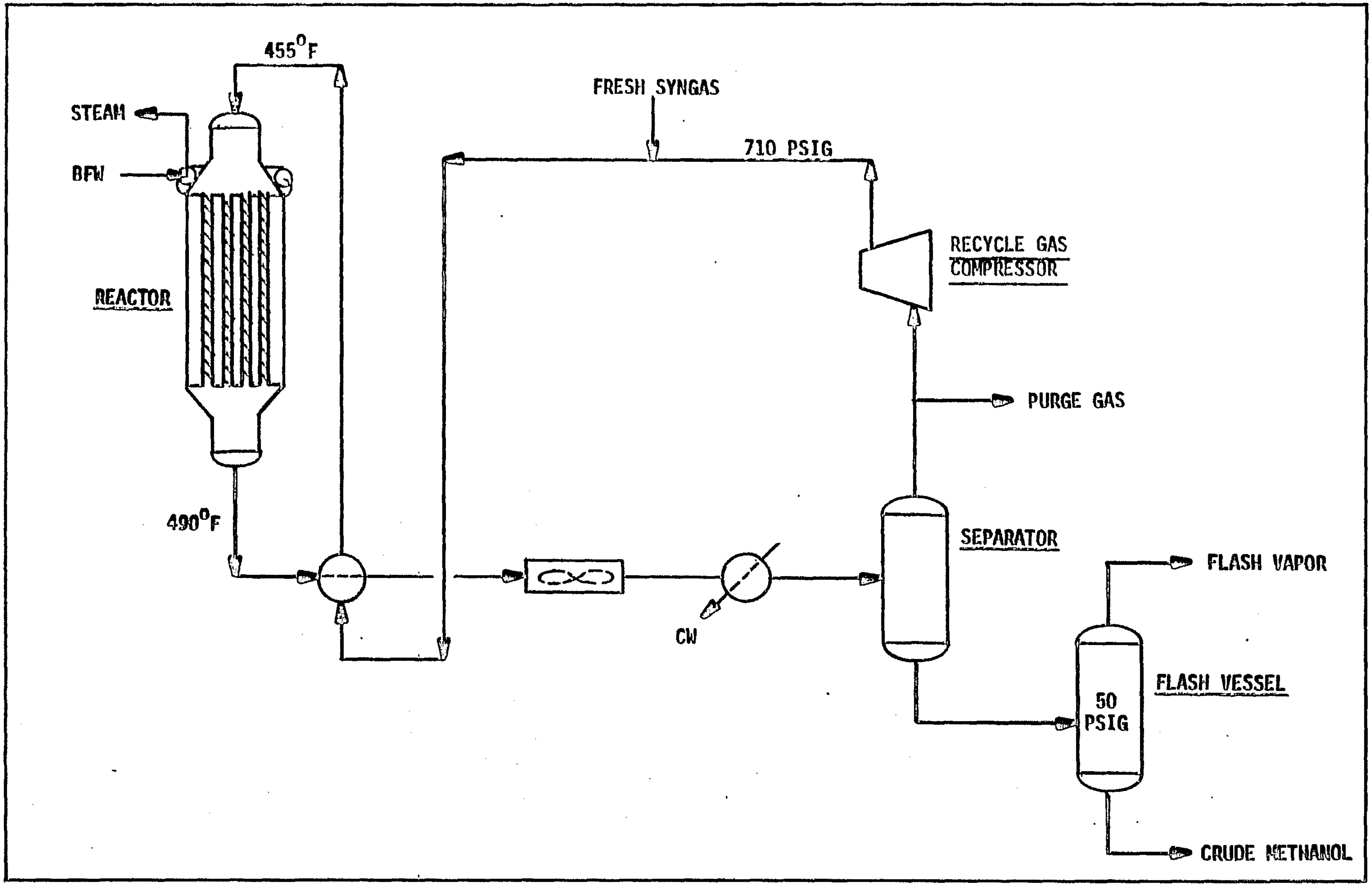

Figure 1 - Flow Diagram
Lurgi LP/LT Methanol Process

PROCESS INFORMATION EXTRACT

PROCESS 3.2.4	Three-Phase Methanol Synthesis
Process Type:	Indirect, methanol
Main Products:	Methanol
Development Status:	Bench Scale
PROCESS DEVELOPER	Chem Systems, Inc.
PROCESS SPONSOR	Electric Power Research Institute (EPRI)

PROCESS DESCRIPTION(117)

The methanol coal liquefaction process entails two major steps:

(1) Production of ($CO+H_2$) synthesis gas from coal

(2) Conversion of synthesis gas to methanol

In the Chem Systems low pressure methanol process (Figure 1) conversion is carried out in a three-phase fluidized-bed reactor. An inert circulating hydrocarbon liquid is used to fluidize the catalyst and control the reaction temperature.

