



Catalysts for upgrading solvent refined lignite
by Nam Kyun Kim

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemical Engineering
Montana State University
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Abstract:

The solvent refined lignite (SRL), made at the University of North Dakota Process Development Unit, was a solid having a nominal melting point of 160°C. The SRL was pulverized and mixed with a donor solvent, tetralin. The SRL to tetralin ratio of 1:1 was selected to pretreat in a high pressure and temperature reactor. The optimized reactor conditions were a reaction temperature of 475°C, an initial hydrogen pressure of 2000 psig and a retention time of 40 minutes. Under these conditions approximately 97% of the SRL was dissolved in tetralin. The resulting solution was used to test the 27 developmental catalysts.

The catalysts were developed by impregnating on the γ -alumina the 3 active metals; MoO₃, CoO, and WO₃, each at 3 levels. The effect of these factors on upgrading of the SRL was evaluated in terms of denitrogenation, desulfurization, and hydrocracking. The multiple linear regression analysis showed that the metal compositions for the best overall catalytic performance were 9.5% MoO₃, 4.3% CoO, and 4% WO₃ (% of carrier weight).

A model was developed based on the results of scanning electron micrographs to explain some of the physical characteristics of the catalysts. The disadvantage of the incipient wetness method used in metal impregnation was explained, and the preferable pore structure and distribution were suggested.

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APPROVAL

of a thesis submitted by

Nam Kyun Kim

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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TABLE OF CONTENTS

	Page
APPROVAL PAGE	ii
STATEMENT OF PERMISSION TO USE	iii
ACKNOWLEDGMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xi
INTRODUCTION	1
BACKGROUND	3
Lignite	5
Solvent Refined Lignite	5
Chemical Structure of Lignite	10
Liquefied Lignite	12
Catalytic Upgrading	15
Catalyst	17
Trickle Bed Reactor	20
Research Objective	20
EXPERIMENTAL	22
Feedstock	22
Preparation of Catalysts	24
Continuous Trickle Bed Reactor	30
Operation of Continuous Trickle Bed Reactor	32
Analytical Procedure	33
RESULTS AND DISCUSSION	34
Preparation of Feed Solution	34
Performance Tests	46
Effect of Metal Compositions on Upgrading	50
Development of A Model for Catalyst	75

	Page
SUMMARY AND CONCLUSIONS	92
RECOMMENDATION FOR FUTURE STUDY	94
LITERATURE CITED	95
APPENDICES	100
A. Surface Area and Pore Distribution of Catalyst Carriers	101
B. Sample Calculation of Pore Volumes	119
C. ASTM D-86 Distillation Data	123
D. Modeling of Katalco Carrier	127

LIST OF TABLES

Table	Page
I. Composition and Characteristics of Feed and Products.....	9
II. Analyses of SRL and North Dakota Lignites.....	23
III. Analysis of Ash.....	24
IV. Systematic Preparation of 27 Catalysts.....	26
V. Summary of the First 15 Batch Runs.....	35
VI. Effect of Water Addition on Catalytic Performance.....	37
VII. SRL Dissolubility at Various Operating Conditions.....	40
VIII. SRL Dissolubility at Extended Operating Conditions.....	42
IX. Catalytic Performances: KT-14 vs. Blank Carrier.....	47
X. Nitrogen Removal With KT Series Catalysts.....	49
XI. Summary of Catalytic Performance.....	52
XII. Analysis of Variance for Three Factors at Three Levels.....	60
XIII. Multiple Regression Analysis for Denitrogenation.....	61
XIV. Analysis of Variance for Desulfurization as Response Variables.....	70
XV. Multiple Regression Analysis for Desulfurization.....	71
XVI. Multiple Regression Analysis for Gasoline Yield.....	76
XVII. Multiple Regression Analysis for Heavy Oil Yield.....	77
XVIII. Comparison of Various Catalysts.....	83
XIX. Pore Volume and Surface Area Following 10% MoO ₃ , 4% CoO, and 8% WO ₃ Impregnation on Katalco Carrier.....	85
XX. Pore Volume and Surface Area Following 10% MoO ₃ , 4% CoO, and 8% WO ₃ Impregnation on Nalco A Carrier.....	86

LIST OF FIGURES

Figure	Page
1. Coal fields in the Northern Great Plains province	4
2. Schematic flow diagram for 50 lb/hr PDU with mass rates and run conditions.	8
3. Chemical precursors of coal.	11
4. Representative partial structures of coal	13
5. Comparison of lignite with other sources of hydrocarbon.	14
6. A theoretical molecule and thermal breakup of coal (Wiser)	16
7. Approximate reaction routines for the HDS, HDN, and HDO from five membered heterorings in the presence of catalyst.	18
8. A 3-D representation of 3 ³ experimental design	27
9. Electric furnace and auxiliary equipment for sulfidation of catalyst.	29
10. Trickle bed reactor arrangement	31
11. Effect of water addition in wt% denitrogenation and wt% desulfurization	38
12. Effect of reactor temperature and retention time at two levels of hydrogen pressure on SRL dissolubility in tetralin	41
13. Effect of reactor temperature on SRL dissolubility in tetralin at two levels of retention time.	44
14. Effect of hydrogen pressure on SRL dissolubility at two different temperature levels	45
15. Effect of retention time on SRL dissolubility in tetralin at 475°C and 2000 psig of H ₂	45
16. Catalytic performance of KT-14 against blank base in denitrogenation	48
17. ASTM D-86 distillation, feed and 8-hr composite product of blank carrier	51

