PART 3

SPECIFIC COAL CONVERSION PROCESSES

I. INTRODUCTION TO PART 3

In Parts 1 and 2 of this report, a number of developments in catalysis and impacting disciplines were discussed which are potentially pertinent to the improvement of catalytic coal conversion processes. Emphasis was placed on those areas in which there has been the greatest interest and progress over the last decade. They are summarized in Table I-1.

Many of the topics shown in Table I-1 have general applicability to all the processes of interest in coal conversion. For example, improvement of the chemical and thermal stability of coal conversion catalysts is highly desirable for both liquefaction and gasification processes. Therefore, developments which impact in this area, such as the use of catalyst-support interactions and the application of new thermally stable materials, have general significance for catalyst development programs in synthetic fuels. A number of other developments, however, are only applicable to specific problems in coal conversion. For example, the use of multimetallic and intermetallic catalysts will not be important in coal liquefaction due to the instability of these materials in the high sulfur levels in the system. It will, on the other hand, be very important in upgrading of coal liquids and possibly in the development of new methanation and Fischer-Tropsch catalysts.

In Part 3, the specific application of the advances in catalysis and related fields to a number of important coal conversion processes are discussed in detail. They include:

TABLE I-1

ADVANCES OF IMPORTANCE TO THE CATALYTIC CONVERSION OF COAL

Subject	Representative Areas of Impact
Multimetallic Catalysis	- Upgrading of coal liquids - Methanation - Fischer-Tropsch Synthesis
Catalyst-Support Interactions	- Thermal & chemical stabilization of catalysts & supports
Catalyst Characterization	- Improvement of coal liquefaction catalysts - Upgrading of coal liquids - Determination of catalyst intrinsic activity
Catalyst Preparation	- New catalyst formulations - Controlled variation in catalyst properties - Higher surface area catalysts
Poisoning and Regeneration	- Effect of sulfur in coal conversion catalysis - Prevention of carbon deposition - removal of carbon
Mechanism and Surface Chemistry	- Better understanding of the important steps in coal conversion - Identification of rate limiting processes, directions for process improvement
Reactor Engineering and Catalyst Testing	- Development of effective catalyst testing procedures - Data interpretation
Inorganic Chemistry	- New catalytic materials and compositions with improved poison tolerance and activity
Materials Science	- Novel support materials and structures - Novel refractory compounds - Understanding of sintering phenomena (catalyst deactivation)
Surface Science	- New characterization techniques

- Upgrading of Coalcon liquids
- Refining of COED, H-Coal and Synthoil liquids to gasoline, jet fuels, and diesel fuels
- Conversion of SRC to low sulfur, low nitrogen liquid boiler fuels
- Liquefaction of coal to low sulfur, low nitrogen boiler fuels
- Shift conversion and methanation
- Catalytic gasification
- The synthesis of diesel fuel, LPG and selected feedstocks from CO and H_2

The discussions will include a brief review of each process and a summary of major problems and constraints associated with the catalytic step. The concepts presented in Parts 1 and 2, which are pertinent to these problems and constraints, are identified and applied where possible. Short range and long range programs are treated separately, as are any developments that are of a more fundamental nature.

II. PREFACE TO SECTIONS III AND IV - AN OVERVIEW OF PERTINENT PETROLEUM REFINING OPERATIONS

Sections III and IV of Part 3 of this study pertain to the upgrading and refining of coal liquids from the Coalcon, COED, H-Coal and Synthoil processes to give high octane motor gasoline, jet fuel, diesel fuel and clean burning boiler fuels. In upgrading coal liquids to these fuels, it is instructive to consider the characteristics of the starting coal liquids feedstock, the characteristics of the desired fuel products and the type of process which could affect the transformation. In this preface, a brief description of the above mentioned refined petroleum fuels is provided, together with a discussion of those petroleum processes which are required to produce these fuels.

A. FUEL PRODUCTS FROM COAL LIQUIDS

The types of fuel products which can potentially be made from coal liquids may be divided into the following classifications:

- Motor Gasoline
- Jet Fuel
- Turbine Fuel
- Diesel Oil
- Heating Oil
- Residual Oil

A brief description of the specifications for these fuels is given below:

1. MOTOR GASOLINE

This fuel is a blend of paraffins, naphthenes and aromatics. It usually contains a substantial fraction of branched paraffins and single-ring aromatics such as benzenes, toluenes and xylenes (BTX), as all of these compounds are high octane components. Optimization of characteristics such as volatility, engine starting, anti-vapor lock, prevention of gum and sludge formation as well as anti-knock, requires careful blending of the above components and is a function of use and climate conditions. As will be mentioned later, the most difficult catalytic step in producing high octane gasolines is the conversion of naphthenic and particularly paraffinic fractions of a petroleum naphtha feed to high octane single ring aromatics components.

2. JET FUEL

Jet fuels are more complex in composition than motor gasolines because of significantly different and more stringent constraints for various applications such as military and commercial use. In general, jet fuels are a highly paraffinic kerosene fraction. The aromatic content is usually limited to less than about 20 vol. %. This gives better control of smoke emissions and optimum energy density. The latter factor is important for aircraft range. Generally, a minimum of 18,400 Btu/lb. of fuel is required. The energy density increases with an increasing H/C ratio and is therefore favored by paraffins and cycloparaffins (naphthenes). The smoke problem is particularly aggravated by polynuclear aromatics (boiling point $>400^{\circ}$F) which also lead to excessive carbon deposition in the engine. Polynuclear aromatics are generally controlled to <3 vol. %. Some single ring aromatic content is desirable to improve the rich mixture performance of the jet aircraft during takeoff. These compounds also contribute to octane, although for jet fuel more effective high octane constituents are branched paraffins (higher energy density than aromatics) and are generally produced by conventional alkylation or isomerization of paraffins. Olefins must also be minimized (<5 vol. %) because they decrease thermal stability and form polymeric gums. Sulfur and mineral constituents present potential problems because they form deposits and facilitate corrosion in the hot section of the jet engine. Mercaptans, for example, are generally limited to a maximum of 0.003 wt.%.

3. GAS TURBINE FUELS

The specifications for gas turbine fuels are primarily concerned with low mineral matter, particularly sodium and potassium (<1 ppm), lead (<1 ppm), vanadium (as low as 0.5 ppm) and calcium (<10 ppm). The constraints on sulfur are currently a maximum concentration of 1.0 wt.%. The nitrogen concentration has to be below environmental specifications for total NO_x emissions. Other physical characteristics are also of concern including specific gravity, viscosity, carbon residue (conradson carbon), flash point and pour point. A summary of typical specifications is given in Table II-1.

4. DIESEL FUELS

In contrast to motor gasolines and jet fuels, the variation in fuel characteristics for diesel fuels is not significant even though diesel engines vary widely in size, speed, power output, and mechanical design. Somewhat analogous to the octane number for motor gasolines, there is an index for diesel fuels which is a measure of ignition quality. It is called the cetane number, and is equal to 100 for cetane (n-hexadecane, $C_{16}H_{34}$) and zero for α-methyl-naphthalene. The cetane numbers usually vary from 35-50 depending on use, and, in general, paraffinic fuels have better ignition qualities than aromatic fuels.

In addition to ignition quality, parameters such as volatility, viscosity, specific gravity, sulfur content, storage stability, pour point, cloud point and flash point are important. Volatility and viscosity are two particularly important physical parameters for diesel engine operation. High speed diesel engines require volatile fuels because high boiling

TABLE II-1

SPECIFICATIONS FOR GAS TURBINE FUELS (a)

CHEMICAL SPECIFICATIONS

Element	Specification (b)
Sulfur (wt.%)	1.0 max.
Hydrogen (wt.%)	11.3 min.
Nitrogen (wt.%)	To meet NO_x standards
Sodium (ppm) Potassium (ppm)	1 max.
Lead (ppm)	1 max.
Vanadium (ppm)	0.5 (c)
Calcium (ppm)	10 max.

