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
Montana State University

Abstract:
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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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Chairperson, Graduate Committee

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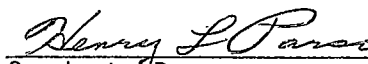

Graduate Dean

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ABSTRACT

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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 Tropsh, 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. SYHTHOIL is hydrogenated using different catalysts at elevated temperatures under hydrogen pressure.

BACKGROUND

The following section will duscuss 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 hyrogen 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

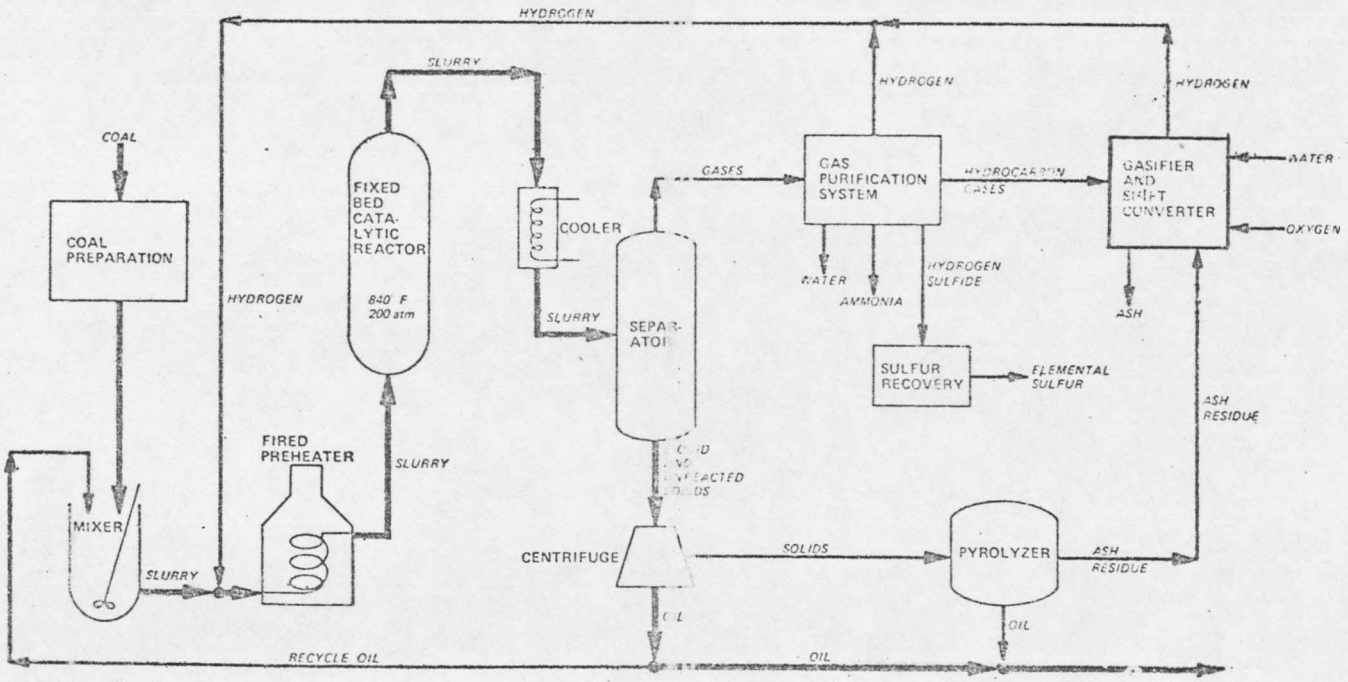

FIGURE 1. SYNTHOIL Process

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 pyrolized 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

Ultimate Analysis, Wt. Pct.

	Coal[1]	SYNTHOIL	Crude Oil[2]
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 stablizied 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 napthobenzothiophenes (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 $CoO/MoO_3/SiO_3/Al_2O_3$ 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, vandium, 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
Solvent Analysis, Wt. Pct. (Ash Free)	
Organic Benzene Insolubles	4.2
Asphaltenes (Pentane Insolubles from Benzene Solubles)	22.5
Oils (Pentane Solubles from Benzene Solubles)	71.8
Ultimate Analysis, Wt. Pct.	
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.