Fresh feed gas and recycle tail gas are preheated to reaction temperature and passed upward through the reactor concurrent with the inert hydrocarbon. Phase separation between solid catalyst, liquid, and gas occurs at the top of the reactor. The catalyst remains in the reactor. The liquid is externally recirculated to the bottom of the reactor via a waste heat boiler, where steam up to 385 psig pressure is generated.

Reactor effluent gases are cooled by heat exchange against the fresh feed and gas recycle, boiler feed water, and finally air or water. Methanol and any vaporized hydrocarbon condensed are phase separated. Methanol and the hydrocarbon liquid are immiscible. Unconverted gases are recycled back to the reactor. Inerts are removed by a continuous purge of recycle gas. The crude methanol contains water and low and high boiling impurities.

OPERATING CONDITIONS(117)

Pressure, psig	1125
Temperature, °F	480
Recycle/Fresh feed,	1
Space Velocity/Residence Time:	
Fresh feed, h^{-1}	2000
Total feed, h^{-1}	4000
Feed	Syngas
Fresh feed $\frac{(H_2 - CO_2)}{(CO + CO_2)}$ Molar/Ratio,	≥2

Conversions*:

Overall, $(CO+H_2)$ %	96
Per pass, $(CO+H_2)$ %	45

*dependent on inerts content

Catalyst:

Low temperature/low pressure active copper-zinc formulation

Reaction Variables (103), (117)

- Pressure: The equilibrium yield of methanol increases with pressure to the second power. Reaction rate increases almost linearly with increased pressure.

- Temperature: The equilibrium yield of methanol decreases with increasing temperature. The rate of reaction increases slowly with temperature above 430°F showing a mild optimum in the region of 445 - 485°F.

- H_2/CO Ratio: Highest methanol equilibrium content is obtained for a stoichiometric H_2/CO mixture. However increased H_2/CO ratio increases equilibrium CO conversion. Reaction rate increases as hydrogen content of the gas increases from a deficient to a stoichiometric balanced region.

- CO_2: A few percent CO_2 significantly increases the overall reaction rate.
- Catalyst Size: Catalyst activity increases with decreasing particle size, but not in direct proportion, over a region of one to three millimeters.

Coals Processed:

Dependent upon suitability of coal for gasification step.

PRODUCTS

Yield

lb water-free crude methanol/1000 SCF ($CO+H_2$) converted = 28.1

Characteristics:

Crude methanol is sulfur, nitrogen, and ash free. Water content of crude methanol is 2.5 to 14% wt (typical) depending on synthesis gas composition. High CO feeds result in high water content crude methanol mixes.

Methanol Properties (dry):

Specific gravity, 20/4	0.792
Higher Heating Value:	
(Btu/lb)	9,760
(Btu/gal)	64,810
Latent heat of vaporization at bp, Btu/lb	502
Octane Rating:	
RON	106
MON	92
Boiling point, °F	148
Freezing point, °F	-144
Flash point, °F	52

Toxicity:

Fatal dose	1 to 4 oz.
Fatal vapor concentration	50,000 ppm for 1 to 2 h

Atmospheric concentrations should not exceed 200 ppm.

INTENDED PRODUCT USE/MARKETS(106), (107)

(1) Boiler Fuel: Methanol can be burned as a clean boiler fuel with only slight modification to existing boilers. Lower (NO_X) emissions are claimed.

(2) Internal Combustion Engine Fuel: Existing gasoline fueled internal combustion engines can be converted to use pure methanol by decreasing the air to fuel ratio, recycling more heat from the exhaust to the carburetor, and providing for cold starts. Methanol gives 5 to 10% more power than gasoline, but twice as much is consumed.

(3) Gasoline Extender: Methanol can be blended up to 15% by volume in gasoline. Blended fuels have cold start problems and some engine throttle response problems due to lean carburetion requirements of the blend. Methanol-gasoline blends undergo phase separation in the presence of very small concentrations of water causing fuel stability problems. Engines using methanol fuel blends have lower (NO_X) emissions than when using gasoline.