Figure	Page
18. Catalytic performance in denitrogenation as a function of MoO_3 concentration	54
19. Catalytic performance in denitrogenation as a function of CoO , WO_3 , and MoO_3 concentrations	55
20. Catalytic performance in denitrogenation as a function of CoO concentration	56
21. Catalytic performance in denitrogenation as a function of MoO_3 , WO_3 , and CoO concentrations	57
22. Catalytic performance in denitrogenation as a function of WO_3 concentration	58
23. Catalytic performance in denitrogenation as a function of MoO_3 , CoO , and WO_3 concentrations	59
24. Catalytic performance in desulfurization as a function of MoO_3 concentration	63
25. Catalytic performance in desulfurization as a function of CoO , WO_3 , and MoO_3 concentrations	64
26. Catalytic performance in desulfurization as a function of CoO concentration	65
27. Catalytic performance in desulfurization as a function of MoO_3 , WO_3 , and CoO concentrations	66
28. Catalytic performance in desulfurization as a function of WO_3 concentration	67
29. Catalytic performances in desulfurization as a function of MoO_3 , CoO , and WO_3 concentrations	68
30. Catalytic performance in hydrocracking as a function of CoO , WO_3 , and MoO_3 concentrations	72
31. Catalytic performance in hydrocracking as a function of MoO_3 , WO_3 , and CoO concentrations	73
32. Catalytic performance in hydrocracking as a function of MoO_3 , CoO , and WO_3 concentrations	74

Figure	Page
33. Scanning electron photomicrographs of various catalysts:	
(A) Katalco blank carrier	78
(B) KT-14 with 10% MoO ₃ , 4% CoO, and 8% WO ₃ on Katalco carrier	78
(C) KT-14 after 8-hr run	78
(D) Union Carbide Linde 13X with 10% MoO ₃ , 4% CoO, and 8% WO ₃	79
(E) Ketjen LA-3P with 10% MoO ₃ , 4% CoO, and 8% WO ₃	79
(F) Nalco A with 10% MoO ₃ , 4% CoO, and 8% WO ₃	80
(G) Harshaw CoMo 0401 with 9% MoO ₃ and 3% CoO	80
34. Three dimensional arrangement of basic granules for Katalco carrier	81
35. Effect of catalyst pore diameter on denitrogenation	84
36. Surface area distribution vs. pore diameter	88
37. Distribution of MoO ₃ vs. pore diameter	89
38. Representative structures of pore	90

ABSTRACT

The solvent refined lignite (SRL), made at the University of North Dakota Process Development Unit, was a solid having a nominal melting point of 160°C. The SRL was pulverized and mixed with a donor solvent, tetralin. The SRL to tetralin ratio of 1:1 was selected to pretreat in a high pressure and temperature reactor. The optimized reactor conditions were a reaction temperature of 475°C, an initial hydrogen pressure of 2000 psig and a retention time of 40 minutes. Under these conditions approximately 97% of the SRL was dissolved in tetralin. The resulting solution was used to test the 27 developmental catalysts.

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A model was developed based on the results of scanning electron micrographs to explain some of the physical characteristics of the catalysts. The disadvantage of the incipient wetness method used in metal impregnation was explained, and the preferable pore structure and distribution were suggested.

INTRODUCTION

Currently the United States consumes close to 80 quadrillion Btu (quads) per year, importing increasing amounts of oil to meet its needs. The United States by 1978 already imported almost 8.5 million barrels of oil per day—over 17 quadrillion Btu per year. It is generally recognized that this level of imports is unhealthy for the U.S. economy. Every worker in the United States consumes 1.55 billion Btu per year for all purposes of employment [1]. If employment is to continue to grow, energy will have to be supplied to the society in increasing amounts from coal. Production of oil and natural gas is declining at an annual rate of about 4 to 5%. Nearly 45% of the petroleum that is currently produced has been obtained by water flooding and other secondary recovery techniques applied to mature fields [2].

In the present United States environment of decreasing availability of petroleum and natural gas, coal is a natural candidate for the raw material for liquids and gases. The reasons for this are that the United States has more energy available in the form of coal than in the combined sources of petroleum, natural gas, oilshale, and tar sands. The use of coal for energy will certainly increase in the United States during the next several decades. Utilization of domestically abundant coal, both for the production of power and as a feedstock in synthetic fuels production, will require processing operations on a large commercial scale [3].

The transportation sector demands exclusively liquid fuels, the residential and commercial sectors depend heavily on gaseous fuels, and three quarters of the energy used by industry are constituted as liquid and gaseous fuels [2]. Consequently, the conversion of

coal to gaseous and liquid fuels in commercial quantities is vital to ensuring the availability of fuel in conventional forms for the major users.

Coal gasification and liquefaction processes were pioneered during the 1920s and 1930s in Germany. They constitute the basis for much of today's technology. The accomplishment of Friederich Bergius [4] brought him the Nobel Prize for chemistry in 1931. His direct hydrogenation of coal at elevated temperature (430°C or 806°F) and pressures (3,000-10,000 psig) led to the production of gasoline and aviation fuel. At the same time Mathias Pier and co-workers found sulfur resistant, coal-hydrogenation catalysts that reduced the severity of the environment for liquefaction while improving conversion efficiency. The production of synthetic fuels from coal will have justification due to the convenience of using liquids and gases and due to the ways in which transportation and domestic systems have been developed [5].

BACKGROUND

The United States Geological Survey estimated that the lignite shares 6% of the demonstrated coal reserve base (437 billion tons). The lignite in the Northern Great Plains (NGP) occurs in relatively thick seams ranging from 5 ft to more than 100 ft and typically with overburden from 50 to 200 ft. The ratio of "overburden volume to lignite volume" is most favorable when compared with that of higher ranking coal [6].

Most significant is the fact that the NGP surface mineable reserve base totals 82.3 billion tons or 58% of the national surface mineable reserve base. More than 95% of these resources are lignite and subbituminous (classified as low rank coals) occurring in the Fort Union and Powder River Regions and the Bull Mountain Field (Figure 1).

Nearly 100% of NGP coal mined since the 1960s has been used to generate electricity, but the future potential for the production of synthetic fuels and chemicals is increasing. Since 1971, plans for construction of seventeen separate mine-mouth coal synfuel plants in the NGP have been announced. These plans include eight separate gasification plants, nine liquefaction plants, and two in-situ gasification pilot operations [7].

