



Catalytic hydrogenation of SYNTHOIL
by Kenneth Norman Runnion

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
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Abstract:

Catalytic hydrogenation of ERDA's SYNTHOIL liquified coal was achieved using commercial hydrotreating catalysts. Twenty-five catalysts were tested in rocking bomb autoclave tests. Successful operation of a continuous reactor was demonstrated with eight catalysts.

The products were analyzed for hydrocracking by ASTM distillation. Heteroatom removal was determined by the quartz tube method for sulfur and Macro-Kjeldahl for nitrogen.

The best catalyst tested was Harshaw HT-500 (3% NiO, 15.5% M0O3 on alumina) which gives a product containing 18% Naphtha, 32% fuel oil, and 22% gas oil. Heteroatom removal was 70% desulfurization and 32% denitrogenation. Nitrogen seems to be the more difficult heteroatom to remove.

The effects of varying liquid hourly space velocity, temperature, and hydrogen flow were studied in the continuous reactor. A temperature of 450°C, a pressure of 800 psi and a hydrogen flow rate of 10,000 scf/bbl gave the best hydrocracking and heteroatom removal. An increase in the LHSV causes a decrease in hydrocracking and heteroatom removal.

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Date March 18, 1977

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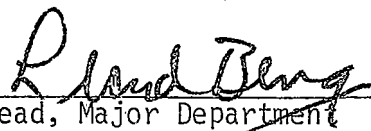
in

Chemical Engineering

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TABLE OF CONTENTS

	<u>Page</u>
VITA.	ii
ACKNOWLEDGMENTS	iii
LIST OF TABLES.	vi
LIST OF FIGURES	vii
ABSTRACT.	ix
INTRODUCTION.	1
BACKGROUND.	3
SYNTHOIL Process	3
Chemistry of Coal.	5
Chemistry of SYNTHOIL.	7
Catalysis and Hydrocracking.	9
RESEARCH OBJECTIVE.	13
MATERIALS, EQUIPMENT, AND PROCEDURES.	14
Coal Analysis.	14
SYNTHOIL Analysis.	15
Catalyst Presulfiding.	16
Bomb Runs.	16
Continuous Reactor	18
Continuous Runs.	21
Analytical Procedures.	24
RESULTS AND DISCUSSION.	26
Preliminary Continuous Runs.	26

TABLE OF CONTENTS (Cont.)

	<u>Page</u>
Bomb Runs.	34
Continuous Runs.	44
CONCLUSIONS	63
FUTURE WORK	64
APPENDICES.	65
APPENDIX A. BATCH RUN CATALYST DESCRIPTION.	66
APPENDIX B. BATCH RUN DATA.	70
APPENDIX C. CONTINUOUS RUN DATA	81
LITERATURE CITED.	89

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	ANALYSIS OF COAL, SYNTHOIL, AND CRUDE OIL.	6
II	ANALYSIS OF FEED COAL TO SYNTHOIL PROCESS.	14
III	SYNTHOIL ANALYSIS.	15
IV	BOMB RUN DISTILLATE YIELDS	36
V	BOMB RUN HETEROATOM REMOVAL.	42

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	SYNTHOIL Process	4
2	Autoclave and Heater Details	17
3	Continuous Reactor	19
4	ASTM Distillation Curve for SYNTHOIL	27
5	ASTM Distillation, Run 1	29
6	ASTM Distillation, Run 2	31
7	ASTM Distillation, Run 3	32
8	ASTM Distillation, Run B4 and Run B25	39
9	ASTM Distillation, Run B15	40
10	Temperature Effects in Bomb Runs	45
11	ASTM Distillation, CoMo-0401	47
12	ASTM Distillation, HT-500	48
13	ASTM Distillation, Run 4	49
14	ASTM Distillation, Run 5	50
15	ASTM Distillation, Run 6	52
16	Percent Desulfurization vs. LHSV	53
17	Percent Denitrogenation vs. LHSV	54
18	Percent Desulfurization vs. Hydrogen Flow	55
19	Percent Denitrogenation vs. Hydrogen Flow	56
20	ASTM Distillation, Run 9	58

<u>Figure</u>		<u>Page</u>
21	ASTM Distillation, Run 7.	59
22	Percent Desulfurization and Denitrogenation vs. Temperatures	60

ABSTRACT

Catalytic hydrogenation of ERDA's SYNTHOIL liquified coal was achieved using commercial hydrotreating catalysts. Twenty-five catalysts were tested in rocking bomb autoclave tests. Successful operation of a continuous reactor was demonstrated with eight catalysts.