(4) Industrial Gas Turbine Fuel: In turbine engine combustion methanol generates lower levels of (NO_X) since both peak temperatures and durations are below those experienced with kerosine. Blade maintenance is estimated to be one-third of that required when methane is burned.

PROCESS EFFICIENCY (117)

Thermal Efficiency:	
Product only, %	86.2
Overall, including net utilities, but excluding feed gas compression, %	97.9
Utilities, per ton methanol (dry basis):	
400 psig steam (produced), MMBtu:	3.01
Power kWh:	
Recycle	4.93
Oil circulation pumps	8.13
BFW pumps	4.27
Hydrogen Consumption ($CO+H_2$), SCF/lb Dry Methanol:	35.5

UNIQUE FEATURES OF PROCESS

Main features of process are: a liquid-gas-fluidized reactor, recovery of synthesis reaction heat as medium pressure steam, high conversions per pass, and low gas recycle rate. Commercial low temperature catalyst used in tests.

PROCESS STATUS

Development Status: Bench scale, exploratory reactor

Patents: U.S. Patents applied for

Location of Development Work: Chem Systems research facilities, Hackensack, New Jersey.

History:

Limited experimental work on liquid phase methanol synthesis conducted by Chem Systems in early 1973, following successful development work on liquid phase methanation, began April 1972. Research and development work later sponsored by EPRI (about 1975).

Problem Areas: No problems reported.

REFERENCES

103. Strelzoff, S., "Methanol: Its Technology and Economics," *Chemical Engineering Progress*, Symposium Series No. 98, Vol. 66, The American Institute of Chemical Engineers, 1970, pp. 54-58.

106. Wigg, E.E., "Methanol as a Gasoline Extender: A Critique," *Science*, Vol. 186, No. 4166, November 29, 1974, pp. 785-790.

107. Bryson, F.E., "Methanol: Old Help for a New Crisis," *Machine Design*, March 21, 1974, pp. 20-26.

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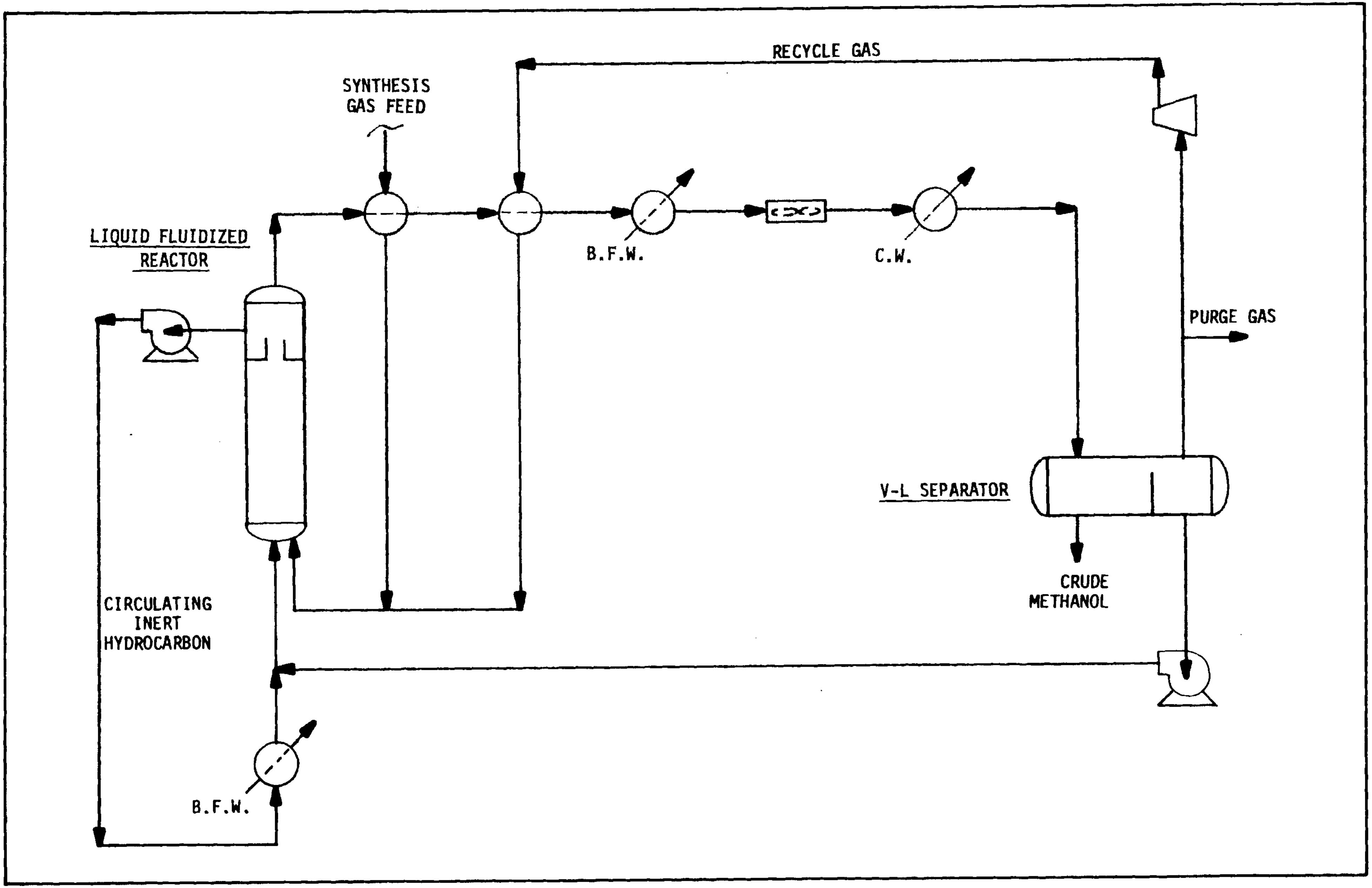

