



Catalysts for hydrotreating Synthoil
by Mark Douglas Anderson

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

Synthoil was hydrotreated with eight commercial and six MSU catalysts in four batch runs and 15 continuous runs. The liquid products were analyzed for sulfur and nitrogen content, and the extent of hydrocracking was determined by performing ASTM-D86 distillations.

Batch runs were used for screening catalysts. Continuous runs were performed to determine the effect of LHSV, hydrogen:oil ratio, temperature, and deactivation on catalyst performance. The standard run conditions were 450°C, 800 psig, LHSV of 1.0, and a H₂:oil ratio of 10,000 scf/bbl. A run using two separate catalytic steps was performed at 410°C.

The extent of hydrocracking and heteroatom removal was shown to be directly proportional to temperature and inversely proportional to LHSV.

Catalyst deactivation during the 12 hour runs was a serious problem which could be lessened by decreasing the temperature from 450°C to 410°C. MSU catalysts were poisoned more rapidly than commercial catalysts.

The two-step run at 410°C gave results that were comparable to those obtained in one step at 450°C.

Shell 324 (Ni-Mo) removed 43% of the nitrogen in Synthoil, and MSU STK-5-2-6 (Co-Ni-Mo) removed 70% of the sulfur. Hydrocracking Synthoil at 450°C increased the distillate yield below 700°F from 44% by volume for the feedstock to an average value of 60% for the products.

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Date August 21, 1978

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by

MARK DOUGLAS ANDERSON

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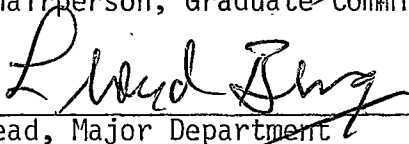
in

Chemical Engineering

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MONTANA STATE UNIVERSITY
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ABSTRACT

Synthoil was hydrotreated with eight commercial and six MSU catalysts in four batch runs and 15 continuous runs. The liquid products were analyzed for sulfur and nitrogen content, and the extent of hydrocracking was determined by performing ASTM-D86 distillations.

Batch runs were used for screening catalysts. Continuous runs were performed to determine the effect of LHSV, hydrogen:oil ratio, temperature, and deactivation on catalyst performance. The standard run conditions were 450°C, 800 psig, LHSV of 1.0, and a H₂:oil ratio of 10,000 scf/bbl. A run using two separate catalytic steps was performed at 410°C.

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INTRODUCTION

The United States is currently facing a serious energy crisis. While the demand for energy is increasing at an annual rate of three to four percent, domestic oil production is decreasing at an annual rate of 0.5 million barrels per day. This discrepancy between supply and demand has forced the U.S. to rely heavily on foreign oil sources at an estimated annual cost of 40 billion dollars (1).

The outlook for the future is no brighter. It is estimated that by the year 2000, oil production in the non-communist world will be 15 to 20 million barrels per day short of demand (2).

Alternate energy sources such as nuclear fission, nuclear fusion, solar, wind, and geothermal power, are being developed but are not expected to make a significant contribution in the near future.

It is estimated that domestic coal reserves comprise 80 percent of the United States' total energy from oil, gas and coal. This vast energy source could last up to 100 years (1).

Combustion of coal in conventional power plants is troubled by transportation and pollution problems which make it an undesirable method of extracting energy from coal. Therefore, a method of converting coal to clean fuels which could be transported and refined in existing facilities is needed.

Although commercial coal conversion processes are being operated in Europe and South Africa, coal conversion processes in the United States remain in the development stage (1).

The United States Department of Energy (D.O.E.) is currently developing coal gasification and liquefaction processes for the conversion of coal to clean fuels. Gasification processes under development include the HYGAS, Bi-Gas and Synthane processes. Liquefaction processes include the Solvent Refined Coal (SRC), Exxon Donor Solvent (EDS), H-Coal, and Synthoil processes (3).

The product of the Synthoil process was originally intended for use as a clean boiler fuel, but at present costs it is more economical to clean up the stack gases than it is to burn a clean fuel (4). Synthoil has a potential use as a synthetic crude oil, but before it can be refined in conventional petroleum refineries, it must be catalytically upgraded or hydrotreated (4).

Therefore, the object of this research is to develop a catalyst which will hydrotreat Synthoil, increasing the hydrogen content and reducing the sulfur and nitrogen content, to produce a more suitable source of clean distillate fuels.

BACKGROUND

Synthoil Process

The Synthoil process is a catalytic coal liquefaction process which converts high-sulfur coal to a low-sulfur, low-ash synthetic fuel oil. A schematic of the process is shown in Figure 1.