The first commercial scale synthetic fuels project, the Great Plains Gasification Plant (GPGP) of Oliver County, North Dakota, has already begun on July 25, 1980 and is scheduled for full gas production by the end of 1984 [8]. Project Lignite, equivalent to the SRC-I, was awarded to the University of North Dakota in 1972 for the purpose of determining the appropriate technological approach to the conversion of lignite to clean fuel. The original plan was expected to extend the two stage conversion of lignite to liquid fuel (equivalent to the SRC-II) with the solvent refined lignite (SRL) as an intermediate solid fuel. The first stage to convert lignite to the SRL has been successfully accomplished,

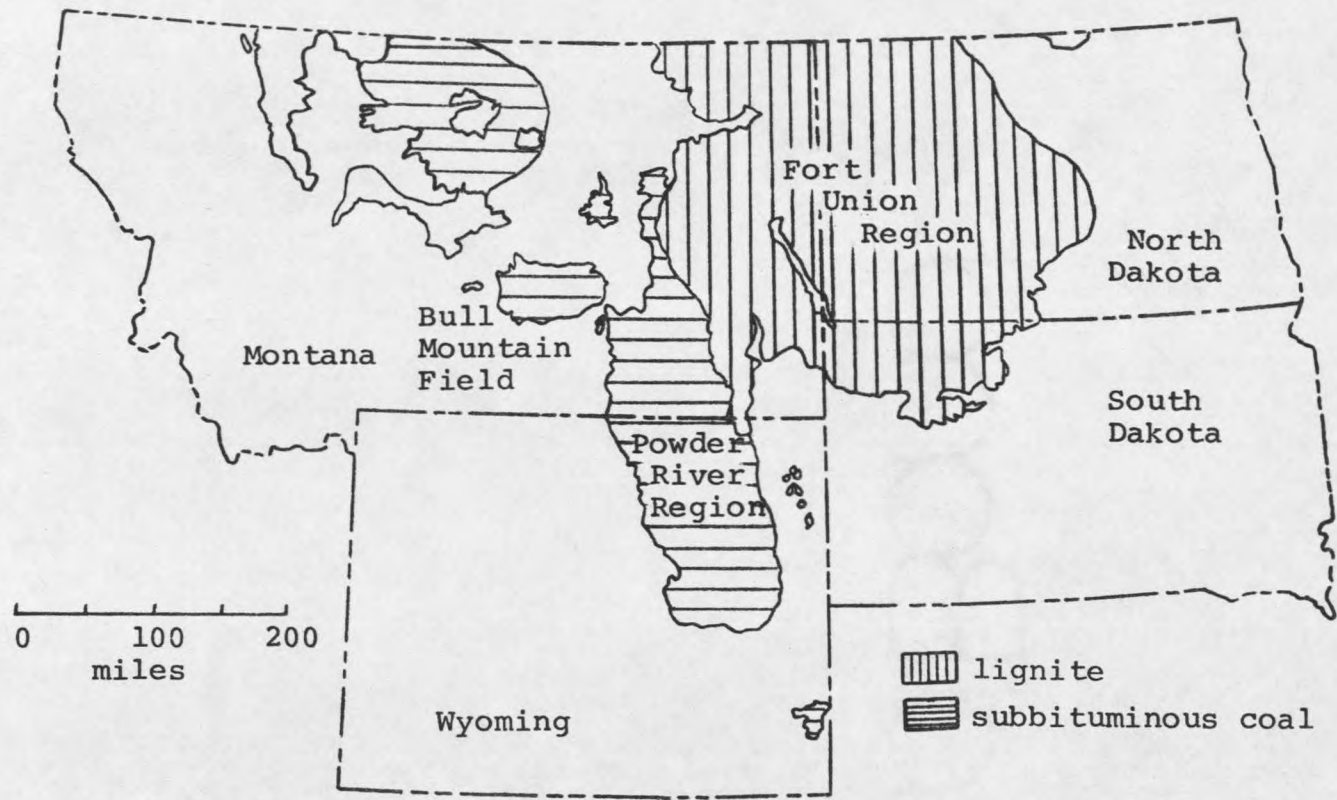


Figure 1. Coal fields in the Northern Great Plains province.

but the second stage that catalytically hydrotreats the SRL to the distillate fuel was not implemented [9].

The objective of this research is to catalytically upgrade the SRL to liquid fuel for immediate industrial use or to clean distillate suitable for conventional refinery feedstock.

Lignite

Lignite is a brownish-black coal that is intermediate in coalification between peat and subbituminous coal. According to the classification system adopted by the American Society for Testing and Materials (ASTM), the lignite is the lowest rank of coals in terms of calorific value (less than 8300 Btu per pound on a moisture, mineral-matter-free basis) and carbonaceous content (47 to 59%) [10].

While the use of lignite to generate electricity will predominate other uses, a strong potential also exists for the conversion of lignite to synthetic fuels. The Great Plains Gasification Plant is designed to convert the North Dakota lignite into pipeline quality synthetic natural gas (SNG) having about 977 Btu per standard cubic foot (scf). Approximately 137 million scf per day of SNG and other byproducts such as anhydrous ammonia, tar, oil, phenols, and naphtha will be produced by processing 22,000 tons per day of lignite. Lignite displays unique properties: (1) its high reactivity evidenced by spontaneous combustion, (2) non-coking and non-swelling nature with high permeability upon heating, and (3) excellent sulfur absorbent qualities [6].

Solvent Refined Lignite

The Project Lignite Process Development Unit [11] has a normal design capacity of 50 pounds of lignite feed per hour and produces light liquids and gases in addition to approximately 15 pounds per hour of SRL having a melting point of 150 to 205°C (300 to 400°F).

Lignite as received is pulverized to slurry with solvent. The slurry is pressurized, preheated and reacted at a selected temperature (normally at 434°C or 814°F) and pressure (2500 psig) in a reducing gas environment. The products are then separated as gases, liquids, and SRL from the unreacted coal and mineral matters. The flow rate of solvent to the slurry mixing tank is controlled by the signals from an orifice in the solvent feed line. The flow out of the tank is controlled by the slurry level in the tank.