PHYSICAL SPECIFICATIONS

Property	Specification (b)
Sp. Gr. @ 60°F	0.46 max.
Kinematic Viscosity	
@ 100°F (cSt)	900 max.
@ 210°F (cSt)	30 max.
Conradson Carbon Residue (wt.%)	1.0 max.

(a) Reference 1
(b) Based on crudes and residual fuels
(c) Untreated with MgO (100-500 ppm if treated)

fractions cannot be vaporized quickly enough for combustion. Incomplete combustion and consequent carbon deposition occurs, with increased engine wear and total emissions. Viscosity control is also important. Excessively high viscosity results in the fuel spray (fuel injection) penetrating too far into the combustion chamber with subsequent wetting of cylinder walls and carbonization on the hot chamber surface. A low viscosity leads to engine wear since the fuel also serves as a lubricant. Both viscosity and volatility are controlled by the molecular weight of the paraffinic fractions.

Low sulfur levels are important for diesel engines not only to minimize emissions, but also because combustion conditions favor the formation of sulfuric acid which leads to corrosion. In addition, SO_3 formed during combustion, particularly for high speed diesel engines, sulfonates the lubricating oil film and forms undesirable sludge deposits. The problem is more significant for high speed because they favor the formation of SO_3 which is substantially more reactive than SO_2.

Typical uses of diesel fuel range from low speed engines such as marine diesels to medium speed railroad diesels as well as high speed applications for buses, trucks and tractors. The boiling range of the fuel varies from 325-550°F to 350-800°F, depending on the application. The sulfur constraint ranges from 1.2 wt.% for low speed use to 0.12 wt.% for high speed use. Nitrogen content varies with the local requirements for total NO_x emissions.

5. HEATING OILS

The last fractions which should be considered as potential products from upgrading coal liquids are heating oils and residual fuels. The most conventional heating oil is commonly called #2 oil. It has an °API gravity of 34, a viscosity (Saybolt Seconds Universal @ 100°F) of 35, an initial boiling point of 325°F and a final boiling point of 645°F. Other specifications require a maximum carbon residue of 0.10 wt.% (on 10% bottoms), a pour point of -5°F, a flash point (Pensky-Martin) of 150°F and a maximum sulfur content of 0.1 wt.%. The oil should have proper viscosity to give optimum atomization and burning characteristics and minimum carbon deposition. The sulfur level is controlled for environmental reasons and to minimize burner corrosion (formation of H_2SO_4).

6. RESIDUAL FUELS

Residual fuels are classified into several grades because of a variety of commercial applications, each having different requirements. The lightest residual fuel oil fraction is called #4 oil, and is used for oil burner installations which do not have facilities for preheating the oil. Grade #5 oil is used for oil burner installations equipped with preheating facilities. The heaviest fraction is #6 oil (sometimes called Bunker C oil), and is used in installations which have high temperature preheating equipment permitting the use of high viscosity fuels.

Residual fuels are produced in a refinery from many sources. These fuels usually contain a residua fraction (bottoms from atmospheric or vacuum distillation) with varying amounts of diluent. Diluents include coker gas oil, visbreaker gas oil, virgin gas oil, catalytic heating oil and heavy catalytic cycle stock. The amount of diluent depends on the grade of the fuel oil. For example, #4 oil is almost totally composed of a distillate diluent and contains only a small amount of residua, whereas #6 oil contains a significant fraction of residua. Properties of primary importance for residual oils are viscosity and sulfur content. With regard to the latter, #1 oil usually contains a maximum of 0.5 wt.% sulfur; #2 1.0 wt.%; and #4, #5, and #6 are limited by local SO_x emission standards.

This section has given a broad overview for the chemical and physical characteristics of fuels which are being considered as potential products from coal liquids. This information will be helpful in discussing the potential catalytic problems involved in the production of these fuels from coal liquids such as those produced by the Coalcon, COED, H-Coal and Synthoil processes. The next section gives a brief discussion of the primary catalytic processes in petroleum refining required to bring about the necessary catalytic conversions.

B. PETROLEUM PROCESSING

There are three types of modern refineries: hydroskimmer, conversion and maximum conversion. The hydroskimmer refinery is the simplest of all and predominantly produces fractions which distill from the atmospheric pipestill, namely gasoline (made by upgrading the naphtha fraction by catalytic reforming), jet fuel, diesel oil, heating oil and fuel oil. This type of refinery is used primarily in Europe and other areas where fuel oil and heating oil are in high demand and where there is not as significant an incentive to maximize the gasoline fraction as in the U. S.

The conversion refinery is the next stage of complexity. This type of refinery is extensively used in the United States because of the significant demand for gasoline (more than half the crude barrel is converted to gasoline in the U. S.). As the term "conversion" implies, additional processing over that for a hydroskimmer refinery is necessary to shift the product slate towards higher gasoline yields. The additional processes include a vacuum pipestill, a catalytic cracking unit, and several additional hydrotreating units. The vacuum pipestill provides a means of distilling off higher molecular weight fractions from the crude oil without substantial thermal degradation of the feedstock. The catalytic cracking unit is used to crack these higher molecular weight fractions to more desirable products.

The maximum conversion refinery is similar to the conversion refinery except for the additional processing of the light and heavy ends to maximize middle distillate fractions. These additional steps include alkylation of paraffins and hydrocracking and coking of heavy fractions.

Of the catalytic processes that are part of these refineries, the most important ones for upgrading coal liquids are catalytic cracking, hydrocracking, naphtha reforming and hydrofining. The latter process encompasses removal of sulfur, nitrogen and oxygen compounds.

In catalytic cracking, a heavy feed containing aromatics, naphthenes and paraffins (usually a virgin gas oil, b.p. 600-1050°F) is contacted with an acidic type catalyst (e.g. aluminosilicates). Usually this is done in a fluidized bed configuration which provides an effective means for withdrawing the catalyst for oxidative regeneration. The objective of the process is to produce gasoline, heating oil and some diesel and jet fuel from heavy feedstocks with minimum excess formation of coke and light gases. Many reactions occur during the process, including cracking, isomerization, alkylation and dehydrogenation. Aromatic rings are the most difficult to crack and also tend to increase coke deposition and thereby decrease the activity maintenance of the catalyst. Coke deposition is characteristic of many high molecular weight petroleum feedstocks which contain substantial amounts of polynuclear aromatics as well as metals like vanadium and nickel which also cause increased coke deposition. It should be noted that in conventional fluidized bed catalytic cracking, an optimum coke deposition level is desirable. The cracking step is endothermic and the process is kept in thermal balance by providing heat from oxidative removal of coke from the catalyst in the regenerator. Interestingly, if no coke or minimum coke were formed, the conventional process would not work. However, heavy coke levels are also detrimental. Typically, catalytic crackers are run between 800 and 980°F at close to atmospheric pressure.

In recent years, hydrocracking has received increased emphasis in refinery operations because it is a process which accomplishes the same function as catalytic cracking with higher molecular weight feedstocks and better control of product distribution. A hydrocracker is operated at elevated pressures, sometimes as high as a few thousand psig, with high pressures of hydrogen and using a bifunctional catalyst. The catalyst contains both acid and hydrogenation sites.

In catalytic reforming, a naphtha containing paraffins, naphthenes and aromatics is converted over a bifunctional catalyst such as Pt/Al_2O_3 to high octane gasoline. This involves maximizing the production of branched paraffins and single-ring aromatics. The process usually operates between 200-600 psig, 800-980°F and at hydrogen flow rates of 5000-8000 SCF/Bbl of naphtha. Finally, the hydrofining operation involves hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) of the various streams in a refinery. It is carried out at high pressures which depend on the type of feedstock. In general, HDN is more difficult than HDS, requiring higher temperatures and high hydrogen pressures. Temperatures range from 600-800°F, with pressures up to 300 psig, and hydrogen feed rates up to 3000 SCF/Bbl. Typical catalysts are cobalt molybdate on alumina and nickel tungsten on alumina for HDS and HDN, respectively.

These brief comments illustrate the variety of processes and products which should be considered in the discussion of the upgrading of coal liquids. They serve as background for the next two sections, which deal with Coalcon liquids and COED, H-Coal and Synthoil liquids, respectively.