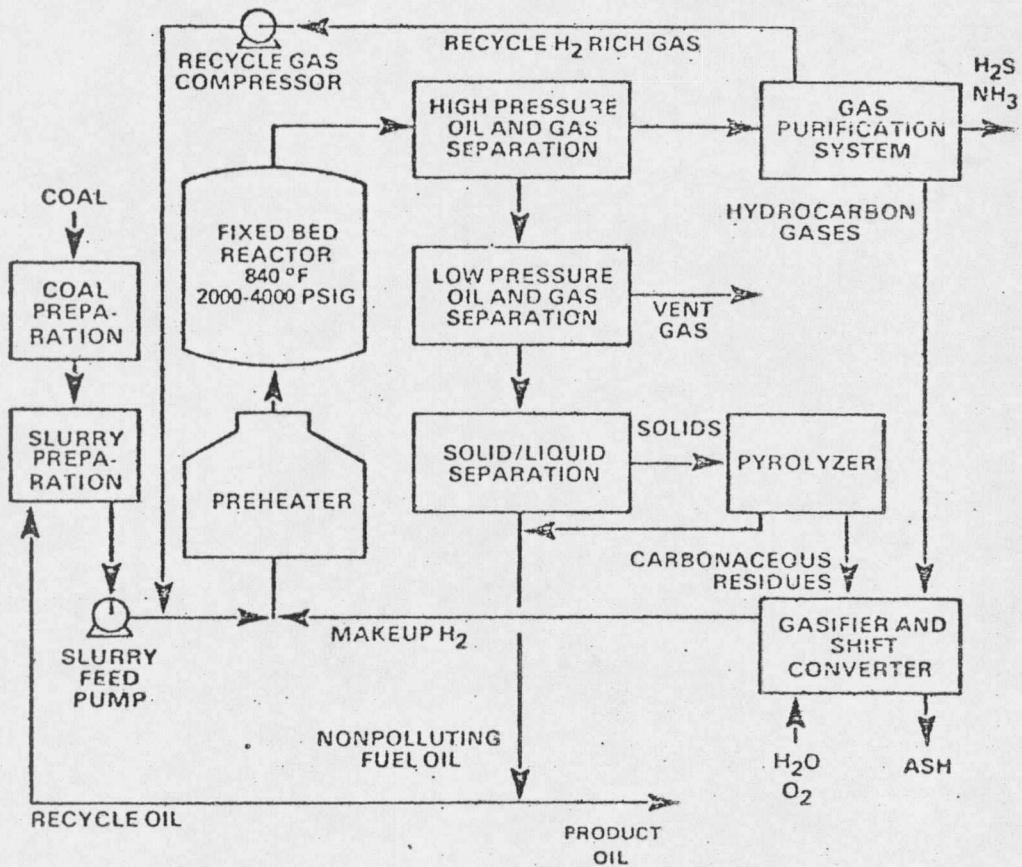


Figure 1. Synthoil Process Schematic

The coal is crushed and dried and then mixed with process product oil to form a slurry of about 40 percent coal. The slurry is combined with hydrogen and fed to a fired preheater.

The preheated slurry is then violently propelled through a fixed-bed catalytic reactor where liquefaction and desulfurization occur. The catalyst is a cobalt-molybdate combination on a silica-alumina support.

After leaving the reactor, the liquids and unreacted solids are separated, and part of the liquid product is recycled as slurry oil. The resulting solids are sent to a pyrolyzer to recover more liquid product, and the remaining carbonaceous residue is fed to a gasifier and shift converter to produce hydrogen.

The process off-gases are separated into five streams: water, ammonia, hydrogen sulfide, hydrocarbon gases, and hydrogen. Elemental sulfur is recovered from the hydrogen sulfide, and the hydrocarbon gases are fed to the gasifier and shift converter. The hydrogen produced in this unit is mixed with the excess hydrogen from the reactor and recycled (5).

Work on this process began in 1969 at the Pittsburgh Energy Research Center (PERC). The initial bench-scale process unit used a 5/16-inch internal diameter reactor that processed five pounds of slurry per hour (5).

Later, a 1/2-ton per day plant was constructed using two inter-connecting 14.5 foot lengths of 1.1 inch inside diameter stainless steel pipe (5). This unit was last operated in August of 1976 (6).

A 10-ton per day process development unit is expected to be completed by 1979, but an operating contractor has not yet been selected (3).

Chemical Properties of Synthoil

Synthoil is an extremely complex mixture of polycyclic aromatic compounds. Exxon Research and Engineering Company (ER&E) has recently published a detailed study of the chemical nature of Synthoil, and some of the results from this study are presented in the following paragraphs. The following information was taken from the Summary of the final report prepared by ER&E (7).