Two dissolvers (or reactors), R-1A and R-1B, are made from 18-ft lengths of 4 7/8-inches OD by 3 7/8-inches ID Incoloy 800 tubing. The inlet of each reactor is at the bottom and the outlet at the top, with another outlet at the center. Thus any multiple of 10 ft lengths up to 40 ft can be assembled. Consequently, residence times for the slurry can be varied four-fold at a constant feed rate.

The gas-slurry mixture then goes to a series of separators at high, intermediate, and low pressures. The vapor products consist primarily of unreacted carbon monoxide and hydrogen, carbon dioxide, hydrogen sulfide, ammonia and light hydrocarbons.

The liquid products consist mainly of water, process solvent, and lighter products. Light end column F-2 is operated at 10 to 15 psig. The overhead product is light oil, essentially a stabilized naphtha, consisting of hydrocarbons ranging from about C₅ to perhaps as high as 350°F to 450°F boiling point. The bottom product is recycled to the slurry mix tank.

Mineral separation consists of a system of vessels and pumps designed for the high temperature extraction of solvent refined lignite plus solvent from the mineral matter and unconverted lignite using toluene as a diluent. The toluene-slurry mixture is then fed to the vacuum flash drum F-1 via the settling tower V-8 (18 inch diameter by 12 ft high) in which the terminal velocity of the settling particles is greater than fluidizing solvent (toluene) and SRL velocity.

The bottoms from the toluene flash vessel V-9 is fed through preheater E-11 and into the vacuum flash drum F-1. The bottoms from F-1 is the SRL product.

A typical PDU operation is shown in a flow schematic for Run M-33C (Figure 2). In this run, 47 lb/hr of average 36.7% moisture lignite was processed with 407 scf/hr of gas containing 50% H₂ and 50% CO, 91 lb/hr of recycle in the liquid-solid separation system. The rough material balance is shown, as well as pressures and temperatures in the important vessels. The 100 lb of moisture and ash free (MAF) lignite produced 57.4 lb of SRL and light organic liquids, consuming 7.8 lb of CO, 0.04 lb of H₂, and 2.38 lb of water with a wt % MAF coal conversion of 93.4 [12].

A typical composition and characteristics of SRL product from Zap lignite are shown in Table I. Generally it has been customary to classify the quality of the coal products in terms of solubility classes. Oils are hexane soluble fractions, while asphaltenes are terms used for benzene or toluene soluble materials. The benzene insoluble material is preasphaltene (some prefer the term asphaltols or polar compounds) which are soluble in pyridine. The primary product of coal is pyridine soluble, but benzene insoluble. This fraction is subsequently converted to both benzene-soluble and hexane-soluble species through liquefaction process.

Hexane-soluble materials (oils) average about 200-300 in molecular weight. They have little or no functionality. Asphaltenes, on the other hand, are predominantly mono-functional compounds. They consist of phenols and basic nitrogens. Molecular weights range from 300 to 700. Asphaltols have multiple functionality. They consist of polyphenols (up to 5 OH/molecule) and multiple basic nitrogens. Molecular weights range from 400 to 2000 or greater [13]. Conversion in this case is defined as conversion of coal to material soluble in pyridine. This fraction is not found in petroleum and suggests a considerable basic difference between coal and petroleum structure. Low hydrogen content and high