The products were analyzed for hydrocracking by ASTM distillation. Heteroatom removal was determined by the quartz tube method for sulfur and Macro-Kjeldahl for nitrogen.

The best catalyst tested was Harshaw HT-500 (3% NiO, 15.5% MoO₃ on alumina) which gives a product containing 18% Naphtha, 32% fuel oil, and 22% gas oil. Heteroatom removal was 70% desulfurization and 32% denitrogenation. Nitrogen seems to be the more difficult heteroatom to remove.

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INTRODUCTION

The demand for energy in the United States continues to increase. More than 75% of this energy comes from limited and declining supplies of petroleum and natural gas. Since the Arab oil embargo of 1973, the price of imported oil has risen sharply. Petroleum has become a dominant force in our economy, but it is far too vulnerable (1).

To become self sufficient in energy the U. S. must develop and commercialize alternative feeds for our refineries. The 600 billion tons of U. S. recoverable coal represents our largest source of fossil fuel (2). The production of synthetic fuels from this coal is vital to the nation's total energy supply.

The Office of Fossil Energy of the Energy Research and Development Administration (ERDA) is conducting a research and development program to provide the technology for rapid commercialization of processes for converting coal to synthetic fuels. ERDA programs are aimed at coal liquefaction, high BTU gas (pipeline gas) from coal, low BTU gas from coal, and direct coal combustion (3).

German war efforts provided the fundamental background for modern coal conversion processes. In 1913, Friedrich Bergius developed a hydrogenation process for converting lignite to crude oil. He was followed in 1925 by Franz Fischer and Hans Tropsch, who devised a catalytic process for turning coal gas directly into gasoline. Coal gasification was developed in 1936 by Lurgi Gesellschaft (4).

Several different processes are used to transform coal into liquids. These include the Char-Oil Energy Development (COED) pyrolysis process, the Solvent Refined Coal (SRC) hydrogenation process, the SYNTHOIL catalytic hydrogenating process, and the H-Coal ebullient-bed catalytic hydrogenation process (5).

One of the problems with coal is its relatively low hydrogen content. Liquefaction processes produce some light oils, but most of the products are heavy oils or tar. Research at Montana State University is directed at catalytic hydrogenation of coal-derived liquids to clean distillate fuels. Specifically, this study deals with catalytic hydrogenation of SYNTHOIL.

The basic goal is to increase the hydrogen to carbon (H/C) atom ratio and decrease the amount of sulfur and nitrogen in the product. SYNTHOIL is hydrogenated using different catalysts at elevated temperatures under hydrogen pressure.

BACKGROUND

The following section will discuss the SYNTHOIL process, chemistry of coal, and chemistry of SYNTHOIL. An overview of catalysis and hydrogenation is also presented.

SYNTHOIL Process

The SYNTHOIL process was originally developed by the U. S. Bureau of Mines. The nominally 1/2 ton/day unit is located at ERDA's Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania. This one-step hydrodesulfurization process uses the rapid turbulent flow of hydrogen to propel a coal slurry through a fixed bed reactor.

Figure 1 is a schematic of the SYNTHOIL process (5).

Coal is dried, pulverized, and mixed with a recycled portion of its own product oil to form the coal slurry that feeds the preheater. A rapid turbulent flow of hydrogen propels the feed through a fixed bed tubular reactor coated with a pelletitized catalyst of cobalt molybdenum on silica activated alumina. Reaction conditions are 840°F and 4000 psig with excess hydrogen.