Figure 1 - Flow Diagram
Chem Systems Three Phase
Methanol Synthesis Process

PROCESS INFORMATION EXTRACT

PROCESS 3.3.1	M-Gasoline (Mobil)
Process Type:	Indirect
Main Products:	Gasoline range hydrocarbons
Development Status:	Bench scale
PROCESS DEVELOPER	Mobil Research and Development Corporation Princeton and Paulsboro, New Jersey
PROCESS SPONSORS	Mobil and DOE

PROCESS DESCRIPTION (118), (119), (120)

The M-Gasoline coal liquefaction process entails three major steps:

(1) Production of synthesis gas ($CO + H_2$) from coal.

(2) Conversion of synthesis gas to methanol.

(3) Conversion of methanol to gasoline range hydrocarbons by the M-Gasoline process.

In the M-Gasoline process (Figure 1), conversion is carried out in two stages in fixed-bed reactors. Feed methanol is fully vaporized by heat exchange with the reactor effluent and by heat input from the reactor charge heater. Vaporized methanol is catalytically converted to a mixture of dimethal ether, methanol, and water, in the first reactor. Some 20 to 30% of the total heat released occurs in this reactor. The reactor effluent is combined with recycled product gas and flows to the second reactor where a zeolite catalyst complets the conversion to hydrocarbons and water.

The first reactor is operated adiabatically with a maximum temperature rise of 200°F. Recycle gas is added to the second reactor feed to limit the temperature rise to 100 to 200°F. Reactor effluent from the second stage is condensed, water and liquid hydrocarbon phases separated, and a portion of the gas recycled as previously described.

Catalyst is regenerated by burning off accumulated coke after several weeks of operation. Mobil R&D Corp. are also operating a fluid bed reactor version of this process.

OPERATING CONDITIONS(119), (120)

	DME Reactor	M-Gasoline Reactor
Pressure, psig:	285	285
Temperature, °F	600 - 770	650 - 850
Recycle/Fresh Feed:	0	4.5 - 9.0
Space Velocity/Residence Time:		
WHSV, lb C_1OH/h/lb catalyst	6	2
Feed: Crude Methanol containing up to 16 wt% water		
Conversions:		
Methanol, %	100	
Catalyst:	zeolite	shape-selective zeolite

Reaction Variables:

- The effect of reaction variables upon the conversion has not been published. The basic equation for the conversion of methanol to hydrocarbons is:

$$n\,CH_3OH \rightleftharpoons (CH_2)_n + n\,H_2O$$

- Since this reaction results in an increase in the number of molecules present, decreasing pressure favors the equilibrium conversion of methanol to hydrocarbons.

Coals Processed:

Dependent upon suitability of coal for gasification step.