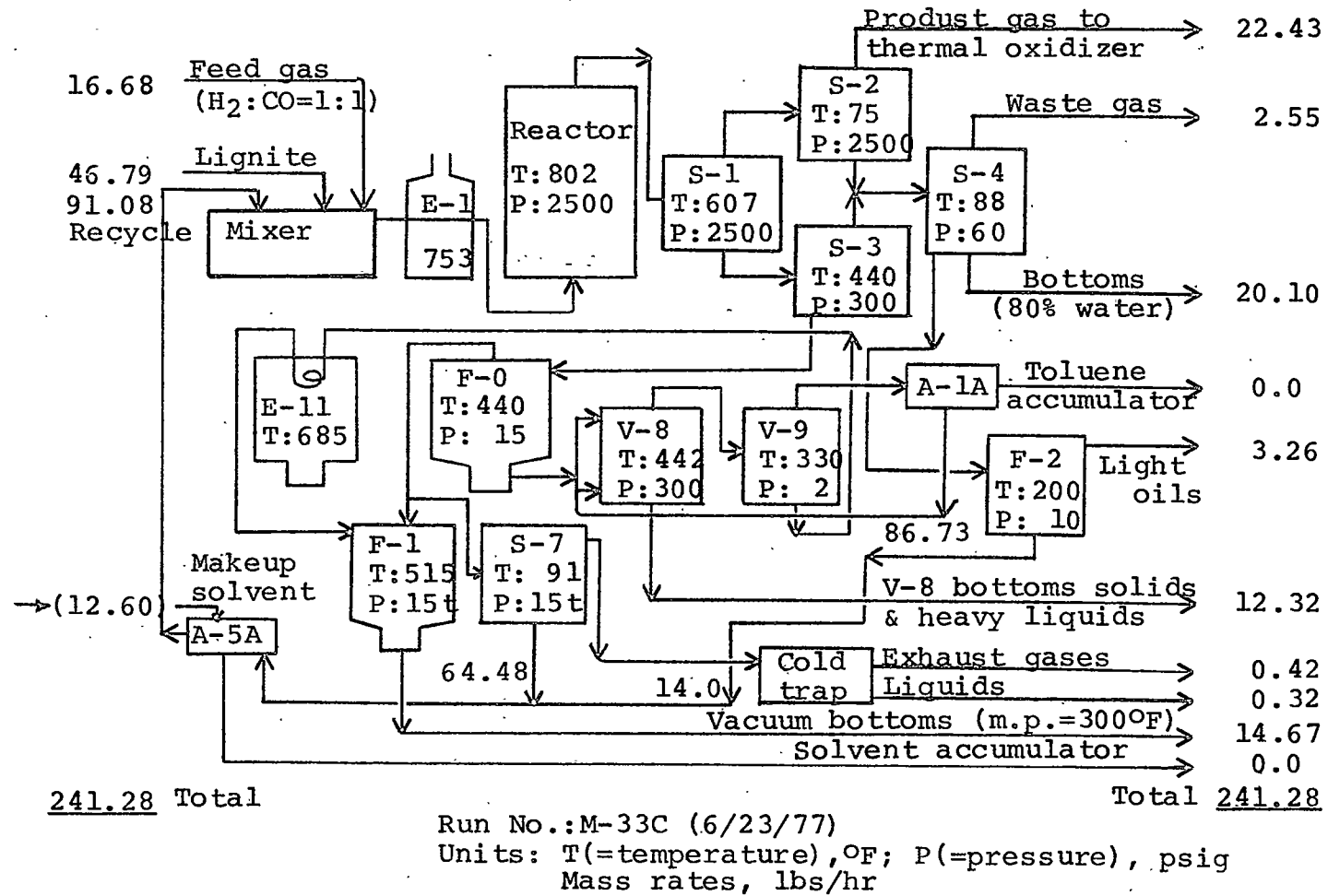


Figure 2. Schematic flow diagram for 50 lb/hr PDU with mass rates and run conditions.

Table I

Composition and Characteristics of Feed and Products

Feed Gas (Project Lignite PDU)

	<u>Vol. %</u>	<u>Wt. %</u>
CO	24.7	81.9
H ₂	75.2	17.8

Material Balance for Gas Components

	<u>Vol% In</u>	<u>Vol% Out</u>	<u>lb/hr In</u>	<u>lb/hr Out</u>
H ₂	75.2	66.2	2.13	1.87
CO	24.7	14.4	9.78	5.81
CO ₂	-	13.2	-	9.91
H ₂ S	-	0.2	-	0.18
CH ₄	-	4.5	-	1.11
C ₂ H ₆	-	1.1	-	0.58
C ₃ H ₈	-	0.3	-	0.33
NH ₃	-	0.1	-	0.04

Ultimate Analysis of Materials

	<u>Lignite Charged</u>	<u>Starting Solvent</u>	<u>Recycle Solvent</u>	<u>Vacuum Bottoms</u>	<u>Deashed SRL</u>
C	45.22	89.03	83.60	80.20	87.42
H	6.43	8.11	9.14	5.20	5.67
N	0.64	0.12	0.20	0.98	1.07
S	0.45	2.23	1.09	0.90	0.98
O*	41.45	0.51	5.97	4.46	4.86
Ash	5.81	0.0	0.0	8.26	0.0

* By difference

Properties of Product SRL

	<u>Measured*</u>	<u>Calculated</u>
Gradient Bar Melting Point, F	327	-
Pyridine Solubles, wt% ash-free	83.5	100
Specific Gravity	1.28	1.25
Heat of Combustion, Btu/lb	14,330	15,990

* F-1 vacuum bottoms

Lignite: North American Coal Co., Zap, N.D.
 Screen size 90%-200 mesh, 100%-60 mesh
 Moisture 31.5%

heteroatom content, compared to petroleum, make coal somewhat intractable with conventional refining technology.

The solvent-refining process consists mainly of conversion of insoluble coal to the pyridine-soluble, toluene-insoluble fraction of SRL. The net result is an increase in aromaticity and some bond breakage, loss of about 20% of the original carbon as gases and volatile liquids, and possible reduction of oxygen, nitrogen, and sulfur.

Chemical Structure of Lignite

It is generally agreed that coal may originate primarily from plants. Through a sequence of evolutionary changes the primary products of the original decomposed plant materials become transformed. The first product is humic acid. Then, the humic acid is transformed eventually into peat, lignite, subbituminous coal, bituminous coal, and finally anthracite [14].

The United States coals consist of primarily vitrinite, usually 80% or more. The composition of this vitrinite is believed to be the result of the coalification of either cellulose or lignin structures, which constitute the majority of the plant components [15]. Some of the chemical precursors of coal are shown in Figure 3.

Lignite is considered to be a crosslinked amorphous polymer, with mostly monoaromatic aggregates connected by relatively weak cross-links. Generally there have been two approaches to deducing chemical structure. One way is to break down the coal material into recognizable fragments and then put them back into an original structure. An alternative approach is direct characterization of solid coal with the use of sophisticated instruments such as IR spectroscopy, NMR spectroscopy and X-ray diffraction. These modern techniques are also severely handicapped because coal is not crystalline and insoluble.

These advanced techniques such as X-ray scattering have been used in the past and conflicting interpretations as to the predominant structure of coal have been reported.