III. UPGRADING OF HYDROCARBONIZATION LIQUIDS FROM THE COALCON PROCESS

A. INTRODUCTION

In 1975 Coalcon Co., an affiliate of Union Carbide and Chemico, received a $237.2 million contract from the Energy Research and Development Administration (then the Office of Coal Research) to build a coal-to-clean-liquid fuels demonstration plant. The project involves the design, construction and operation of a 2,600 ton/day demonstration plant using a hydrocarbonization process for producing 3,990 bbl/day of liquid product and 22 million cu. ft./day of pipeline quality gas.

Phase one of this project, already underway, entails a conceptual design of the demonstration plant. In phase two, additional work will be performed on this design. Both of these phases are being funded by ERDA. Phase three, plant construction scheduled for completion in 1979, and phase four, operation of the plant through mid-1983, will be co-funded by ERDA and private industry.

The process involves carbonization or pyrolysis of coal in the presence of a moderate hydrogen pressure ($\sim$550 psig). The coal is heated in the hydrocarbonization reactor producing liquid, gas and a solid product. The gas is separated from the liquid to produce synthetic natural gas (SNG) and liquified petroleum gas (LPG). The liquid is separated into a light and heavy fraction. These fractions have characteristics similar to a light to heavy petroleum naphtha and a light to medium gas oil, respectively. The solid char is used for fuel and hydrogen generation.

The Coalcon process, while based on known process steps (e.g. hydrocarbonization), is a relatively new project, and therefore little has been published in the literature concerning product quality and general process operation. However, sufficient data (2) do exist for the former to make judgments as to the catalytic processes which might be used for upgrading the liquid products. The purpose of this section is to discuss these processes and identify pertinent areas for research and development. First, a description is given of the conceptual design and operation of the Coalcon process. Next, the nature of the Hydrocarbonization liquid product is treated in some detail to provide a basis for defining the expected catalytic problems in upgrading these liquids. After summarizing these problems, the potential impact of research and development in catalysis (Part 1) and impacting disciplines (Part 2) on their solution is discussed in three parts: short term developments, long term developments and supporting research.

B. PROCESS DESCRIPTION

A simplified flow diagram for the Coalcon Hydrocarbonization process is shown in Figure III-1 (2). In a full size plant, coal containing 10% or less ash and 2.9% sulfur will be stockpiled at the mine and delivered to the Hydrocarbonization plant by conveyor at the rate of 15,000 tons per day. The coal will then be dried and sized to 50% through 100 mesh. Although the Coalcon process was originally developed to use low rank western coals of high moisture, high oxygen, high ash and low sulfur content, recent emphasis has been on the use of high volatility, high sulfur and medium ash coals. For example, Pittsburgh No. 8, Illinois No. 6 and Western Kentucky No. 11 are considered particularly attractive coals.

After preheating to 617°F, the coal is fed to the Hydrocarbonization reactor as a dense fluid phase from lock hoppers which operate at 900 psig.

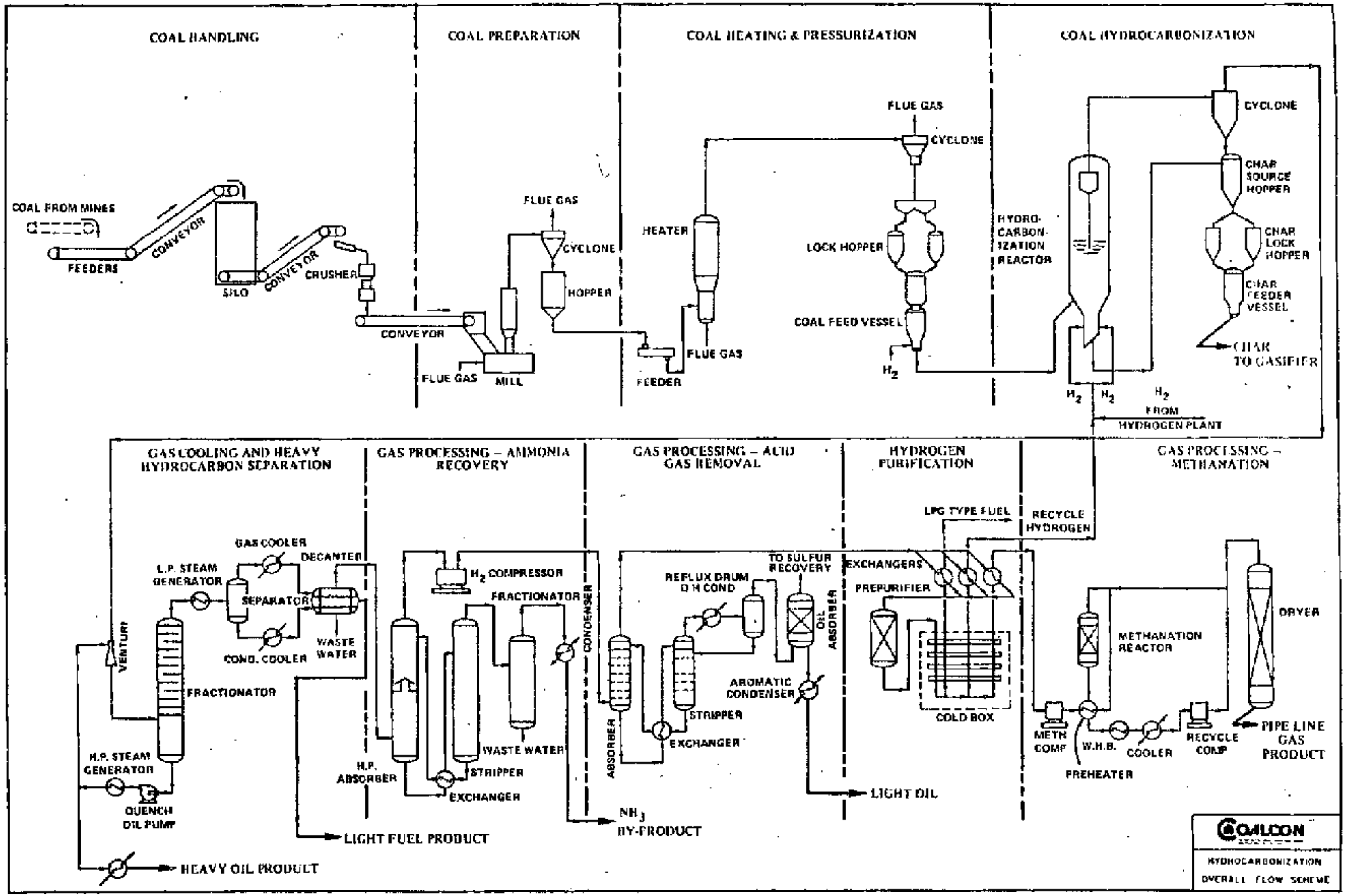

Figure III-1. Coalcon's Hydrocarbonization Process Flow Diagram (2)

Hydrogen is used as the carrier gas. Additional hydrogen from the Hydrogen Production Plant is mixed with recycled hydrogen, preheated and fed into the Hydrocarbonization reactor to fluidize the coal. The hydrocarbonization reaction takes place at 1040°F and 550 psig. Hydrocarbon vapors and gas leave the top of the reactor and char is discharged at the bottom.

The char exits through lock hoppers after being cooled to 600°F and stripped of hydrocarbons. It is ultimately cooled to about 200°F, pulverized and fed either to the Hydrogen Production Plant or to the plant steam boilers, which produce steam for process and steam turbine equipment.

The vapors which leave the top of the Hydrocarbonization reactor are cooled and condensed into heavy fuel oil and light hydrocarbons. The residual gases are treated by conventional technology to remove ammonia, hydrogen sulfide and carbon dioxide. The dried process gases are then separated cryogenically. Hydrogen is recycled to the reactor and a carbon monoxide, hydrogen, methane stream is fed to a methanation plant to make high Btu pipeline gas (SNG).

Hydrogen for the process is produced using the Texaco process which involves partial oxidative gasification of char, followed by carbon monoxide conversion in a water-gas shift converter and hydrogen sulfide removal. The purified hydrogen is then mixed with recycle gas and fed to the gasification reactor.