PRODUCTS (119), (120)

Yield:	wt % pure methanol
Hydrocarbons	43.67
Water	55.73
CO, CO_2	0.36
Coke, other	0.24
	100.00

Hydrocarbon yield based on (CH_2) charged = 99.8 wt %

Characteristics:

Composition Component	Product wt%	
C_1	1.4	
C_2 =		
C_2		
C_3 =	0.2	
C_3	5.5	
C_4 =	1.1	
C_4	11.9	(i C_4/n C_4 = 2.61)
C_5 -C_{10}	79.9	
	100.0	

Typical Gasoline Product:

Distillation, °F

	TBP	ASTM
IBP	11	87
10	85	132
30	130	156
50	194	201
70	279	272
90	337	319
EP	449	409
°API		57.9
MW		93.6
RON		90-95

PONA Analysis

	vol%
Paraffins	47
Olefins	14
Naphthenes	9
Aromatics	30
	00

All products: oxygen, sulfur, nitrogen, and ash free.

INTENDED PRODUCT USE/MARKET

(1) Alkylation feedstock: Olefins and iso-butane to be separated and alkylated to additional gasoline.

(2) Gasoline: Gasoline composition is similar to that produced by petroleum refining. Octanes exceed current requirements of unleaded regular or leaded premium grade gasoline.

Durene (C_{10} alkylbenzene) is present in relatively large amounts (3 to 6 wt % depending upon process conditions). In concentrations greater than 4 wt % durene can result in unsatisfactory engine operation caused by crystallizing out of the durene in the carburetor. Durene levels can be maintained at suitable levels by careful process control or by blending. Gasoline paraffins and olefins are highly branched.

PROCESS EFFICIENCY(120)

Thermal Efficiency:

Product only %	95.5

Overall, including net utilities, %	93.5
Utilities, per ton methanol:	
(Pilot plant data):	
Power. kWh	14.4
Cooling water, gpm	7.2

Hydrogen Consumption:

Methanol ($CO + H_2$) Equivalent, SCF/lb Gasoline - 90.0

Catalyst Consumption:

Catalyst life, 1 year
(at 7.5:1 gas recycle ratio)

UNIQUE FEATURES OF PROCESS

Use of a shape selective zeolite cracking catalyst to produce a highly branched hydrocarbon mixture, containing no hydrocarbons above C_{10}, from methanol and other oxygen compounds.

PROCESS STATUS

Development Status:

Zeolite catalyst developed and tested on bench scale. Fixed-bed and fluid-bed reactors tested. Design package for a 100-BPSD pilot plant completed (1976).

Mobile Patents: U.S. 3,931,349
3,969,426

Location of Development Work: Mobile R&D Corp. Laboratories, near Princeton, New Jersey

History:

Mobil has been engaged in the development of zeolite cracking catalysts for petroleum refining since the 1950s. One type of shape-selective zeolite developed by Mobile was found to have a unique channel structure which permitted the conversion of methanol and other oxygenates to a narrow range of molecular weight hydrocarbons.

The M-Gasoline was first reported in the literature in 1976.

Problem Areas:

Coke accumulation on catalyst requires regeneration of catalyst after a few weeks on stream.

REFERENCES

118. Meisel, S.L. et al, "Gasoline from Methanol in One Step," *Chemical Technology*, 6, 1976, p. 86.

119. Wise, J.J. and A.J. Silvestri, "Mobile Process Efficiently Converts Methanol to Gasoline," *The Oil and Gas Journal*, November 22, 1976, p. 141.

120. Daviduk, N. et al, *Design of a 100 BPD Pilot Plant to Convert Methanol to Gasoline Using the Mobile Process*, 11th Meeting IECEC, p. 320.