The product leaves the reactor and is sent to a vapor liquid separator. Gases then go to a purification system where they are separated into water, ammonia, hydrogen sulfide, hydrogen, and hydrocarbon gases. The hydrogen sulfide is converted to elemental sulfur. Hydrogen is recycled. The hydrocarbon gases are sent to a gasifier and shift converter where they are combined with water and

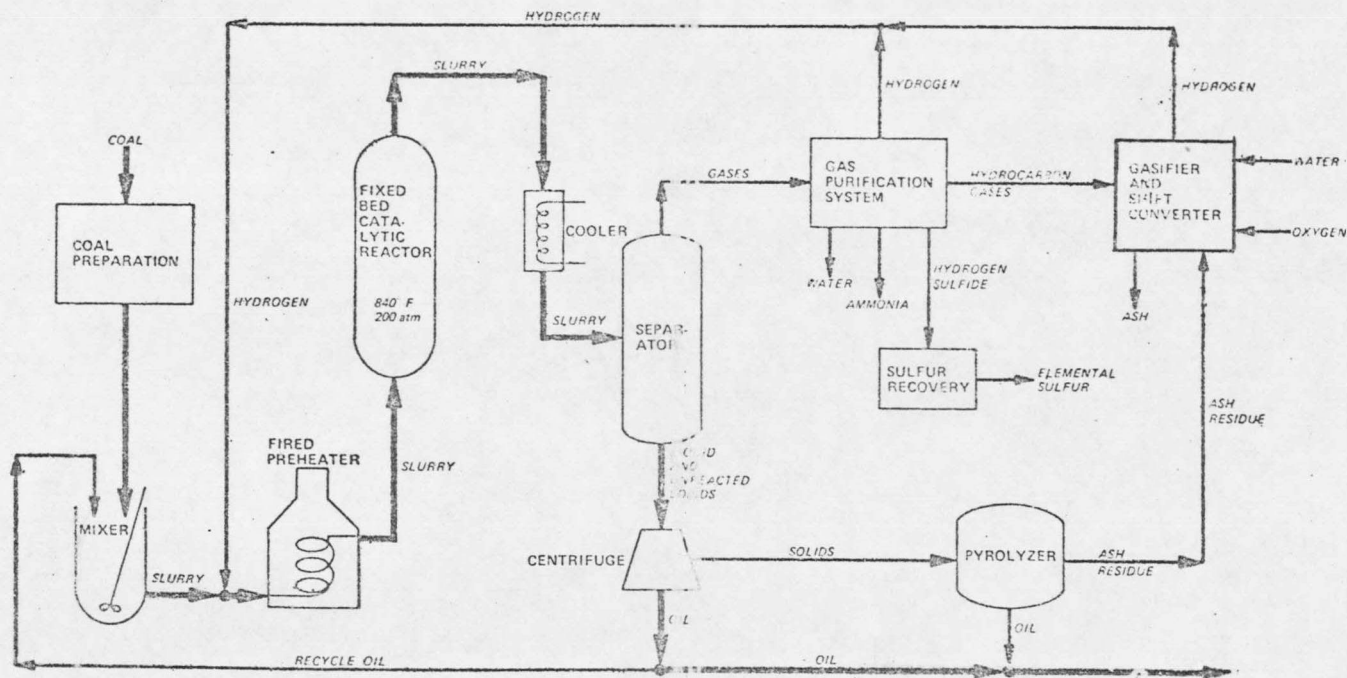


FIGURE 1. SYNTHOIL Process

oxygen to make hydrogen.

From the separator the liquids go to a centrifuge to remove the solid residue from the product oil. Part of this product oil is then recycled to be slurried with the feed coal. The solids are pyrolyzed to yield product oil and ash residue. The ash, which contains some carbonaceous material, is sent to the gasifier and shift converter to aid in hydrogen production.

The SYNTHOIL product is a heavy oil that is essentially free of sulfur and de-ashed.

Chemistry of Coal

Analytical characterization of coal is important in the liquefaction process. Coal can be characterized as a compound consisting of a low H/C ratio, high amounts of sulfur, nitrogen, oxygen, and mineral matter (ash). The ultimate analysis of the West Virginia bituminous coal used as feed in the SYNTHOIL process is given in Table I.