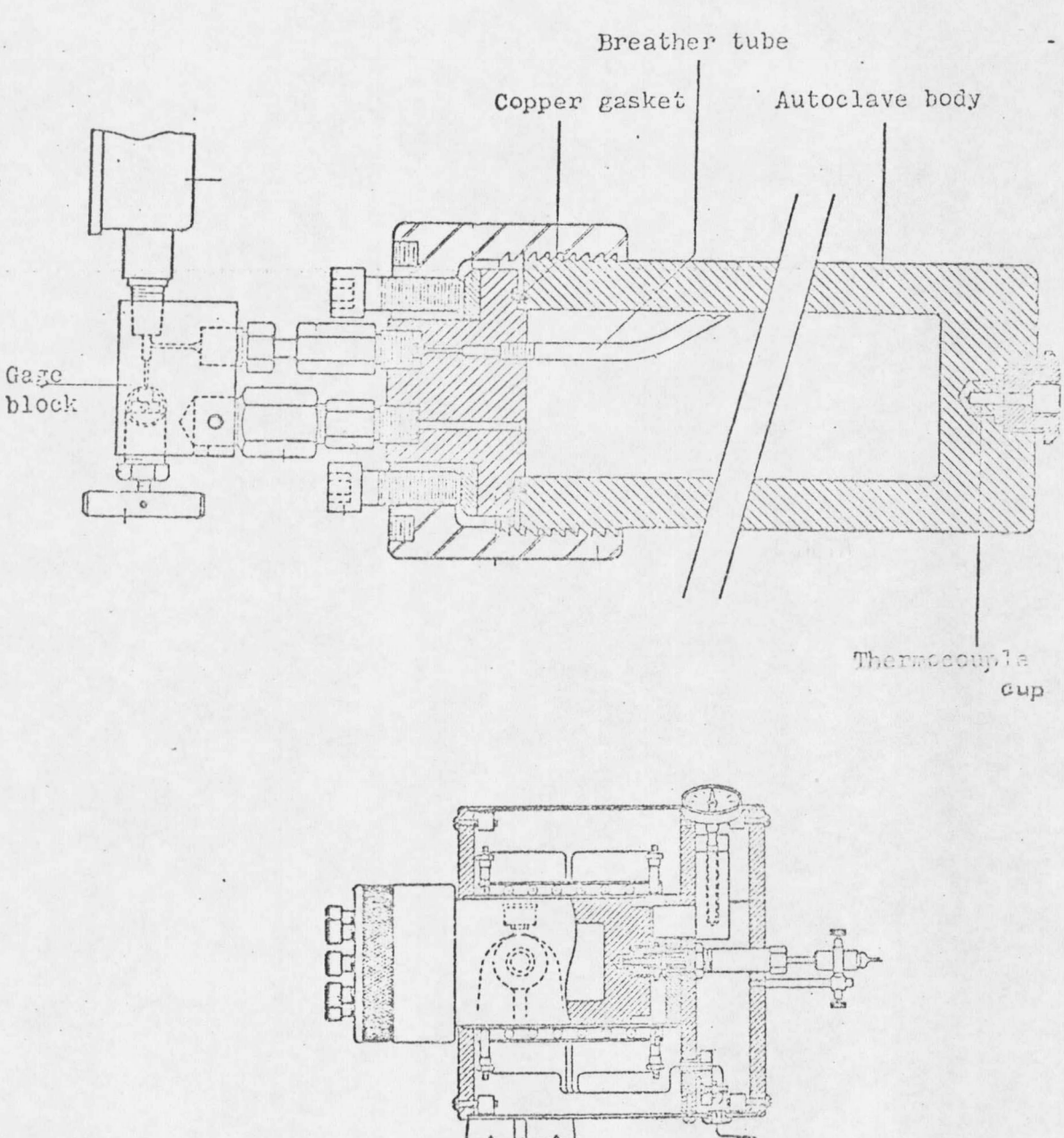

FIGURE 2. AUTOCLAVE AND HEATER DETAILS

The bomb was pressurized with 2000 ± 100 psig of hydrogen using a Haskel gas booster (19). If no leaks were detected, the bomb assembly was inserted into the rocker heater. The bomb was anchored with the retaining bolt that screws into the bomb base. An iron-constantan thermocouple inserts into the hole of the retaining bolt. Temperature was recorded on a Honeywell temperature recorder.