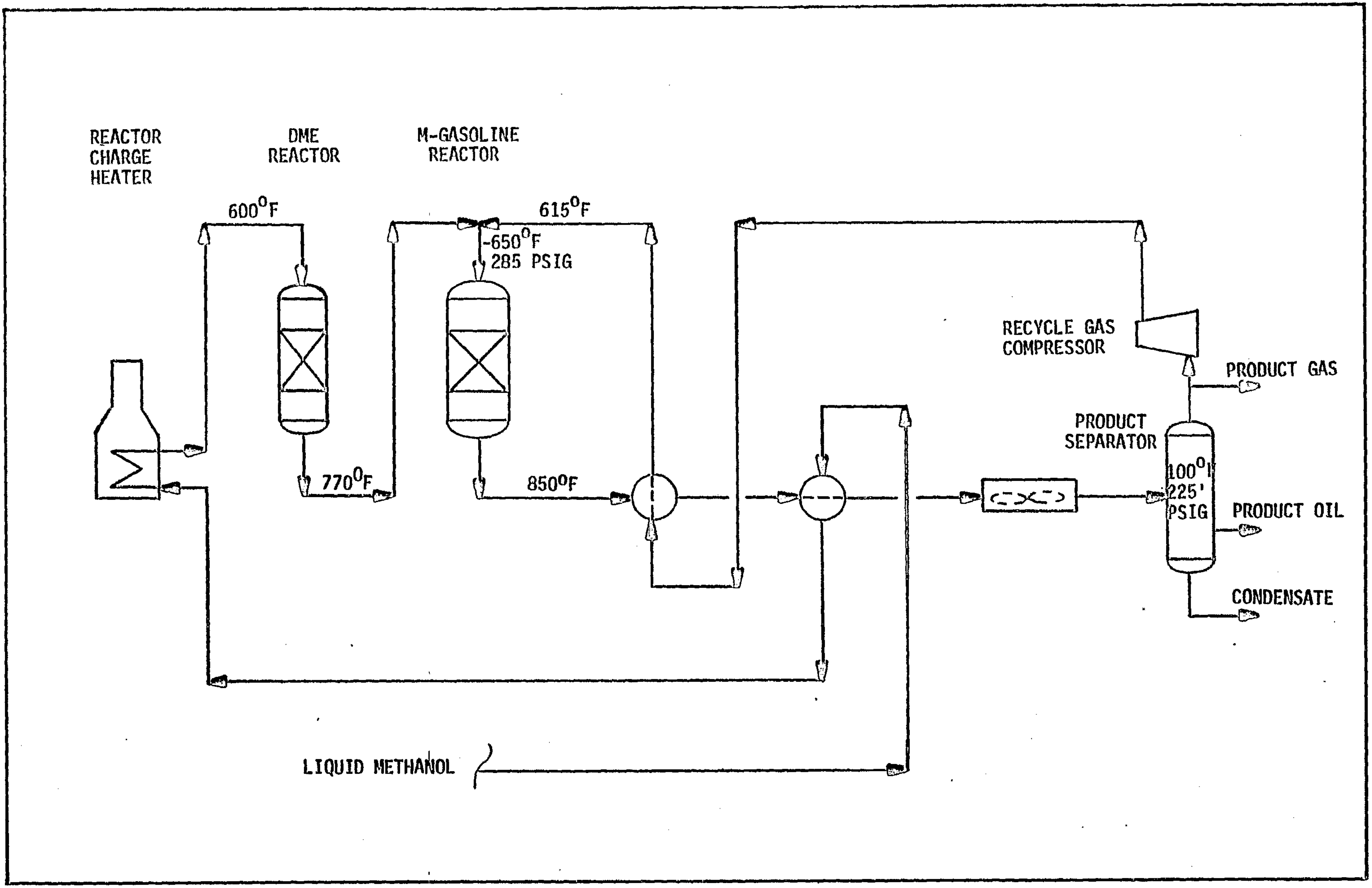

Figure 1 - Flow Diagram
M-Gasoline Process (120)

PROCESS INFORMATION EXTRACT

PROCESS 4.1.1	Supercritical Gas Extraction (SCE)
Process Type:	Solvent Extraction
Main Products:	Gas Extract Residue
Development Status: (123)	Laboratory-scale; 1/4-TPD unit under construction

PROCESS DEVELOPERS (123)

Laboratory and process development:

National Coal Board
Coal Research Establishment
Stoke Orchard
Cheltenham, Glos
England

Conceptual design:

Catalytic Inc., a subsidiary of
Air Products and Chemicals, Inc. (APCI)

PROCESS SPONSOR

National Coal Board

DESCRIPTION OF PROCESS (Refer to Figure 1)

Coal is fed to the lock hopper system where it is pressurized and then charged to the extractor. The extractor is also charged with gaseous toluene which is heated in a fired heater to maintain the extractor at about 750°F. This is above the critical temperature of toluene (606°F) but below the cracking or destructive-distillation temperature of the coal liquids. The reactor pressure is maintained at about 1500 psia. The extractor conditions are such that the gaseous toluene acts as a solvent to "dissolve" the coal tar liquids.

"Undissolved residue" is discharged to the Residue Lock Hopper system where it is depressurized and steam stripped to recover entrained toluene. Overhead extractor vapors, consisting of toluene, extract, water vapor, and hydrocarbons are cooled to condense solvent and extract. Uncondensed hydrocarbon vapors are separated in the Degasser. The solvent-extract condensate is flashed at near atmospheric pressure. Most of the toluene and water are removed as vapors leaving a solution of extract in toluene. The vapors are condensed and phase-separated to recover toluene as recycle solvent and send the aqueous phase to wastewater treatment. The extract solution is fractionated in an atmospheric column to recover the extract as bottoms and toluene as recycle solvent.