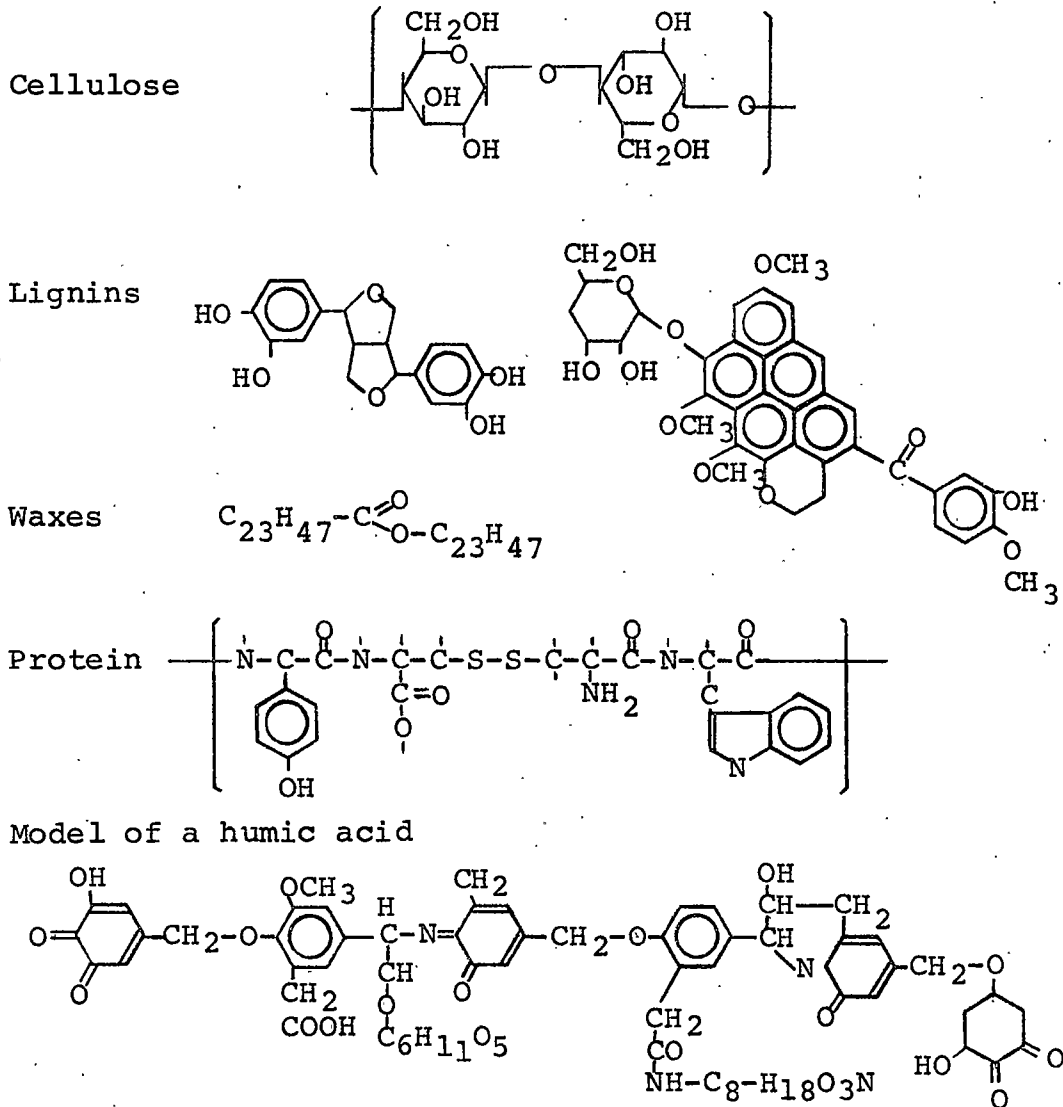


Figure 3. Chemical precursors of coal.

New instruments have evolved recently that are capable of direct characterization in its solid form. The most promising of these tools is a solid state CP-C¹³ NMR developed by Pines [16].

Wender indicated that the carbon skeleton of coals can be considered as consisting of hydroaromatic structure with aromaticity increasing from low-rank to high-rank coals. Figure 4 shows some frames of reference for various ranks of coal [17].

Liquefied Lignite

Coal has chronic problems in utilization. It is a solid of non-uniform composition inorganic material and environmentally objectionable elements such as sulfur, nitrogen, mercury, etc. Conversion of lignite to liquids or gases substantially reduces these disadvantages for lignite. The most important chemical change required for this conversion is the addition of hydrogen (hydrogenation). The amount of hydrogen addition determines the quality of the synthetic product. A comparison of some representative fuels illustrates in Figure 5 the scale of hydrogen/carbon mole ratio [14]. Lignite has a lower hydrogen content than that characteristic of premium quality transportation fuels like gasoline and diesel oil. It can be seen that there is a long path necessary in the conversion of lignite to high quality products.

Liquefaction of coals where the liquid products are the main product has been known for many years since the first work by Bergius. Subsequent development of the process of coal liquefaction have led to a variety of process conditions for producing liquids. The term liquid may need to be defined since some products of coal liquefaction are solids at room temperatures. The degree of conversion can be measured by the amount of material soluble in a certain organic solvent [2].

Wiser [18] showed in 1975 a schematic representation of structural groups and connecting bridges in bituminous coal. It may consist of layers of condensed aromatic and