Table I. gives a summary of the analysis of a West Virginia Ireland Mine feed coal and liquid product FB-46 made from the coal using the Synthoil process.

The sample of Synthoil used in this research product was also produced from coal from the Ireland Mine, so its analysis should be similar to that of product FB-46.

Coal liquids are generally separated into these three fractions: oil, asphaltenes and residue. Oil is defined by Exxon as the fraction that is soluble in cyclohexane. Asphaltenes are defined as cyclohexane insolubles-benzene solubles and the residue fraction is insoluble in

Table I. Chemical Composition of Synthoil and Feed Coal¹

Classes of Components	Weight Percent in Sample	
	W. Va. Ireland Feed Coal	Synthoil FB-46 Batch 55
<u>Oil</u>	0.660	69.49
• Saturates	0.114	5.27
Paraffins	0.037	1.19
Naphthenes	0.077	4.07
• Aromatics	0.312	33.67
Hydrocarbons	0.260	31.63
Thiophenes	0.027	0.56
Furans	0.025	1.48
• Polars	0.234	30.56
Mono-oxygen compounds	0.066	15.29
Di-oxygen compounds	0.012	2.07
Nitrogen compounds	0.010	7.25
Other	0.006	0.42
Residue	0.139	5.53
<u>Asphaltenes</u>	0.150	17.22
<u>Residue</u>	95.77	9.04

¹Data taken from Reference 7.

benzene. Table I shows that in liquefaction, all but about 9 percent of coal's residual material is converted to oils or asphaltenes.

The oil fraction can be further separated into saturate, aromatic and polar compounds. Table II lists some of the specific compound types identified in each of these fractions.

Exxon found 13 compound types and 225 carbon number homologs in the saturate fraction. About 80% of the saturates in product FB-46 are naphthenes.

The aromatic fraction of Synthoil contains condensed ring structures containing up to 8 rings. Exxon isolated 135 compound types and 1150 carbon number homologs. Polycyclic rings containing oxygen, nitrogen, and sulfur were also identified. Some of these compound types are listed in Table III.

The polar fraction contains one to eight ring hydroxyaromatics and dihydroxyaromatics, and aromatic pyrroles and pyridines. A total of 158 compound types and 1150 homologs were found.

Asphaltenes are complex ring systems containing 7 to 11 aromatic rings and 1 to 4 naphthenic rings per molecule. Approximately 80 percent of the carbon is located in aromatic rings, and the average alkyl group is less than 2 carbons in length. There are 1 to 3 oxygen atoms, 1/2 to 1 nitrogen atoms, and 0.03 to 0.16 sulfur atoms per molecule (7).

Table II. Typical Compounds Found in Synthoil¹

Fraction	Typical Compounds	
<u>Oil</u>		
Saturates	n-paraffins, C ₁₄ - C ₂₂ naphthenes	
Aromatic	naphthalenes acenaphthenes fluorenes phenanthrenes pyrenes fluoranthrenes benzanthracenes chrysenes benzopyrenes	benzoperylene coronenes tetralins tetrahydroacenaphthenes hexahydrofluorenes dibenzothiophenes phenanthrenothiophenes dibenzofurans phenanthrenofurans
Polar	1 - 8 ring hydroxyaromatics and dihydroxy- aromatics aromatic pyrroles, pyridines	
<u>Asphaltenes</u>	aromatic phenols, pyrroles	

¹Taken from Reference 7.

Table III. Aromatic Compounds Containing Sulfur, Nitrogen and Oxygen¹

Heteroatom	Typical Compounds
Sulfur	benzothiophenes dibenzothiophenes phenanthrenothiophenes
Nitrogen	pyrroles pyridines quinolines carbazoles acridines
Oxygen	dibenzofurans phenanthrenofurans hydroxybenzenes hydroxyindanes tetralins

¹Taken from Reference 7.

The following trace metals have been found in Synthoil: Si, Al, Fe, Ti, K, Na, Mg, Ca, Pb, V, and Ni. The concentrations of these metals range from 1348 ppm for Si down to 1 ppm for Ni. It is believed that the high silicon and aluminum concentrations originate from the Si-Al catalyst used in the Synthoil process (8).

Hydrorefining Coal Liquids

As mentioned in the Introduction, before Synthoil can be processed into clean distillate fuels in conventional petroleum refineries, it must be catalytically hydrotreated. The process is known as hydrorefining (4). Hydrorefining is necessary because Synthoil contains excessive concentrations of residual carbon, polynuclear aromatics, complex heterocycles containing sulfur, nitrogen and oxygen, and ash (9).