C. NATURE OF THE PRODUCT

To identify catalytic problems with the upgrading of Coalcon liquids, it is necessary to first discuss the nature of the liquid product. As mentioned earlier, the Coalcon process produces four primary fuel products:

- Liquified Petroleum Gas - LPG (7.3%)
- Synthetic Natural Gas - SNG (44.7%)

- Light Hydrocarbons (gasoline range) (14.3%)
- Heavy Fuel Oil (similar to No. 6 fuel oil) (33.7%)

From these data and those in Table III-1, it is clear that SNG and heavy fuel oil are primary products. A model which identifies the nature of the product composition has been developed to treat pilot plant results for eastern coals (2). The results are given in Tables III-2 to III-6, and are reported to have an accuracy of ± 10% (2). A detailed material balance for the various product streams from the Hydrocarbonization reactor is given in Tables III-7 to III-11. These data have been estimated by extrapolation of actual pilot plant results for Wyoming coal to that expected for eastern coals. It will be noted from the data in Tables III-7 to III-13 that the product slate involves very simple molecules. This may reflect an inadequacy in the extrapolation procedure or in the model itself. Because the information of the Coalcon process is not readily available and has been published only in a detailed report (reference 2), Tables III-1 to III-11 have been reproduced in their entirety. For the purpose of the present study, Tables III-10 and III-11 are of primary interest, as they present data which are representative of the heavy and light liquid fractions. The nature of these two fractions will now be discussed in more detail. (It should be noted that the exact distribution of each fraction can be modified to a certain degree by a change in process variables. However, such changes will not affect the present discussion).

1. HEAVY LIQUID FRACTION

The heavy liquid fraction from the Hydrocarbonization reactor has an approximate initial boiling point of 400°F and a final boiling point of 840°F (see Table III-6). As can be seen in Table III-12, this corresponds to a light and medium gas oil petroleum fraction with some

TABLE III-1

PRODUCT SUMMARY (2)

	Flow	Flow, #/hr	HHV Btu/lb	HHV Millions Btu/hr	HHV Percent of Coal
Heavy Fuel – Oil	13,153 Bbl/Day	207,212	16,441(3)	3,407	22.67
Gasoline Fraction	6,788 Bbl/Day	77,228	18,601(3)	1,437	9.56
LPG Fraction	4,387 Bbl/Day	34,695	21,421(1)	743	4.94
Pipeline SNG	105.00 MMSCFD	206,282	21,862(2)	4,510	30.01
Anhydrous Ammonia	48.8 T/D	4,070	9,674	39	0.26
Elemental Sulfur	352.4 T/D	29,366	3,980	117	0.77
Total Output				10,253	68.21
Feed Coal, MAF Basis	12,292 T/D	1,024,352			
Feed Coal, ROM (10% H_2O)	15,023 T/D	1,251,973			
Feed Coal, Dry Solids	13,521 T/D	1,126,777	13,336	15,026	100.0

(1) HHV = 96,800 Btu/Gallon (Gaseous Fuel Basis)

(2) HHV = 1,031 Btu/SCF

(3) HHV = 14,935 C + 51,319 H - 4,875 ϕ + 4,050 S (C, H, ϕS = Wt. Fr. Carbon, Hydrogen, Oxygen, Sulfur)

TABLE III-2

POSTULATED HYDROCARBON TYPE COMPOUND DISTRIBUTION IN REACTOR PRODUCT (2)

Postulated Reactor Effluent Composition	Percent
Hydrogen	7.66
Nitrogen	1.92
Carbon Monoxide	8.08
Methane	13.32
Ethane	6.59
Carbon Dioxide	5.38
Hydrogen Sulfide	1.90
Organic Sulfur Comp. (Carbonyl Sulfide, Carbon Disulfide, Thiophene)	0.35
Ammonia	0.53
Propane	3.07
N-Butane	1.05
N-Pentane	0.37
Cyclopentane	1.24
Benzene	0.65
Water	11.92
Toluene	1.89
Pyridine	3.18
P-Xylene	0.43
Propylbenzene	0.31
Mesitylene	1.27
Decane	3.35
Phenol	1.39
O-Cresol	1.97
Naphthalene	2.30
3,5 Xylenol	0.77
1-Methylnaphtalene	0.77
2-Naphtol	1.61
3-Methylphenanthrene	1.65
1-2 Benzofluorene	4.11
Chrysene	10.80
Char MAF Basis	0.10
Ash	0.03
Hydrochloric Acid	0.04
Total	100.0

TABLE III-3

CRUDE GAS PRODUCT FROM REACTOR (2)

	Percent	MMBtu/Day
Methane	66.9	59,222.4
Ethane	33.1	27,396.0
	100.0	86,618.4

TABLE III-4

CRUDE LPG COMPOUNDS FROM REACTOR (2)

	Percent	MMBtu Day
Propane	74.4	12,379.2
Butane	25.6	4,178.4
	100.0	16,557.6

TABLE III-5

LIGHT LIQUID HYDROCARBON COMPOUNDS FROM REACTOR (2)

(BP MINUS 400°F)

	ABP°F	Percent	MMBtu Day
N-Pentane	96.8	2.3	1,454.4
Cyclopentane	120.8	7.7	4,654.8
Benzene	176.2	4.0	2,147.5
Toluene	231.1	11.8	6,368.4
Pyridine	240.0	19.8	8.651.0
P-Xylene	280.5	2.7	1.470.5
Propylbenzene	319.0	1.9	1,077.4
Mesitylene	328.5	7.9	4,427.8
Decane	345.4	20.9	12,853.0
Phenol	358.7	8.7	3,822.2
O-Cresol	376.7	12.3	5.310.2
TOTAL		100.0	52,237.2

TABLE III-6

HEAVY LIQUID HYDROCARBON COMPOUNDS FROM REACTOR (2)

(Boiling Point +400°F)

	ABP°F	Percent	MMBtu Day
Naphthalene	411	10.5	7,382.2
3, 5 Xylenol	427	3.5	2,208.0
1-Methyl Naphthalene	468	3.5	2,508.5
2-Naphtol	563	7.3	4,439.5
3-Methyl Phenatrene	662	7.5	5,304.5
1-2 Benzofluorene	748	18.6	12.981.6
Chrysene	839	49.1	33,950.4
TOTAL		100.0	68,774.7

TABLE III-7

MATERIAL BALANCE
HYDROCARBONIZATION REACTOR PRODUCT (2)