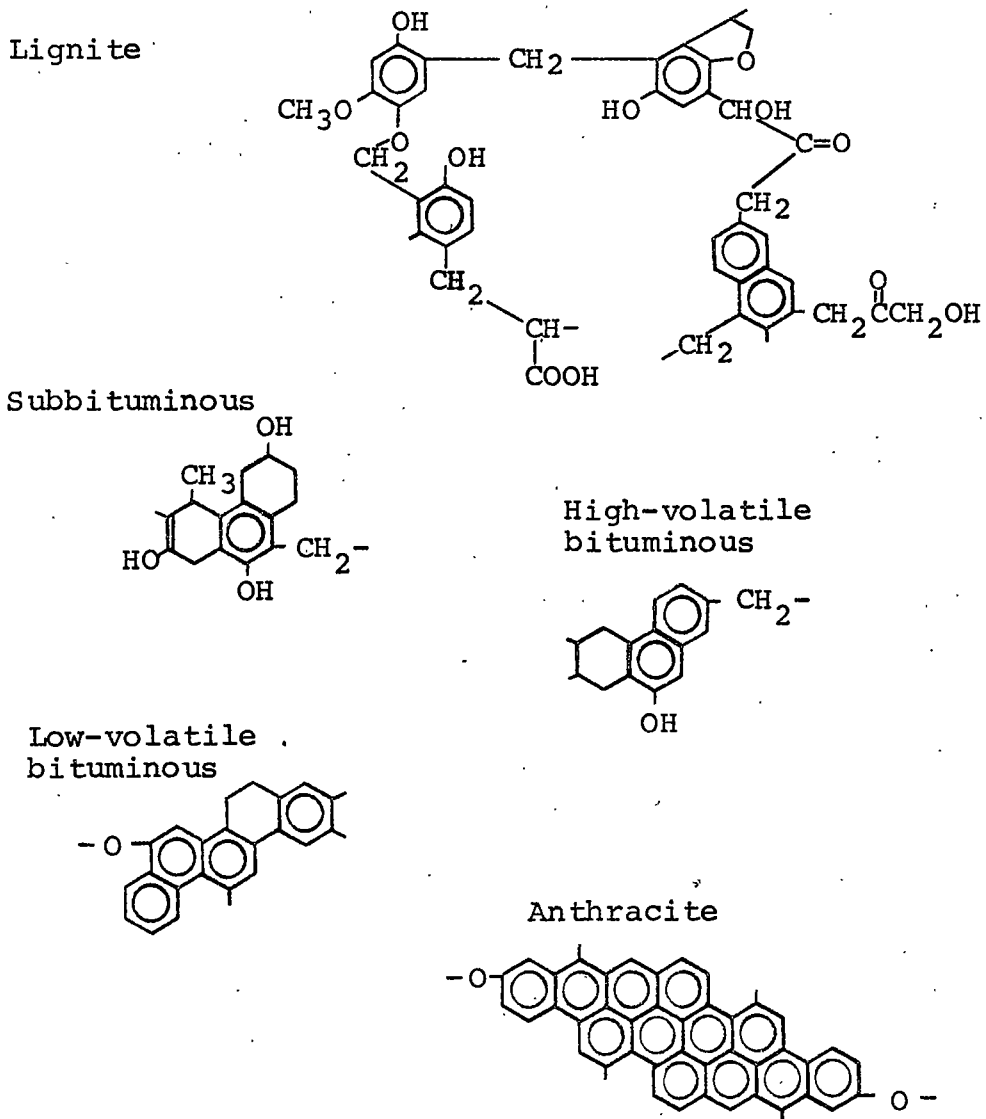


Figure 4. Representative partial structures of coal.

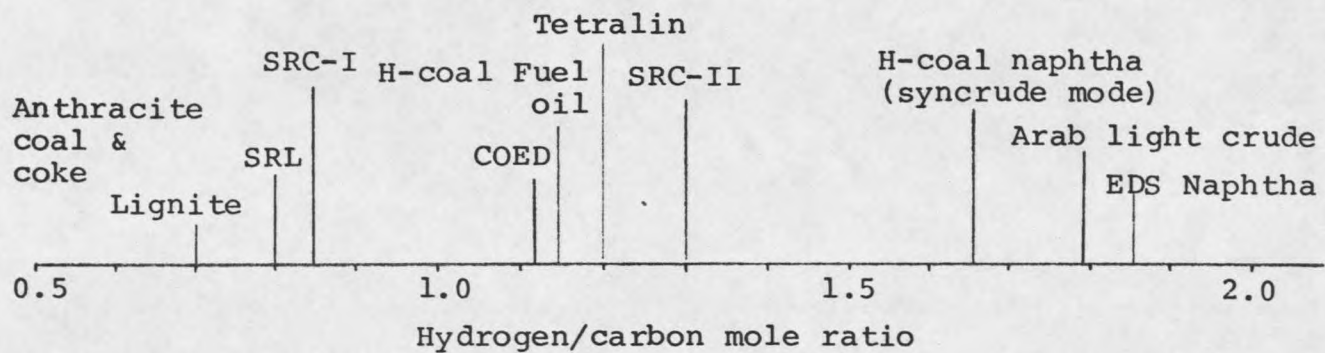
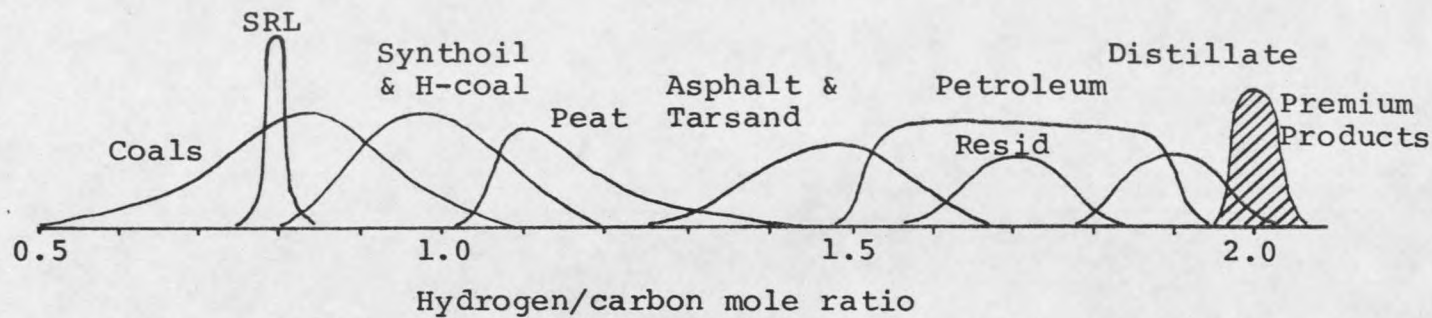


Figure 5. Comparison of lignite with other sources of hydrocarbon.

hydroaromatic clusters ranging in sizes from one to several rings per cluster with an average of three rings per condensed configuration. The significance of these theoretical molecules is the location of a number of relatively weak bonds indicated by arrows which can account for the easy thermal breakup of coal into smaller more soluble fragments (Figure 6).

Catalytic Upgrading

In the process of the hydrogenation of lignite to produce synthetic liquid some removal of heteroatoms (sulfur, nitrogen, and oxygen) is also accomplished. Sulfur and nitrogen contents of lignite are often greater than 1% and oxygen content is sometimes over 20%. Such heteroatoms are responsible for some of the coal conversion and upgrading problems. Upgrading process not only improves the heating value of the fuel but also makes resulting products more environmentally acceptable.