The rocker was activated by a switch in the back of the heater base. The temperature was controlled manually with a Powerstat variable transformer. Reaction time was one hour at 450°C.

After the run, the bomb was removed from the heater and cooled in room air. The pressure was slowly bled off to assure no loss of product. The product was stored in sample bottles until analysis could be performed.

Continuous Reactor

Design and fabrication of the continuous reactor was conducted by the Chemical Engineering Department at Montana State University. The continuous reactor apparatus is shown in Figure 3.

The reactor consists of a one inch I.D., three feet long piece of Inconel pipe. The reactor fits into an aluminum block which is wrapped with nichrome heating wires. This is all enclosed in a metal container filled with zonolite insulation to limit heat loss.

A 1/4 inch stainless steel rod runs down the middle of the

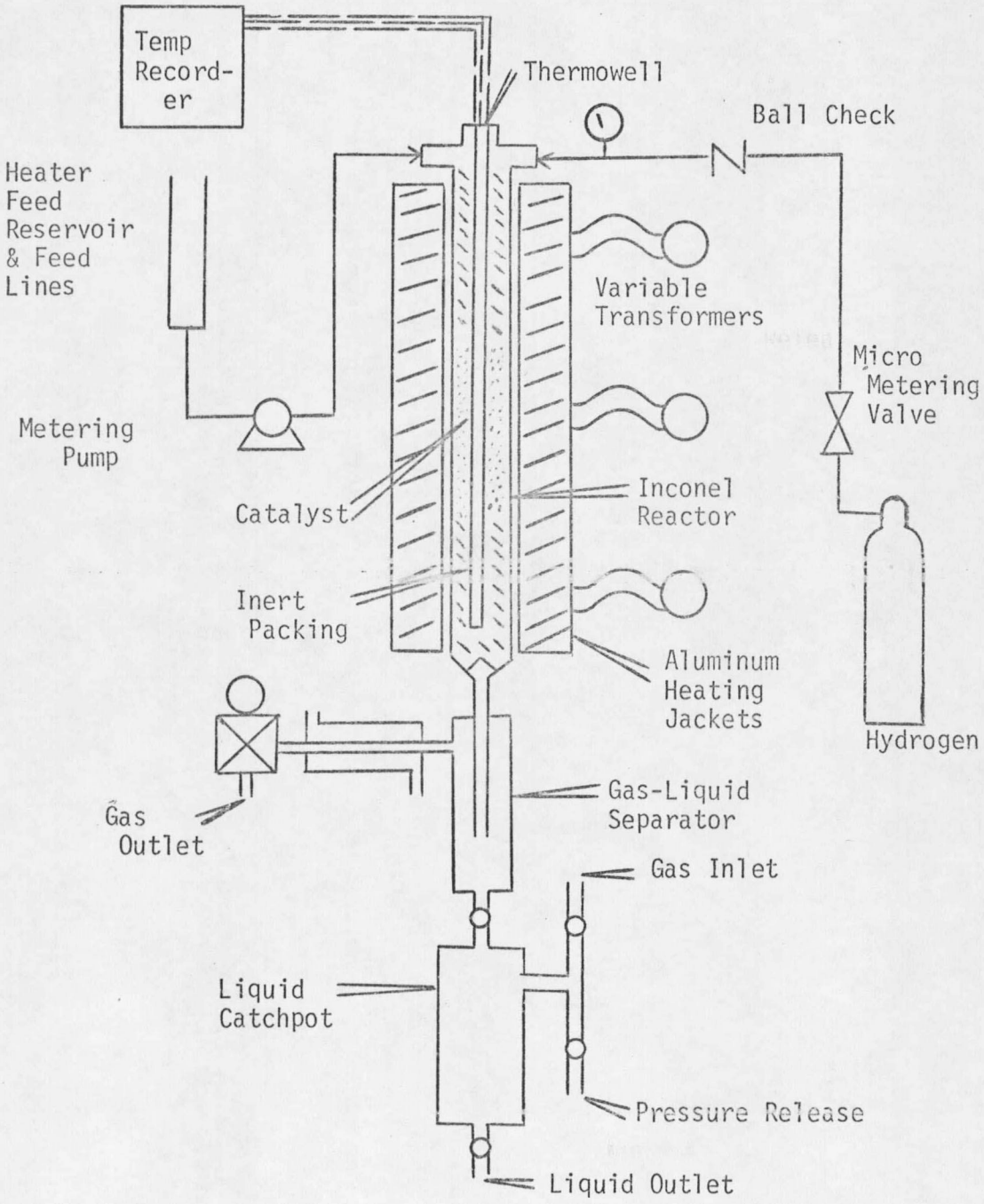

FIGURE 3. Continuous Reactor

reactor and serves as a thermowell. Three iron-constantan thermocouples measure the temperature at the top, middle, and bottom of the reactor. The thermocouples are connected to a Honeywell temperature recorder.

The top section of the reactor is packed with inert Norton Denstone bed support to preheat and distributed the reactants. The catalyst, which fills the middle section, is mixed with inert support to eliminate hot spots. More Denstone support fills the bottom of the reactor.

Because of the viscous nature of SYNTHOIL, the glass feed reservoir and 1/8 inch stainless steel feed lines are wrapped with heating tapes. They are heated to approximately 80°C. The heated SYNTHOIL is pumped under pressure to the top of the reactor with a Hills-McCanna chemical proportioning pump.

Technical grade hydrogen flows through a micro metering valve and then a ball check valve to the top of the reactor.

SYNTHOIL and hydrogen flow concurrently through the trickle bed type reactor. The products from the bottom of the reactor are separated in a gas-liquid separator. The gases then pass through a Grove back pressure regulator valve that controls the pressure of the system. The gases are scrubbed with sodium hydroxide and vented to the atmosphere.

The liquid product is collected in the catchpot. When the receiver becomes full, the valve between the separator and catchpot

is closed. The pressure is bled off and the liquid product collected from the outlet on the bottom of the catchpot. The pressure release valve and liquid valve are closed after the product dump. Nitrogen is used to repressurize the liquid catchpot through the gas inlet. When the valve from the separator is reopened, there is no interruption to the system pressure. Continuous flow is maintained in the reactor.

Continuous Runs