	Description	Formula	Mol/Wt	Lb/Hr	Mol/Hr	Mol Fr
1.	Hydrogen	H_2	2.02	59354.47	29441.70	0.588644
2.	Nitrogen	N_2	28.01	14888.93	531.49	0.010626
3.	Carbon Monoxide	CO	28.01	62726.21	2239.39	0.044773
4.	Methane	CH_4	16.04	103339.54	6441.41	0.128787
5.	Ethane	C_2H_6	30.07	51142.15	1700.77	0.034004
6.	Carbon Dioxide	CO_2	44.01	41724.15	948.06	0.018955
7.	Hydrogen Sulfide	H_2S	34.08	14719.58	431.96	0.008636
8.	Carbonyl Sulfide	COS	60.07	107.53	1.79	0.000036
9.	Propane	C_3H_8	44.10	23831.73	540.44	0.010805
10.	Ammonia	NH_3	17.03	4113.60	241.54	0.004829
11.	N-Butane	C_4H_{10}	58.12	8175.14	140.65	0.002812
12.	N-Pentane	C_5H_{12}	72.15	2879.55	39.91	0.000798
13.	Carbon Disulfide	CS_2	76.13	768.16	10.09	0.000202
14.	Cyclopentane	C_5H_{10}	70.13	9614.11	137.08	0.002741
15.	Benzene	C_6H_6	78.11	5039.13	64.51	0.001290
16.	Thiophene	C_4H_4S	84.14	1847.63	21.96	0.000439
17.	Water	H_2O	18.02	92488.90	5133.28	0.102644
18.	Toluene	C_7H_8	92.14	14639.36	158.88	0.003177
19.	Pyridine	C_5H_5N	79.10	24670.24	311.88	0.006236
20.	P-Xylene	C_8H_{10}	106.17	3331.60	31.38	0.000627
21.	Propylbenzene	C_9H_{12}	120.19	2394.28	19.92	0.000398
22.	Mesitylene	C_9H_{12}	120.19	9839.16	81.86	0.001637
23.	Decane	$C_{10}H_{22}$	142.29	25979.35	182.59	0.003651
24.	Phenol	C_6H_6O	94.11	10817.39	114.94	0.002298
25.	O-Cresol	C_7H_8O	108.14	15307.27	141.55	0.002830
26.	Naphthalene	$C_{10}H_8$	128.17	17855.50	139.31	0.002785
27.	3, 5 Xylenol	$C_8H_{10}O$	122.17	5993.53	49.06	0.000981
28.	Methylnaphthalene	$C_{11}H_{10}$	142.20	5966.75	41.96	0.000839
29.	2-Naphthol	$C_8H_{10}O$	144.17	12521.46	86.85	0.001736
30.	Methylphenanthrene	$C_{15}H_{12}$	192.26	12830.17	66.73	0.001334
31.	1-2 Benzofluorinc	$C_{17}H_{12}$	216.28	31870.33	147.35	0.002946
32.	Chrysene	$C_{18}H_{12}$	228.29	83806.73	367.10	0.007340
33.	Hydrogen Chloride	HCL	36.46	298.26	8.18	0.000164
	Coal, MAF Basis			0.00		
	Char, MAF Basis			805.44		
	Ash			194.56		
	Total		15.49	775881.94	50016.18	
	Carbon	C	12.01	447051.80		
	Hydrogen	H	1.01	135780.28		
	Nitrogen	N	14.01	22653.65		
	Oxygen	O	16.00	154627.43		
	Sulfur	S	32.06	15288.64		
	Chlorine	CL	35.45	290.58		
	Ash			194.56		
	Total			775881.9HWS		
	Pressure, PSIA			555.00		
	Temperature, Deg. F			1040.00		

TABLE III-8

MATERIAL BALANCE - PIPELINE (2)

	Description	Formula	Mol/Wt	1099 Lb/Hr	1099 Mol/Hr	1099 Mol Fr
1.	Hydrogen	H_2	2.02	1482.57	735.40	0.063793
2.	Nitrogen	N_2	28.01	6628.28	236.64	0.020527
3.	Carbon Monoxide	CO	28.01	288.51	10.30	0.000893
4.	Methane	CH_4	16.04	139199.98	8676.68	0.752662
5.	Ethane	C_2H_6	30.07	48973.20	1628.64	0.141277
6.	Carbon Dioxide	CO_2	44.01	1232.27	28.00	0.002429
7.	Hydrogen Sulfide	H_2S	34.08	0.00	0.00	0.000000
8.	Carbonyl Sulfide	COS	60.07	0.00	0.00	0.000000
9.	Propane	C_3H_8	44.10	201.96	4.58	0.000397
10.	Ammonia	NH_3	17.03	0.00	0.00	0.000000
11.	N-Butane	C_4H_{10}	58.12	0.00	0.00	0.000000
12.	N-Pentane	C_5H_{12}	72.15	0.00	0.00	0.000000
13.	Carbon Disulfide	CS_2	76.13	0.00	0.00	0.000000
14.	Cyclopentane	C_5H_{10}	70.13	0.00	0.00	0.000000
15.	Benzene	C_6H_6	78.11	0.00	0.00	0.000000
16.	Thiophene	C_4H_4S	84.14	0.00	0.00	0.000000
17.	Water	H_2O	18.02	20.00	1.11	0.000096
18.	Toluene	C_7H_8	92.14	0.00	0.00	0.000000
19.	Pyridine	C_5H_5N	79.10	0.00	0.00	0.000000
20.	P-Xylene	C_8H_{10}	106.17	0.00	0.00	0.000000
21.	Propylbenzene	C_9H_{12}	120.19	0.00	0.00	0.000000
22.	Mesitylene	C_9H_{12}	120.19	0.00	0.00	0.000000
23.	Decane	$C_{10}H_{22}$	142.29	0.00	0.00	0.000000
24.	Phenol	C_6H_6O	94.11	0.00	0.00	0.000000
25.	O-Cresol	C_7H_8O	108.14	0.00	0.00	0.000000
26.	Naphthalene	$C_{10}H_8$	128.17	0.00	0.00	0.000000
27.	3, 5 Xylenol	C_8H_{100}	122.17	0.00	0.00	0.000000
28.	Methylnaphthalene	$C_{11}H_{10}$	142.20	0.00	0.00	0.000000
29.	2-Naphthol	C_8H_{100}	144.17	0.00	0.00	0.000000
30.	3-Methyl Phenantrene	$C_{15}H_{12}$	192.27	0.00	0.00	0.000000
31.	1-2 Benzofluorine	$C_{17}H_{12}$	216.29	0.00	0.00	0.000000
32.	Chrysene	$C_{18}H_{12}$	228.29	0.00	0.00	0.000000
33.	Hydrogen Chloride	HCL	36.46	0.00	0.00	0.000000
34.	Argon	Ar	39.95	8255.27	205.64	0.017925
	Coal, MAF Basis					
	Char, MAF Basis			0.00		
	Argon					
	Total		17.68	206282.04	11527.99	
	Carbon	C	12.01	143963.85		
	Hydrogen	H	1.01	46356.13		
	Nitrogen	N	14.01	6628.28		
	Oxygen	O	16.00	1078.52		
	Sulfur	S	32.06	0.00		
	Chlorine	CL	35.45	0.00		
	Ash			0.00		
	Argon			8255.27		
	Total			206282.04		
	Pressure, PSIA			800.00		
	Temperature, Deg. F			146.00		

TABLE III-9

MATERIAL BALANCE - LPG (2)

	Description	Formula	Mol/Wt	963 Lb/Hr	963 Mol/Hr	963 Mol Fr
1.	Hydrogen	H_2	2.02	0.00	0.00	0.000000
2.	Nitrogen	N_2	28.01	0.00	0.00	0.000000
3.	Carbon Monoxide	CO	28.01	0.00	0.00	0.000000
4.	Methane	CH_4	16.04	0.00	0.00	0.000000
5.	Ethane	C_2H_6	30.07	318.14	10.58	0.014906
6.	Carbon Dioxide	CO_2	44.01	0.00	0.00	0.000000
7.	Hydrogen Sulfide	H_2S	34.08	0.00	0.00	0.000000
8.	Carbonyl Sulfide	COS	60.07	0.00	0.00	0.000000
9.	Propane	C_3H_8	44.10	22465.66	509.46	0.717772
10.	Ammonia	NH_3	17.03	0.00	0.00	0.000000
11.	N-Butane	C_4H_{10}	58.12	7017.31	120.73	0.170095
12.	N-Pentane	C_5H_{12}	72.15	1908.39	26.45	0.037265
13.	Carbon Disulfide	CS_2	76.13	0.00	0.00	0.000000
14.	Cyclopentane	C_5H_{10}	70.13	2984.95	42.56	0.059962
15.	Benzene	C_6H_6	78.11	0.00	0.00	0.000000
16.	Thiophene	C_4H_4S	84.14	0.00	0.00	0.000000
17.	Water	H_2O	18.02	0.00	0.00	0.000000
18.	Toluene	C_7H_8	92.14	0.00	0.00	0.000000
19.	Pyridine	C_5H_5N	79.10	0.00	0.00	0.000000
20.	P-Xylene	C_8H_{10}	106.17	0.00	0.00	0.000000
21.	Propylbenzene	C_9H_{12}	120.19	0.00	0.00	0.000000
22.	Mesitylene	C_9H_{12}	120.19	0.00	0.00	0.000000
23.	Decane	$C_{10}H_{22}$	142.29	0.00	0.00	0.000000
24.	Phenol	C_6H_{60}	94.11	0.00	0.00	0.000000
25.	O-Cresol	C_7H_{80}	108.14	0.00	0.00	0.000000
26.	Naphthalene	$C_{10}H_8$	128.17	0.00	0.00	0.000000
27.	3, 5 Xylenol	C_8H_{100}	122.17	0.00	0.00	0.000000
28.	Methylnaphthalene	$C_{11}H_{10}$	142.20	0.00	0.00	0.000000
29.	2-Naphthol	C_8H_{100}	144.17	0.00	0.00	0.000000
30.	Methylphenanthrene	$C_{15}H_{12}$	192.26	0.00	0.00	0.000000
31.	1-2 Benzofluorine	$C_{17}H_{12}$	216.28	0.00	0.00	0.000000
32.	Chrysene	$C_{18}H_{12}$	228.29	0.00	0.00	0.000000
33.	Hydrogen Chloride	HCL	36.46	0.00	0.00	0.000000
	Coal, MAF Basis			0.00		
	Char, MAF Basis			0.00		
	Ash			0.00		
	Total		48.88	34694.45	709.78	
	Carbon	C	12.01	28556.27		
	Hydrogen	H	1.01	6138.18		
	Nitrogen	N	14.01	0.00		
	Oxygen	O	16.00	0.00		
	Sulfur	S	32.06	0.00		
	Chlorine	CL	35.45	0.00		
	Ash			0.00		
	Total			34694.45		
	Pressure, PSIA			435.00		
	Temperature, Deg. F			104.00		