OPERATING CONDITIONS (125)

Temperature	650° – 750°F
Pressure	100 Atm.
Solids residence time	10 min.
Conversions	Tar-extract yields up to 30 wt% of D.A.F. coal feed
Catalyst	None

Reaction Variables:

Included in the list of variables investigated and their effect on extract yields are:

(1) Injection of reducing gases, such as H_2, CO, and/or H_2O in the reactor which was found to increase extract yields up to 60% by weight.

(2) Volatile content of coal feed: an increase in the volatiles of the feed also increase the extract yields.

Coals Processed:

Bituminous coals from 10 – 30 wt% V.M. content of D.A.F.

PRODUCTS

Typical Yields (estimated from Reference 124)

	Wt% of Dry Coal to Reactor
Gas	2.2
Water	1.6
Extract	33.2
Residue	63.3
	100.3 (0.3% toluene consumed)

Characteristics:

Analysis of a Typical Supercritical Extract, Coal Feed and Residue[a]

Material	Coal Feed	Extract	Residue
Carbon, % wt	82.7	84.0	84.6
Hydrogen, % wt	5.0	6.9	4.4
Oxygen, % wt	9.0	6.8	7.8
Nitrogen, % wt	1.85	1.25	1.90
Sulfur, % wt as received	1.55	0.95	1.45
H/C ratio, atomic	0.72	0.98	0.63
OH, % wt	5.2	4.4	4.8
Ash, % wt dry basis	4.1	0.05	5.0
Volatile Matter, % wt	37.4	-	25.0
Molecular Weight	-	490	-

---

[a] All values are moisture and ash-free (MAF) except as noted.

INTENDED PRODUCT USE/MARKETS(124)

(1) Gas: It is to be used internally as plant fuel.

(2) Extract: The extract is a low-melting glossy solid which has a low ash content (0.1 wt%). It represents the hydrogen-rich fraction of the coal, and has a generally open-chain polynuclear aromatic structure linked by ether and probably methylene groups. Its composition indicates that it could be hydroconverted to hydrocarbon fuels and chemicals.

(3) Residue: The residue is a porous devolatilized char similar in size distribution to the parent coal but more reactive. It is also non-caking and is considered to be a premium quality feed for gasification or as a fuel for power generation in a fluidized bed combustion unit.

PROCESS EFFICIENCY

	% of Coal Feed HHV to Dryer + Pulverizer
Yields(124)	
Extract	33.9%
Residue	51.1%
	85.0%
Thermal Efficiency(123), (124)	82-85%
Excluding Utilities	99.5%

UNIQUE FEATURES OF PROCESS

- The technique of gas extraction makes use of the solvent power of compressed gases near the critical temperature and the increased volatility of the extracted liquids at higher dissolving gas partial pressures. In this way, the technique is a combination of extraction and distillation principles. The gas, which is above its critical temperature, is at an elevated partial pressure. Hence, the density of the gas approaches its liquid density and acts as a solvent. The elevated partial pressure also acts to increase the volatility of the coal liquids to be vaporized.

- The separation of extract liquids from the solvent is easier compared to other solvent extraction coal processes because:
  - After cooling and flashing the solvent and extract, the gas densities and viscosities are significantly lower than those of solutions of coal in liquids.
  - The volatility difference of the gas solvent to the coal liquids is much larger than the volatility of typical liquid solvents and coal liquids.
- The gas solvent is pressured to system pressure as a liquid by a pump. Vaporization takes place in the heater and hence no compressors are required.

PROCESS STATUS

Development Status:

The NCB has acquired data over the last five years in laboratory scale, batch-type equipment. A 1/4-TPD (10 kg/h) PDU continuous reactor is under construction. The purpose of this plant is to obtain a first demonstration of the continuous operation of the process and to identify the preferred extraction conditions. To investigate other engineering aspects, such as use of lock hoppers in the process, a pilot plant of at least 24-TPD capacity is presumed necessary. The final development stage before commercialization would be a 2,400-TPD demonstration plant, which is thought to be about the largest throughput which can be accommodated in one extraction vessel.

Location of Development Work: Stoke Orchard, Cheltenham, Glos, England.