The following discussion on operating procedures for the continuous reactor represents the "best" method developed. Since this was the first study using the apparatus, the procedures were refined through the course of the research. Any refinements that may affect the results will be noted in the Results and Discussion section.

The Inconel reactor was first filled with inert support and catalyst. The top section was packed with 50 ml of 1/4 inch spheres of Norton Denstone support, then 100 ml of 1/16 inch extrusions of Norton inert support. A 50-50 mixture of presulfided catalyst and inert packing constituted the reaction section, The volume varied depending on the desired space velocity. Inert support and 1/4 inch spheres filled the reaminder of the reactor. A conical shaped piece of steel screen was inserted into the bottom of the reactor to hold the catalyst and support materials in place.

The reactor was then inserted into the aluminum heating block. The feed lines, separation apparatus, vent lines and thermocouple leads were then attached onto the reactor. The system was pressurized and tested for leaks. If no leaks were found, the apparatus was ready for operation.

The micro metering valve regulated the flow of hydrogen to the reactor. A wet test meter was connected to the vent line after the sodium hydroxide scrubber system. The micro metering valve was calibrated with the wet test meter before each run and a calibration curve drawn.

The Powerstat variable transformers manually controlled the temperature of the reactor. Continuous monitoring of the temperature by the Honeywell temperature recorder helped maintain isothermal conditions. Heating tapes, controlled by Variacs, supplied heat to the feed reservoir, pump head, and feed lines.

When the reaction temperature was reached, the metering pump was started. The flow of SYNTHOIL was measured by recording the level in the graduated glass feed reservoir. Frequent readings were necessary because of fluctuations in the metering pump performance.

Readings were made of the hydrogen bottle pressure, inlet pressure, reactor pressure, and back pressure regulator. Observations were also noted for the bubbling action in the scrubber.

Once the desired flow rates and temperatures were achieved, the

reactor was allowed to operate at constant operating conditions for several hours before a product sample was taken. When operating parameters were changed, the system was again allowed to reach steady state before product samples were collected. The samples were obtained as noted previously in the discussion of apparatus. Each sample was approximately 150 to 250 ml.

The runs usually took about twelve hours. No attempt was made to run continuously for more than one day, because it was felt that continuous monitoring of the reactor pressures was necessary to insure that the reactor system did not plug. More will be noted on plugging and run times in the Results and Discussion section.