TABLE III-10

MATERIAL BALANCE - HEAVY OIL PRODUCT (2)

	Description	Formula	Mol/Wt	609 Lb/Hr	609 Mol/Hr	609 Mol Fr
1.	Hydrogen	H_2	2.02	0.28	0.10	0.000078
2.	Nitrogen	N_2	28.01	0.00	0.00	0.000000
3.	Carbon Monoxide	CO	28.01	0.00	0.00	0.000000
4.	Methane	CH_4	16.04	4.97	0.31	0.000242
5.	Ethane	C_2H_6	30.07	9.32	0.31	0.000242
6.	Carbon Dioxide	CO_2	44.01	41.81	0.95	0.000743
7.	Hydrogen Sulfide	H_2S	34.08	29.31	0.86	0.000672
8.	Carbonyl Sulfide	COS	60.07	0.00	0.00	0.000000
9.	Propane	C_3H_8	44.10	14.55	0.33	0.000258
10.	Ammonia	NH_3	17.03	7.49	0.44	0.000344
11.	N-Butane	C_4H_{10}	58.12	15.11	0.26	0.000203
12.	N-Pentane	C_5H_{12}	72.15	15.15	0.21	0.000164
13.	Carbon Disulfide	CS_2	76.13	12.94	0.17	0.000133
14.	Cyclopentane	C_5H_{10}	70.13	129.05	1.84	0.001438
15.	Benzene	C_6H_6	78.11	117.95	1.51	0.001180
16.	Thiophene	C_4H_4S	84.14	63.94	0.76	0.000594
17.	Water	H_2O	18.02	60.17	3.34	0.002011
18.	Toluene	C_7H_8	92.14	472.68	5.13	0.004010
19.	Pyridine	C_5H_5N	79.10	13160.15	166.37	0.180061
20.	P-Xylene	C_8H_{10}	106.17	202.78	1.91	0.001493
21.	Propylbenzene	C_9H_{12}	120.19	234.38	1.95	0.001524
22.	Mesitylene	C_9H_{12}	120.19	1495.23	12.44	0.009725
23.	Decane	$C_{10}H_{22}$	142.29	990.31	6.96	0.006441
24.	Phenol	C_6H_6O	94.11	3801.24	40.39	0.031575
25.	O-Cresol	C_7H_8O	108.14	14748.19	136.38	0.106616
26.	Naphthalene	$C_{10}H_8$	128.17	17855.92	139.31	0.108907
27.	3, 5 Xylenol	C_8H_{100}	122.17	5735.76	46.95	0.036703
28.	Methylnaphthalene	$C_{11}H_{10}$	142.20	5966.75	41.96	0.032803
29.	2-Naphthol	C_8H_{100}	144.17	12521.46	86.85	0.067896
30.	Methylphenanthrene	$C_{15}H_{12}$	192.26	12829.58	66.73	0.052167
31.	1-2 Benzofluorine	$C_{17}H_{12}$	216.28	31869.30	147.35	0.115192
32.	Chrysene	$C_{18}H_{12}$	228.29	83806.73	367.10	0.286983
33.	Hydrogen Chloride	HCL	36.46	0.00	0.00	0.000000
	Coal, MAF Basis			0.00		
	Char, MAF Basis			805.44		
	Ash			194.56		
	Total		161.21	207212.43	1279.17	
	Carbon	C	12.01	187104.74		
	Hydrogen	H	1.01	12405.09		
	Nitrogen	N	14.01	2349.59		
	Oxygen	O	16.00	5063.56		
	Sulfur	S	32.06	89.34		
	Chlorine	CL	35.45	0.56		
	Ash			194.56		
	Total			207212.43		
	Pressure, PISA			14.70		
	Temperature, Deg. F			104.00		

TABLE III-11

MATERIAL BALANCE -
LIGHT OIL PRODUCT (2)

	Description	Formula	Mol/Wt	640 Lb/Hr	640 Mol/Hr	640 Mol Fr
1.	Hydrogen	H_2	2.02	0.10	0.05	0.000065
2.	Nitrogen	N_2	28.01	0.00	0.00	0.000000
3.	Carbon Monoxide	CO	28.01	0.00	0.00	0.000000
4.	Methane	CH_4	16.04	6.74	0.42	0.000542
5.	Ethane	C_2H_6	30.07	51.42	1.71	0.002206
6.	Carbon Dioxide	CO_2	44.01	131.59	2.99	0.003857
7.	Hydrogen Sulfide	H_2S	34.08	126.08	3.70	0.004773
8.	Carbonyl Sulfide	COS	60.07	3.60	0.06	0.000077
9.	Propane	C_3H_8	44.10	661.01	14.99	0.019337
10.	Ammonia	NH_3	17.03	36.11	2.12	0.002735
11.	N-Butane	C_4H_{10}	58.12	687.03	11.22	0.015248
12.	N-Pentane	C_5H_{12}	72.15	891.79	12.36	0.015945
13.	Carbon Disulfide	CS_2	76.13	309.09	4.06	0.005237
14.	Cyclopentane	C_5H_{10}	70.13	6347.22	90.51	0.116760
15.	Benzene	C_6H_6	78.11	4719.65	60.42	0.077943
16.	Thiophene	C_4H_4S	84.14	1301.58	15.47	0.019957
17.	Water	H_2O	18.02	0.00	0.00	0.000000
18.	Toluene	C_7H_8	92.14	14112.32	153.16	0.197580
19.	Pyridine	C_5H_5N	79.10	5974.55	75.53	0.097435
20.	P-Xylene	C_5H_{10}	106.17	3109.66	29.29	0.037785
21.	Propylbenzene	C_9H_{12}	120.19	2146.68	17.86	0.023040
22.	Mesitylene	C_9H_{12}	120.19	8337.93	69.37	0.089489
23.	Decane	$C_{10}H_{22}$	142.29	24989.69	175.63	0.226567
24.	Phenol	C_6H_{60}	94.11	2590.00	27.52	0.035501
25.	O-Cresol	C_7H_{80}	108.14	435.81	4.03	0.005199
26.	Naphthalene	$C_{10}H_8$	128.17	0.00	0.00	0.000000
27.	3, 5 Xylenol	C_8H_{100}	122.17	257.77	2.11	0.002722
28.	Methylnaphthalene	$C_{11}H_{10}$	142.20	0.00	0.00	0.000000
29.	2-Naphthol	C_6H_{100}	144.17	0.00	0.00	0.000000
30.	3-Methyl Phenantrene	$C_{15}H_{12}$	192.26	0.00	0.00	0.000000
31.	1-2 Benzofluorine	$C_{17}H_{12}$	216.28	0.00	0.00	0.000000
32.	Chrysene	$C_{18}H_{12}$	228.29	0.00	0.00	0.000000
33.	Hydrogen Chloride	HCL	36.46	0.00	0.00	0.000000
	Coal, MAF Basis			0.00		
	Char, MAF Basis			0.00		
	Ash			0.00		
	Total		99.63	77228.11	775.18	
	Carbon	C	12.01	65791.69		
	Hydrogen	H	1.01	8836.78		
	Nitrogen	N	14.01	1037.62		
	Oxygen	O	16.00	635.18		
	Sulfur	S	32.06	876.84		
	Chlorine	CL	35.45	0.00		
	Ash			0.00		
	Total			77228.11		
	Pressure, PSIA			14.70		
	Temperature, Deg. F			104.00		