The basic goals of hydrorefining are to saturate and partially crack polynuclear aromatics and to remove sulfur, nitrogen and oxygen. This results in a higher hydrogen to carbon ratio, prolonged catalyst life in subsequent processing, and reduced concentrations of potential air pollutants.

The following sections will discuss catalysts in general, specific reactions that occur in hydrorefining, and catalyst presulfiding, poisoning and testing.

Catalysts in general. Catalysts are useful in hydrorefining because they allow reactions to proceed by lowering the activation energies of the reaction steps and providing alternate reaction paths (10). The activity and selectivity of a catalyst is determined by the following properties: nature of the support, chemical composition, surface acidity, total surface area, pore volume, and pore-size distribution among others (9). Activity is also influenced by pretreatment and catalyst poisons. The effects of these properties on catalytic activity are discussed in the following sections.

Reactions. Three important reactions that occur in hydrorefining are hydrocracking, hydrodesulfurization (HDS), and hydrodenitrogenation (HDN). Effects of catalyst properties on these reactions and simple mechanisms are discussed.

1. Hydrocracking. Hydrocracking catalysts are important because they promote saturation and partial cracking of polynuclear aromatic compounds. Hydrocracking is believed to proceed through a multi-step mechanism involving hydrogenation, isomerization, cracking, and rehydrogenation. These reactions produce saturated cyclic and branched compounds and reduce coke deposition caused by polynuclear aromatics (9).

The majority of currently used hydrocracking catalysts are based on crystalline silica-alumina combinations impregnated with cobalt, molybdenum, nickel or tungsten in varying proportions. These catalysts act

as high temperature acids which accounts for their activity (11). Pore size distribution and surface area are also important parameters (9).

2. Hydrodesulfurization (HDS). Sulfur is undesirable in coal liquids because it is readily adsorbed on the catalyst and acts as a poison. Sulfur present in fuels also acts as an air pollutant (9).

Studies of dibenzothiophene, a constituent of Synthoil, have shown that sulfur extraction occurs predominately before the aromatic rings are completely saturated. Sulfur is removed as H_2S . The HDS reaction was found to be first order with respect to the sulfur-containing compound (12). In general, as the molecular weight of the compound increases, the difficulty of HDS and HDN increases. Sulfur is easier to remove than nitrogen (11).

The most common HDS catalysts are Co-Mo combinations on alumina or silica-alumina supports. HDS activity increases with increasing surface area and average pore size (11).

3. Hydrodenitrogenation (HDN). Basic nitrogen compounds are undesirable because they react with the acid centers of the catalyst and inhibit cracking. They also act as coke precursors and, if present in fuels, act as air pollutants (11).

Studies on the HDN of quinoline, a constituent of Synthoil, have shown that complete hydrogenation must occur before the C-N bond is broken (12). Nitrogen is removed as NH_3 .

The most common HDN catalysts are Ni-Mo, Ni-W or Ni-Co-Mo combinations on alumina or silica-alumina supports. These catalysts must be presulfided for proper activity.

Presulfiding. Hydrorefining catalysts are presulfided to increase hydrogenation activity and decrease the initial rate of carbon deposition by minimizing hydrocracking. Presulfidation decreases HDS, but most HDS catalysts are sulfided in the reactor by feeds containing more than one percent sulfur (9).

Catalyst poisoning. Catalyst deactivation or poisoning can occur by four mechanisms: adsorption of sulfur and nitrogen compounds, coke deposition, deposition of organometallic compounds, and sintering. Sulfur and nitrogen poisoning have already been briefly discussed, so this section will concentrate on the problems of coking and organometallic compounds. Sintering will not be discussed.

1. Coking. Catalyst poisoning due to coke deposition during the hydrorefining of coal liquids is a serious problem. This is because of the high concentration of polynuclear aromatic compounds, especially those containing nitrogen, found in these liquids (9).

Coking occurs when the free-radicals that are formed during hydrogenation and hydrocracking reactions are not quenched with hydrogen but react with other free-radical containing fragments. The result is

repolymerization or condensation of large polynuclear compounds that are resistant to further fragmentation (9,13).

Although this type of poisoning is not permanent, coking occurs rapidly and causes the catalyst to lose 70 to 90 percent of its activity. This loss of activity is caused by the loss of pore volume and surface area as the carbon is deposited throughout the pore structure. These deposits tend to fill up pores that have a radius smaller than 30 Å. Regeneration can restore 90 to 94 percent of the catalyst's virgin activity (14).