The coal structure consists of aromatic ring clusters generally no larger than 6 or 7 rings tied together by bridge linkages. These connecting aliphatic chains in the coal polymer are limited essentially to three carbon atoms (6).

The objective of coal liquefaction is to rupture the linkages to obtain the ring structures as individual molecules and then to further break the aromatic clusters. It is postulated that coal is

TABLE I. ANALYSIS OF COAL, SYNTHOIL, AND CRUDE OIL

	<u>Ultimate Analysis, Wt. Pct.</u>		
	<u>Coal⁽¹⁾</u>	<u>SYNTHOIL</u>	<u>Crude Oil⁽²⁾</u>
Carbon	73.8	87.62	86.0
Hydrogen	5.3	7.97	10.0
Oxygen	7.6	2.08	0.5
Nitrogen	1.4	0.97	0.5
Sulfur	3.8	0.43	3.0
Ash	8.1	1.50	-
H/C ⁽³⁾ Ratio	0.86	1.09	1.40

(1) West Virginia bituminous coal

(2) Approximate analysis for typical petroleum crude

(3) Atom Ratio

thermally split to form reactive fragments. The fragments either polymerize to form benzene-insoluble products or are stabilized by the addition of hydrogen to form soluble products (7).

Since coal contains perhaps 7 to 15 percent oxygen and also substantial nitrogen and sulfur, these elements must be eliminated. Most of the oxygen is converted to water in conventional coal liquefaction using hydrogen. Sulfur comes in three forms: (1) inorganic (pyrites), (2) sulfates, and (3) organic (mercaptans and thiols). Desulfurization occurs most readily, because many sulfur compounds are desulfurized and then hydrogenated. Nitrogen is part of and linked to coal and is hard to separate.

Chemistry of SYNTHOIL

SYNTHOIL is a coal liquefaction product that resembles a tar or heavy fuel oil. The hydrogen to carbon atom ratio of this coal liquid is lower than the corresponding ratio for petroleum crudes (See Table I). The heteroatom level of SYNTHOIL is higher however, specifically oxygen and nitrogen. Sulfur is lower than most petroleum crudes that are refinery feed stocks.

The one outstanding chemical characteristic of SYNTHOIL is the small amount of any individual compound.

Characterizing the SYNTHOIL coal liquid shows how it compares to crudes. SYNTHOIL exhibits slightly higher carbon content, but

significantly lower hydrogen content. These data suggest both a higher degree of aromaticity and a more highly condensed ring structure for SYNTHOIL. The coal liquid contains significantly more material in the asphaltene fractions than do the petroleum liquids.

The saturate fractions of SYNTHOIL are all predominately naphthenic with varying amounts of 1 to 6 ring naphthenes being detected.

Olefinic hydrocarbons observed in SYNTHOIL liquids may arise from hydrothermal cracking in the coal liquefaction process (8).

Nitrogen compounds in SYNTHOIL consists of pyridines, quinolines, and indoles. In hydrodenitrogenation, C=C would hydrogenate first and C-N hydrogenolysis is considered to be the rate determining step (9).

Of the two principal forms of sulfur in coal, the pyritic sulfur is eliminated completely while 60-80 percent of the organic sulfur is eliminated in the SYNTHOIL process. Sulfur compounds consist of thiophenes, benzothiophenes and naphthobenzothiophenes (10). In hydrodesulfurization, aromatic saturation is not a prerequisite for C-S bond breaking (9).

Trace metal analysis of SYNTHOIL revealed the following metals in descending quantitative order: Si, Al, Fe, Ti, K, Na, Mg, Ca, Pb, V, and Ni. The unusually high concentrations for silicon and aluminum may be due to small amounts of catalyst or other inorganic contaminants from the SYNTHOIL process (8).