TABLE III-12

PROPERTIES OF COMMON PETROLEUM FRACTIONS

Fraction	Carbon Number Range	Approximate Boiling Range, °F
Gases (LPG)	C_1-C_4	32
Light Naphtha	C_5-C_7	80-200
Heavy Naphtha	C_6-C_{10}	200-350
Kerosene	C_9-C_{15}	300-500
Light Gas Oil	C_{13}-C_{18}	400-650
Medium Gas Oil	C_{16}-C_{25}	600-750
Heavy Gas Oil	$>C_{22}$	>725-1050
Lube Oils/Waxes	$>C_{22}$	>725-1000
Residuum	$>C_{40}$	>1050

TABLE III-13

SUMMARY OF PERTINENT DATA FOR HEAVY LIQUID HYDROCARBON COMPOUNDS FROM COALCON PROCESS

COMPOUND	AMOUNT IN LIQUID PRODUCT	
	WEIGHT PERCENT	MOLE PERCENT
P-N-A FRACTION		
Paraffins		
Decane	0.5	0.06
Others	0.03	0.111
Total Paraffins	0.53	0.171
Naphthenes		
Cyclopentane	0.6	0.144
Aromatics		
Benzene	0.06	0.118
Toluene	0.20	0.401
p-Xylene	0.10	0.149
Propylbenzene	0.10	0.152
Mesitylene	0.70	0.973
Naphthalene	8.6	10.89
Methylnaphthalene	2.9	3.28
Methylphenanthrene	6.2	5.22
1-2 Benzofluorene	15.4	11.52
Chrysene	40.4	28.70
Total Aromatics	74.66	61.40
HETEROATOM FRACTION		
Oxygenated Compounds		
Phenol	1.8	3.16
o-Cresol	7.1	10.66
3,5 Xylenol	2.8	3.67
2-Naphthol	6.0	6.79
Total Oxygenated Compounds	17.7	24.28
Sulfur Compounds		
Thiophene	0.03	0.06
Nitrogen Compounds		
Pyridine	6.4	18.0
Miscellaneous		
Ash	0.9	-
H_2O	0.03	0.20

contribution from the heavy gas oil fraction. Pertinent data from Table III-10, which give a material balance for the heavy oil product, are summarized in Table III-13. The hydrocarbon constituents may be conveniently divided into two broad groups, the paraffin-naphthenic-aromatic (P-N-A)[a] fraction and the heteroatom fraction (cf. Table III-13).

The data of Table III-13 show that the liquid product is primarily aromatic, with aromatic compounds comprising almost 75 wt.% of the total and 99% of P-N-A fraction. The aromatic constituents in the P-N-A fraction are primarily polynuclear aromatics as indicated by the relatively large amounts of two and four ring compounds such as chrysene and 1-2 benzofluorene which reportedly comprise 75 wt.% of the aromatic fraction. The benzene, toluene and xylene (BTX) fraction is very low, about 1.6 wt.% of the total aromatic content. The fact that there are no data reported for more complex molecules such as those described in Section IV for the H-coal, COED and Synthoil processes is an indication of the limitation of this model. Therefore, these compounds can be considered only as representative of the qualitative aspects of composition.

The heavy liquid fraction contains a substantial amount of heterocyclic compounds, with 24 wt.% of the total liquids containing sulfur, nitrogen or oxygen. The primary heteroatoms are oxygen and nitrogen, the former making up 17.7 wt.% of the total liquids and 73 wt.% of the heterocycles, and the latter 6.4 wt.% of the total liquids and 26 wt.% of the heterocycles. The data suggest that the oxygen is spread throughout a number of hydroxyaromatics whereas the nitorgen is concentrated predominantly in pyridine. Similarly, the small amount of sulfur present in these liquids (.03 wt.%) is in the form of thiophene. Although this distribution may be correct, it is likely

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[a] Not to be confused with polynuclear aromatic fraction

that more complex pyridine and thiophene molecules are involved. A final point to note for the heavy liquid fraction is that it contains about .09 wt.% ash which could present processing problems by deposition on the catalyst.

2. LIGHT LIQUID FRACTION

The light liquid fraction boils in the 97-377°F range which corresponds to a light to heavy petroleum naphtha (cf. Tables III-5 and III-12). The data from Table III-11, which gives a material balance for the light oil product, are summarized in Table III-14. As with the heavy oil product, the constituents have been divided into two groups, the P-N-A fraction and the heteroatom fraction.

In contrast to the heavy oil product, the light oil is less aromatic. The P-N-A fraction makes up 84.8 wt.% of the total light liquid product and of this 40.7 wt.% is paraffinic, 9.7 wt.% naphthenic and 49.6% wt.% aromatic. The paraffinic product is weighted towards higher molecular weights (93.6 wt.% of paraffin product is decane). The only naphthene identified is cyclopentane and this is present at a relatively low level (8 wt.%) as compared to most petroleum naphtha fractions. As with the heavy oil fraction, the light oil product contains a large fraction of aromatics (~42 wt.%). As will be discussed later and as is apparent from Table III-15, the BTX aromatic constituents have good octane blending characteristics.

The heteroatom content is lower than that found in the heavy oil, however, it is still substantial. It accounts for 13.7 wt.% of the total light oil with 31 wt.% of this fraction being oxygenated compounds (hydroxyaromatics), 12 wt.% thiophenic sulfur and 57 wt.% heterocyclic nitrogen as pyridine.

The above mentioned chemical compositions will be used later in a discussion of catalytic upgrading and the problems which are expected to be involved in such processes.

TABLE III-14

SUMMARY OF PERTINENT DATA FOR LIGHT OIL PRODUCT HYDROCARBON COMPOUNDS FROM COALCON PROCESS

COMPOUND	AMOUNT IN LIQUID PRODUCT WEIGHT PERCENT	 MOLE PERCENT
P-N-A FRACTION		
Paraffins		
Methane	0.009	0.05
Ethane	0.067	0.22
Propane	0.080	1.93
n-Butane	0.89	1.53
n-Pentane	1.15	1.60
Decane	32.36	22.66
Total Paraffins	34.556	27.99
Naphthenes		
Cyclopentane	8.22	11.68
Aromatics		
Benzene	6.11	7.78
Toluene	18.27	19.76
p-Xylene	4.03	3.78
Propylbenzene	2.78	2.30
Mesitylene	10.80	8.95
Total Aromatics	41.99	42.58
HETEROATOM FRACTION		
Oxygenated Compounds		
Phenol	3.35	3.55
o-Cresol	0.56	0.52
3,5 Xylenol	0.33	0.27
Total Oxygenated Compounds	4.24	4.34
Sulfur Compounds		
Thiophene	1.69	2.00
Nitrogen Compounds		
Pyridine	7.74	9.74

TABLE III-15

BLENDING RESEARCH OCTANE NUMBER FOR PURE HYDROCARBON CONSTITUENTS IN THE LIGHT OIL FRACTION FROM THE COALCON PROCESS (3)

Compound	RON (Clear)[a]
n-Butane	113
n-Pentane	62
Benzene	99
Toluene	124
P-xylene	146
n-Propylbenzene	127
Mesitylene	171

(a) Calculated value of pure hydrocarbon from research method rating of clear mixture of 20% hydrocarbon and 80% primary reference fuel (60% iso-octane + 40% n-heptane).