Hydrogenation of liquefied coal is slower than that of petroleum crudes because of the abundance of the polynuclear aromatic compounds. Oxygen is removed primarily as carbon dioxide and water with small amounts of carbon monoxide. About 40-50% of the oxygen and organic sulfur is relatively easy to remove. It is believed to be the result of exchange of OH or carbonyl oxygen by sulfur, due to biological activity in the sediment [19]. The remaining sulfur is much more resistant to removal and is probably present in heterocyclic ring structures.

Removal of S, N, and O from SRL under reducing conditions and in the presence of an industrial catalyst is associated with elimination of hydrogen sulfide, ammonia, and water. Prior to these reactions, C-Y (Y = S, N, or O) bonds may have to be broken, and the fission of one of these bonds may be the rate controlling step [20].

Heterocyclic S, N, and O containing rings are well known for their high resistivity to removal. Ring saturation may be required for N containing compound, while there is some

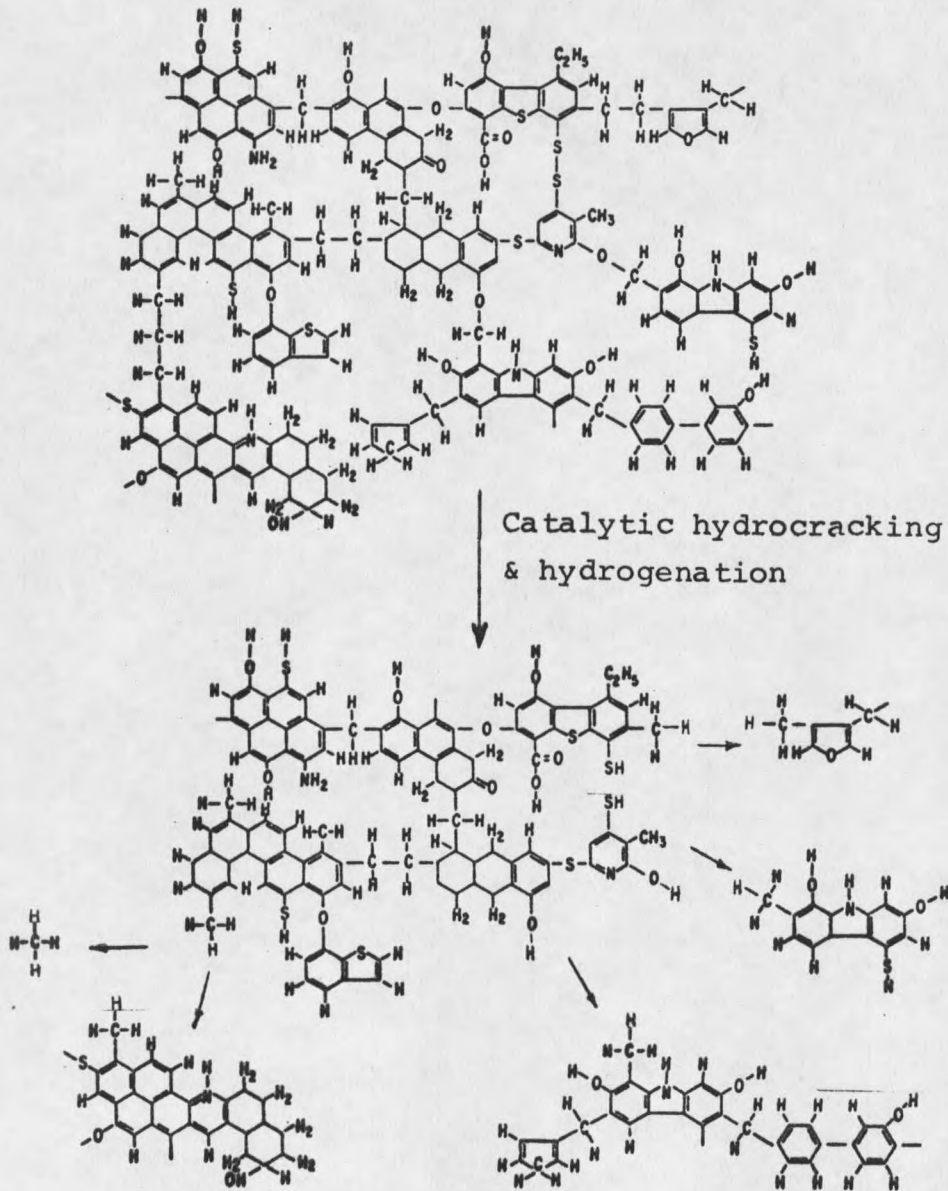


Figure 6. A theoretical molecule and thermal breakup of coal (Wiser).

experimental evidence for the HDS with or without preliminary heteroring hydrogenation [21].

The basic routes for hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) of heterocyclic compounds are shown in Figure 7 as suggested by Furimsky [22]. The hydrogenation of the heteroring is an equilibrium process affected by the concentration of hydrogen [23].

Hydrocracking is extensively practiced commercially in petroleum refining to produce high quality gasoline, jet fuel, diesel, high quality lubricant [24,25,26,27]. Some of the commercially proven catalytic hydrocracking methods are the Standard Oil of Indiana Ultracracking Process and Union Oil Unicracking Process. These processes can tolerate feedstocks with a nitrogen content of as high as 0.3% [28,29].

Under trickle bed catalytic hydrotreating conditions the denitrogenation is always accompanied by other reactions such as hydrogenation, hydrocracking, desulfurization, deoxygenation, coking, and demetallization.

Catalyst

It has long been known that the rates of chemical reactions can be accelerated by small amounts of alien material. Such material is termed a catalyst and it is defined as a substance which increases the rate at which a chemical reaction approaches equilibrium, without being consumed in the process [30]. An appropriate catalyst plays a key role in removing sulfur, nitrogen, and oxygen simultaneously as gaseous hydrogen sulfide, ammonia, and water from the syncrude oil.

The carrier, quite often alumina, refers to a major catalyst constituent that serves as a base or binder for the active metals and promoters. A carrier may be catalytically active or inert. The major function of a carrier is to provide a large surface area so that catalytically active metals can be spread out or dispersed as a monolayer, if possible [31,32,33].