Scanning electron microscope analysis of aged $\text{CoO}/\text{MoO}_3/\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst pellets from the SYNTHOIL process showed inorganic and organic contaminants both on the exterior surface and in the pore mouths of the catalyst. Ferrous sulfide contaminated 50 to 70% of the catalyst. Aluminum and silicon contaminated 10 to 20% of the catalysts. Trace metals were variably distributed through the catalyst (11).

This same kind of deactivation due to residue lay-down will probably not be as severe in catalytic upgrading of the SYNTHOIL liquified coal, because of the elimination of inorganic ferrous sulfide, decrease in trace metals, and the lower ash content (10,11).

Catalysis and Hydrocracking

Development of improved hydrocracking catalysts is very important to the coal liquefaction process. This section will discuss the basics of catalysis and give direction for this study and future catalysis work.

A catalyst is effective in increasing the rate of a reaction by offering an alternative mechanism path which has a lower activation energy than the uncatalyzed process. Development of hydrocracking catalysts is aimed at improving selectivity and stability.

The hydrocracking catalyst is dual functional. The two functions that it serves are (1) cracking of high molecular weight hydrocarbons, and (2) hydrogenation of the unsaturates formed either during the

cracking step or otherwise present in the feedstock. The dual functional nature is provided by incorporating a metal hydrogenation component onto a high surface area cracking component. In a way hydrogenation helps cracking. The metal hydrogenation sites keep the acid sites of the cracking catalyst clean and active by hydrogenating the coke precursors (12).

A typical cracking catalyst is silica-alumina. The hydrogenation component is usually a metal oxide such as cobalt, nickel, molybdenum, tungsten, vanadium, platinum, etc. Combinations of two or more of these components can be used, for example, cobalt and molybdenum (13). The metals are usually converted from the oxide forms into the sulfide forms by pretreatment with hydrogen sulfide.

It is important to not only look at the metal loading and chemical composition of the support, but also the physical properties of the catalyst such as surface area, pore size, particle size, and morphology. Catalyst studies with heavy feedstocks and coal tars have indicated that a large pore diameter gives better results (12, 14). Heating above a certain critical temperature may cause it to lose activity. This observation suggests that it is the physical or crystalline structure which somehow imparts catalytic activity to a material (9).

Molecular sieve zeolites have increased in use in catalysis as supports due to their greater acidity and increase in number of sites as compared to amorphous supports. The zeolites higher activity

may be seen in more selectivity, greater tolerance for nitrogen compounds, and the ability to convert high boiling point feedstocks (9,13,15).

As mentioned above, most catalysts are presulfided with hydrogen sulfide. Presulfiding helps maintain catalyst activity. The hydrogen sulfide acts as a hydrogen carrier and saturates cyclic olefins which might otherwise form high-boiling polymers and thus foul the catalyst surface. Hydrogen sulfide increases hydrodenitrogenation by increasing the hydrocracking activity of the catalyst. However, sulfided catalysts lower hydrodesulfurization (9).

In heterogenous catalysis it is important to determine the rate of each step in the catalysis process. The sequence of steps for converting reactants to products is as follows (16):

1. Diffusion of reactants to exterior catalyst surface
2. Diffusion of reactants in catalyst pores
3. Adsorption onto active sites
4. Chemical reaction
5. Desorption of products
6. Diffusion of product out of catalyst pore
7. Diffusion of product away from exterior catalyst surface

The effects of mass transfer on the catalyst could determine the reaction rate. The diffusional processes can be studied to determine their effect (17).

Film diffusion tests consist of making two series of runs at two different constant catalyst charges varying the liquid feed rate. The weight of catalyst/feed rate is plotted versus conversion. If the curves coincide diffusion has no effect. For fixed bed reactors with large flow rates, diffusion resistance is usually negligible.

As size of the catalyst decreases, the resistance to pore diffusion decreases because the path of diffusion becomes shorter. Pore diffusion tests involve two series of runs at two different catalyst pellet sizes. Pore resistance is negligible if you get the same conversion at the same ratio of catalyst weight to feed rate.