D. SUMMARY OF CONSTRAINTS AND PROCESS REQUIREMENTS FOR UPGRADING COALCON LIQUIDS

To identify the catalytic problems in upgrading Coalcon liquids to refined fuel products, it is useful to consider the physical and chemical characteristics of the starting liquid feedstock and the catalytic processes which might be used for conversion to a product with the desired specifications. In contrast to the situation for synthoil, H-Coal and COED liquids, few data have been reported for Coalcon liquids upgrading. Therefore, anticipated processing problems by necessity must be extrapolated from the reported chemical and physical properties of Coalcon liquids, and by analogy to processing of similar coal liquids or petroleum fractions. For convenience, the upgrading of heavy and light Coalcon liquid fractions are treated separately in the following discussion.

1. UPGRADING OF THE HEAVY LIQUID FRACTION: GENERAL PROBLEMS

The heavy liquid fraction (b.p. 400-800^{o}F) is similar in physical and chemical characteristics to No. 6 fuel oil. In terms of the common refined fuels discussed in Section II-A, one can consider upgrading this feed to gasoline, stationary turbine fuel, and refined (low sulfur and nitrogen) heating oils. Because of the high aromatic character of this feedstock, jet and diesel fuels are not practical candidates for primary products as the combustion characteristics for these fuels require a substantial paraffinic component. However, it should be noted that with more severe conversion it would be possible to produce a light aromatic blending stock which could be used in jet and diesel fuels. Upgrading to gasoline, turbine fuel and refined heating oils presents two basic problems: selective cracking of the high molecular weight polynuclear aromatic constituents to lighter aromatics and reduction of the heteroatom content to an acceptable level.

The aromaticity is particularly a problem, since 75 wt.% of the heavy liquid fraction is aromatic and of this, 99 wt.% consists of high molecular weight polynuclear aromatics, primarily 1-2 benzofluorene and chrysene. These four ring compounds must be selectively cracked to one and two ring compounds to reduce molecular weight and thereby give improved burning characteristics. For a gasoline fraction, selective cracking leads to high octane constituents (BTX). In any cracking process, high levels of polynuclear aromatics also promote carbon deposition and consequent catalyst deactivation. This is less of a problem for hydrocracking than catalytic cracking because the catalysts used in the former process contain a hydrogenation function which improves activity maintenance by hydrogenating coke precursors. Selective cracking is also important to minimize light gas (C_4^-) production and thereby maximize the liquid (C_5^+) yield.

The high level of heteroatom content in the Coalcon heavy liquid product presents the second general problem. As mentioned in Section III.C, 24 wt.% of the total heavy liquid product contains heterocyclic sulfur, nitrogen and oxygen, and primarily the latter two elements. Nitrogen, reported as pyridine, makes up 17.7 wt.% of this 24 wt.% and hydroxyaromatics make up most of the remainder. The sulfur level (as thiophene) is low at .03 wt.%. The implications of these figures are that nitrogen must be reduced to a level which gives an environmentally acceptable NO_x emission upon combustion. In upgrading these liquids to motor gasoline or lighter aromatic feedstocks, an additional constraint presents itself: <u>the basic pyridine structure can poison catalysts containing an acid function</u>. Thus, cracking of the heavy coal liquid feed (without denitrogenation) and subsequent blending with naphtha or middle distillate stocks which are ultimately processed either in a cracking or reforming operation could lead to catalyst poisoning for the latter two processes. Therefore, the pyridine content must be reduced not only for environmental reasons, but also to prevent catalyst poisoning in processing the heavy liquid or derivative products.

The high oxygen and ash content of the heavy liquids is also a potential problem. The presence of hydroxyaromatics can affect the stability of these liquids, in particular during storage. However, it should be noted that the oxygen is likely to be removed in any hydrodenitrogenation operation by carbon-oxygen hydrogenolysis reactions. (It is difficult to anticipate at this point how much of this oxygen must be removed.)

Finally, mention should be made of the ash levels, which are reported to be of the order of 0.1 wt.%. While this is not substantial, it is definitely a problem for a fixed-bed process in which all of the ash can be deposited on the catalyst. It could be a problem for special applications such as turbine fuels. It may be necessary to reduce the ash level by about one order of magnitude for a continuous catalytic upgrading step. An alternative would be to vacuum distill and leave the bottoms for boiler fuel or hydrogen production.

2. UPGRADING OF THE HEAVY LIQUID FRACTION: SPECIFIC APPLICATIONS

As mentioned above, the heavy oil fraction is best suited for upgrading to refined heating and fuel oils, motor gasoline and turbine fuels. While jet and diesel fuels are potential products, their production would involve extensive hydrocracking and the use of large quantities of costly hydrogen since these fuels are highly paraffinic in nature.

Refined heating and fuel oils would require some cracking to reduce the molecular weight of the Coalcon heavy liquid fraction to give the appropriate properties (e.g. viscosity, pour point, flash point, gravity, etc.) for a given application. Heating oils usually have a boiling range of 325-645°F, however, heavier fuel oils correspond quite closely in boiling range (400-840°F) to the Coalcon heavy oil product. The primary upgrading step which is necessary is denitrogenation. Some hydrocracking would be necessary to make lighter fuel oils (e.g. #3 or #4).

Conversion of the heavy oil fraction to <u>motor gasoline</u> would require hydrocracking and denitrogenation to a product which is primarily one and two ring aromatics. The presence of a substantial amount of polynuclear aromatics (primarily 1-2 benzofluorene and chrysene) is likely to promote carbon deposition during catalytic cracking. It will also be difficult to selectively crack these large aromatic molecules to single ring aromatics with minimum gas (C_4^-) production.

The requirements for upgrading the Coalcon heavy oil fraction to <u>turbine fuel</u> can be deduced from the specifications in Table II-1. The constraint of 1.0 wt.% maximum sulfur is easily met by the heavy oil product (.03 wt.% sulfur as thiophene). The hydrogen content of the oil, however, is low and will have to be increased. This can be seen by the fact that chrysene ($C_{18}H_{12}$) contains 5.3 wt.% hydrogen. The minimum specification for hydrogen in a stationary turbine fuel is 11.3 wt.% (Table II-1). For comparison, benzene has a hydrogen content of 7.7 wt.%, cyclohexane 14.3 wt.% and heptane 16 wt.%. It is expected that some hydrocracking would be necessary to meet the hydrogen specification and also to give the appropriate specific gravity, viscosity and conradson carbon content shown in Table II-1. Denitrogenation would also be necessary to meet existing and anticipated NO_x standards. Finally, the stringent constraint of minimizing mineral content (particularly sodium, potassium, lead, vanadium and calcium) is pertinent in view of the 0.1 wt.%

mineral content in the Coalcon heavy liquid product. This level could cause substantial degradation of turbine blades if a significant fraction of this mineral content included the above mentioned elements. It is probable that any hydrofining operation which reduced molecular weight and removed nitrogen would also remove some of the mineral content by deposition on the catalyst. This is especially the case for a fixed bed process. However, this of course can lead to catalyst deactivation.

A final option for upgrading the heavy liquid product would be recycle hydrocracking to extinction to produce a light gasoline blending stock, a heavy naphtha catalytic reforming feedstock, and a jet and diesel fuel blending stock.

3. LIGHT LIQUID FRACTION

The light liquid fraction from the Coalcon process is similar to motor gasoline. However, as shown in Table III-14, the paraffinic component is primarily decane, it is low in naphthenes (only cyclopentane reported) and is highly aromatic in character. The only upgrading which need be considered for this fraction is desulfurization (1.69 wt.% thiophene) and denitrogenation (7.74 wt.% pyridine). HDS and HDN should be easier for this fraction than the heavier fraction. After hydrotreating to remove the sulfur and nitrogen to adequate levels, this fraction could be blended to give high octane gasoline. If the high level of decane presents an engine operability problem, two options are apparent. First, the hydrotreated light liquid fraction could be mixed with a light naphtha stock and processed through a reformer. This would convert a substantial fraction of the decane to higher octane branded paraffinic isomers (isomerization) and aromatics (dehydrocyclization). A second option would be to use the light liquid as an aromatic blending stock for jet fuel. The