Coking can be reduced by using more active catalysts at a lower temperature to prevent free-radical formation (9). In a study of petroleum residual oils, increasing the hydrogen pressure decreased the amount of coking but did not decrease the rate of formation (11).

2. Organometallic compounds. Poisoning by the deposition of organometallic compounds occurs at a much slower rate than coking, but it is irreversible. Irreversibility occurs because permanently bound metal oxides are formed during catalyst regeneration (14).

The ash in Synthoil contains four known catalyst poisons. They are Fe, Ni, Ti, and V (11,14).

Catalyst testing. Catalyst testing takes place in three general reactor types: differential, pulsed micro, and integral.

While differential reactors are useful for obtaining kinetic data, and pulsed microreactors for screening catalysts, integral reactors can be used for both purposes. Since integral reactors operate at high conversion levels, they more nearly simulate the real catalytic process (9).

A trickle bed reactor is a fixed bed integral reactor in which liquid and gas flow concurrently down through the reactor. While this type of reactor is useful in catalyst screening, resistance to heat and mass transfer can give misleading results.

Catalytic reactions involve seven steps (15):

1. Diffusion of reactants through the external film to the catalyst surface.
2. Diffusion of reactants through pores.
3. Adsorption of reactants on active sites.
4. Reaction.
5. Desorption of products.
6. Diffusion of products through pores.
7. Diffusion of products through the external film.

If heat and mass transfer limitations are significant, the reaction will not be controlled by steps 3, 4, and 5 making it difficult to observe the kinetic effect of catalysts (10).

Three types of transport limitations that occur are: intraparticle, interphase and interparticle. These limitations and the methods of testing for them are discussed below.

If intraparticle transport limitations are significant, the catalyst effectiveness factor η will be inversely proportional to the catalyst diameter. Increasing conversion with decreasing particle size is a positive test for this limitation (16).

Interphase transport limitations are severe in trickle bed reactors because of the liquid film which surrounds the catalyst pellet. If conversion increases with increasing mass flow rate at a constant liquid hourly space velocity, interphase limitations are important (16).

Interparticle limitations can lead to radial temperature gradients in the catalyst bed. To prevent deviations from ideal plug flow due to channelling and axial dispersion, the catalyst bed should be diluted with inert particles. Mears (16) suggests the following criterion for dilution:

$$\frac{L}{d_p} > 250 \frac{b}{\delta}$$

L = catalyst + diluent bed length

d_p = particle diameter

b = cm^3 inert : cm^3 catalyst ratio

δ = relative experimental error in conversion

This discussion of hydrorefining illustrates the complexity of the problem of obtaining clean distillate fuels from coal liquids. Because of this complexity, it is essential that catalyst properties and operating conditions are well defined and carefully controlled.

RELATED RESEARCH

Synthoil has been catalytically upgraded by at least three other groups of investigators through the support of the U.S. Department of Energy. In general, these investigators used more severe processing conditions and obtained better results than were obtained in this investigation. This related research was completed by the School of Chemical Engineering at Oklahoma State University, UOP, and Dow. Their processing conditions and results are summarized below.

Oklahoma State University

A Synthoil liquid was treated at OSU under a variety of reactor conditions in a one-step catalytic process (17). The catalysts used were Co-Mo and Ni-Mo combinations on Si-Al supports. The processing conditions and heteroatom removal results from one run are presented below in Table IV.

Table IV. Upgrading Synthoil at OSU

	Catalyst: Ni-Mo			Wt. % S	Wt. % N
	T (°C)	P (psig)	LHSV (hr ⁻¹)		
Feed	--	--	--	1.02	1.19
Product	427	1500	1.0	0.12	0.58

UOP

Synthoil was treated in a two-step catalytic process at UOP using catalysts containing group VI and group VIII metals on high surface

area refractory supports (18). Before being hydrotreated (Step I) and hydrocracked (Step II), the Synthoil was filtered to remove ash and washed to remove NH_4Cl . The operating conditions for Steps I and II were in the following ranges:

Temperature: 375-450°C.

Pressure: 2000-3000 psig

LHSV: .25-1.0 hr^{-1}

Their results are summarized in Table V.

Table V. Upgrading Synthoil at UOP

	Wt. % S	Wt. % N
Feed	.55	1.46
Step I Product	.02	.376
Step II Product	--	.076

DOW

Synthoil was studied by Dow to determine its suitability as a petrochemical feedstock (19). The first step was to distill the Synthoil product to obtain the 350-650°F fraction (Step I). This distillate was then hydrocracked (Step II) and then hydrotreated (Step III). The product from Step III was then catalytically reformed to produce a maximum yield of aromatics. Typical conditions and results are presented in Table VI.