RESEARCH OBJECTIVE

The objective of this research work is catalytic conversion of ERDA's SYNTHOIL liquified coal to clean distillate fuels. Clean distillate fuels means more distillable liquid product, one that shows an increase in conversion in the ASTM distillation graphs. An effective catalyst will also reduce the amount of sulfur and nitrogen in the product.

The research plan consisted of hydrotreating SYNTHOIL with commercial hydrocracking catalysts, usually from the petroleum industry, in rocking bomb autoclave tests. Successful operation of the continuous reactor was demonstrated with the best catalysts from bomb runs. The effects of varying liquid hourly space velocity, temperature, and hydrogen flow rate were studied in the continuous reactor.

It is hoped this work will give direction to future studies in the hydrocracking of SYNTHOIL.

MATERIALS, EQUIPMENT, AND PROCEDURES

Coal Analysis

A 55-gallon drum of centrifuged SYNTHOIL (FB-49C) was received from the United States Energy Research and Development Administration, Pittsburgh Energy Research Center, Pittsburgh, Pennsylvania.

This 55-gallon drum sample of centrifuged SYNTHOIL was made from a West Virginia coal, the source is the Pittsburgh Seam from Ireland Mine. Analysis of the feed coal as received is listed in Table II.

TABLE II. ANALYSIS OF FEED COAL TO SYNTHOIL PROCESS

Proximate Analysis, Wt. Pct. (as received)

Moisture	1.6
Volatile Matter	41.6
Fixed Carbon	48.6
Ash	8.1

Ultimate Analysis, Wt. Pct.

Hydrogen	5.3
Carbon	73.8
Nitrogen	1.4
Oxygen	7.6
Sulfur	3.8
Ash	8.2

Forms of Sulfur, Wt. Pct.

Sulfate	0.09
Pyritic	1.79
Organic	1.92
Calorific value, BTU/lb	13,400

SYNTHOIL Analysis

The SYNTHOIL sample was produced using Pittsburgh Energy Research Center's nominally 1/2 ton/day unit with a 14.5 foot long catalytic reactor. Conditions were 4,000 psig, 450°C, liquid feed rate at 25 lb. per hour. The catalyst was 1/8" pellets of cobalt molybdenum on silica alumina. Analysis of the SYNTHOIL sample drum is listed in Table III.

TABLE III. SYNTHOIL ANALYSIS

Sulfur in Product, wt. pct.	0.41
Ash in Product, wt. pct.	1.50
Viscosity of Product, SSF @ 180°F	50.5
Specific Gravity of Product	1.103
<u>Solvent Analysis, Wt. Pct. (Ash Free)</u>	
Organic Benzene Insolubles	4.2
Asphaltenes (Pentane Insolubles from Benzene Solubles)	22.5
Oils (Pentane Solubles from Benzene Solubles)	71.8
<u>Ultimate Analysis, Wt. Pct.</u>	
Carbon	87.62
Hydrogen	7.97
Oxygen	2.08
Nitrogen	0.97
Sulfur	0.43
Ash	1.50

Catalyst Presulfiding

Commercial catalysts as received were dried and sulfided. Sulfiding the catalysts promotes hydrocracking and thus hydrodenitrogenation (9).

The sulfiding apparatus consists of a two foot long, one inch I.D. piece of steel pipe. The pipe is loaded with 1/4 inch Norton alumina supports and the catalyst to be sulfided. Exit gases were scrubbed with water and sodium hydroxide.

A mixture of hydrogen and 10% hydrogen sulfide flows through the sulfiding reactor for twelve hours. The temperature was maintained at 350°C with an electric pipe heater. Flow of the gas mixture continues until the catalyst has cooled. The sulfided catalysts were stored in sealed containers to minimize exposure to air and moisture.

Bomb Runs

Batch runs were made in a Parr series 4000 pressure reaction apparatus (18). Details of the autoclave and heater are shown in Figure 2.

The 500 ml, Inconel Parr bomb was charged with 150 ml of SYNTHOIL and 25 ml of sulfided catalyst. The head was placed on the body and secured with the screw cap. A copper gasket between the head and body insure a tight fit. After the eight cap screws had been torqued down, the gauge block was connected to the head.