After the run, the SYNTHOIL flow, the hydrogen flow, and heat were stopped. Heavy motor oil, pumped through the system, helped clean out the lines and loosen the catalyst and support material in the reactor. The feed line was disconnected from the reactor and toluene was pumped through the line to clean the feed reservoir, check valves in the pump head, and feed lines. Caution! Toluene should not be pumped through the hot reactor.

After the reactor has cooled to room temperature, toluene may be pumped through the reactor. The reactor is then taken apart. Some of the catalyst and support material will fall out of the reactor, but usually the reactor must be drilled out. The reactor, gas-liquid separator, liquid catchpot and back pressure regulator valve are then

cleaned with toluene and dried with acetone.

Analytical Procedures

The products from the rocking bomb autoclave and continuous reactor were analyzed to determine the extent of cracking, desulfurization, and denitrogenation. Samples were completely mixed to give a representative sample. Drying the samples with Drierite (anhydrous $CaSO_4$) to remove water was found to be ineffective. Loss of product occurred due to the drying process and the excess handling of sample. Centrifuging of the product did not yield any water.

The amount of cracking was determined by ASTM atmospheric distillation (20,21). This test determines the amount of product that boils at temperatures up to 700 F. The data from the distillation was plotted on the same graph as the ASTM distillation data for the SYNTHOIL feed. Comparisons between the products and feed, and among the products will be discussed.

The weight percent sulfur in the samples was determined by the quartz tube combustion method using a Bico-Brown Shell design sulfur determination apparatus (22,23). Interference from chlorides and/or nitrogen in the samples, necessitated using a gravimetric procedure which precipitates the sulfate using barium chloride rather than direct titration with a standard sodium hydroxide solution (24).

Analysis of SYNTHOIL feed showed a 0.44 weight percent sulfur.

The Pittsburgh Research Center reports a 0.41 weight percent sulfur for the SYNTHOIL sample. Results are presented as weight percent desulfurization based on a SYNTHOIL feed of 0.44 weight percent sulfur.

The Macro Kjeldahl method was used for nitrogen determination (24,25,26). The nitrogen content for SYNTHOIL has been reported as 0.97 weight percent (8). Analyzing six SYNTHOIL samples and taking an average yielded a value of 1.06 weight percent nitrogen. Results are presented as weight percent denitrogenation based on a SYNTHOIL feed of 1.06 weight percent nitrogen.

Chromatograph analysis of the off-gases from the continuous reactor before scrubbing was attempted. No hydrocarbon gases, hydrogen sulfide or ammonia could be detected due to excess hydrogen which diluted the samples.

No products were sent out for complete analysis, because of the many compounds found in coal liquids. It was felt that comparison of ASTM distillation curves provided good and inexpensive results.

RESULTS AND DISCUSSION

Twenty-eight rocking bomb autoclave tests were performed on twenty-four commercial catalysts and one chloride catalyst impregnated on a support at Montana State University. Continuous runs were made on eight catalysts in nine runs.

The products from each run were analyzed for cracking by ASTM atmospheric distillation. Heteroatom removal was determined by the quartz tube method for sulfur and the Macro Kjeldahl method for nitrogen.

The data and results from the runs are presented in the Appendix. All the catalysts tested in bomb runs are described by manufacturer, size, metal loading, support, and support properties in Appendix A. The data from the bomb runs is given in Appendix B. Appendix C lists the continuous run catalysts, data, and results.

This section will discuss the most important results from these appendices. The discussion is arranged mostly in chronological order with preliminary continuous runs, bomb runs, and then continuous runs.