History:

Since 1970, the National Coal Board has been gathering experimental data on extraction of coal with supercritical gas solvents. Early work involved batch extractions and later, under the auspices of the National Coal Board and the European Coal and Steel Community (ECSC), the emphasis changed to semi-continuous work which allowed a closer approach to the kinetics of a continuous process. A 1/4-TPD PDU is now under construction.

Problem Areas:

- High pressure solids feed system
- High cost solvent (toluene)

REFERENCES

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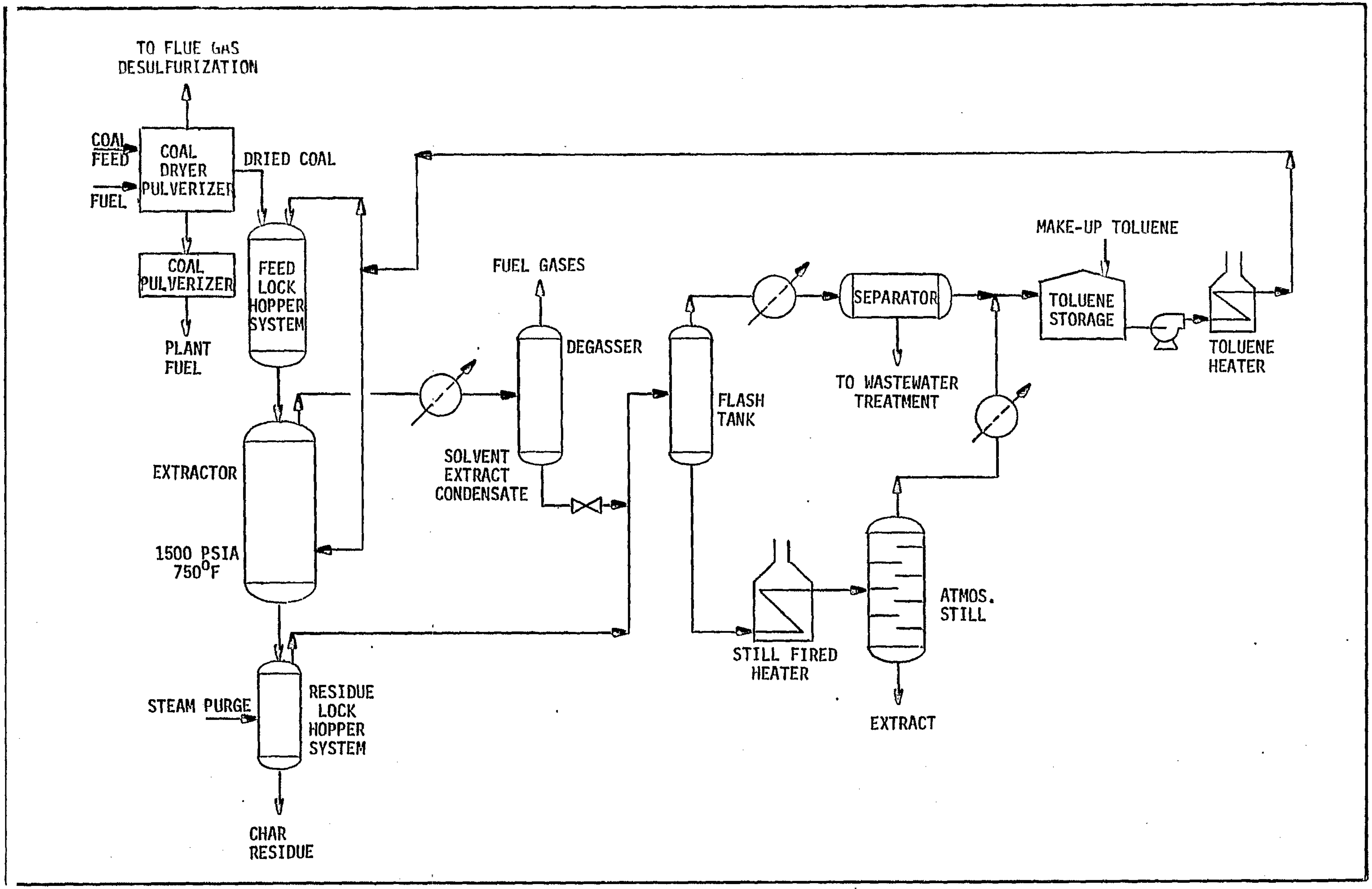

Figure 1 - Flow Diagram
The Supercritical Gas Extraction
of Coal Process - British Coal Board (124)

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