Preliminary Continuous Runs

To determine if any hydrogenation and cracking have taken place and to give a quantitative comparison of the SYNTHOIL feed and run products, ASTM distillation of SYNTHOIL is used as a basis for comparison. Figure 4 is a distillation curve for SYNTHOIL. The percent SYNTHOIL is plotted vs. the temperature in degress Fahrenheit up to 700°F which is the end point for distillation at 640 mm. The

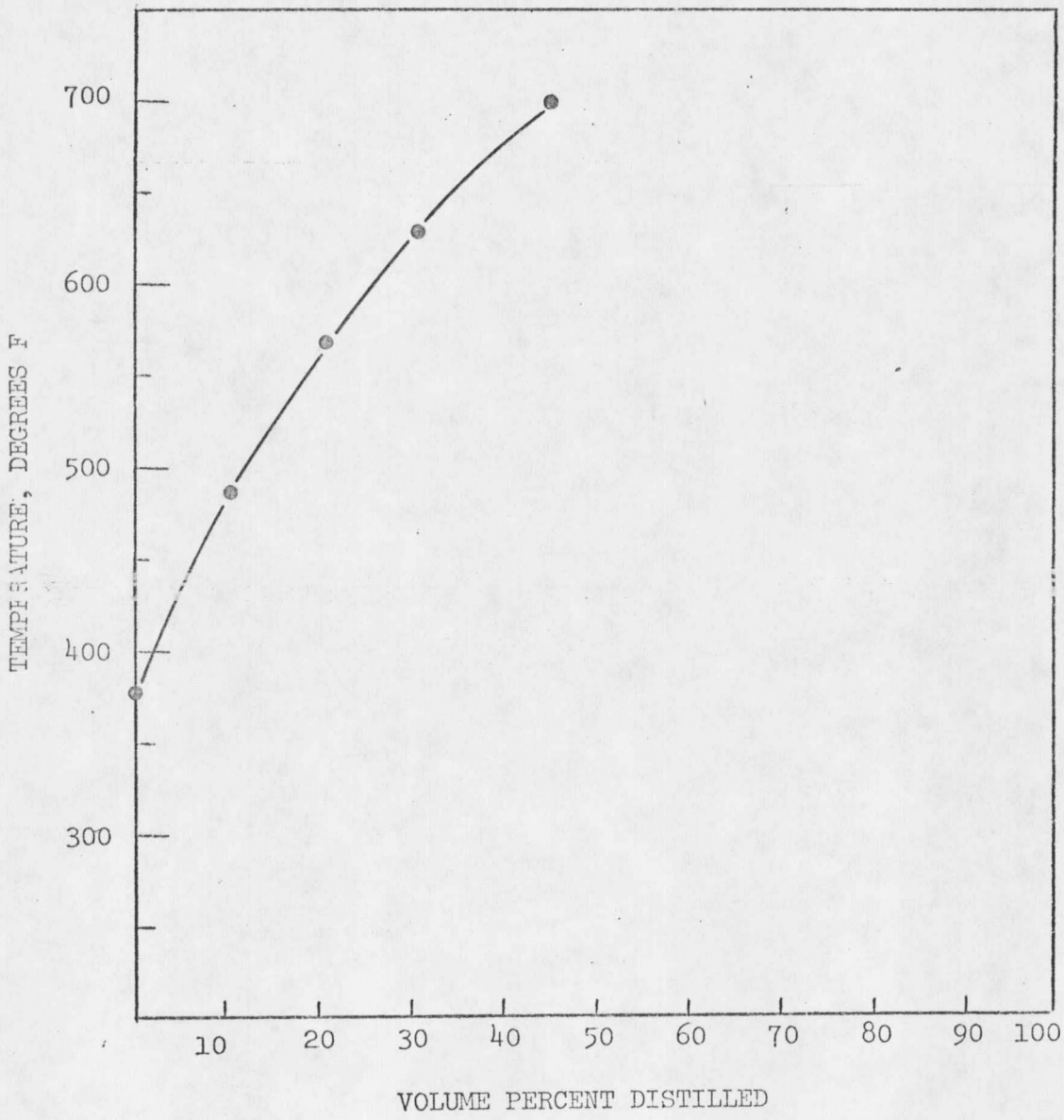

FIGURE 4. ASTM Distillation Curve for SYNTHOIL

objective of this research is to shift this curve to the lower right.

When the research was started, it was planned to test all catalysts in the continuous reactor. In the first reactor design both the liquid and gaseous products flowed through the back pressure regulator valve rather than being separated before the valve as in Figure 3.

Figure 5 is a comparison of distillation of the SYNTHOIL feed and the product from Run 1. See Appendix C for continuous run data and results. SYNTHOIL was fed to the reactor at a liquid hourly space velocity (LHSV) of 4. The run conditions were a temperature of 450°C and a pressure of 800 psig. The catalyst was sulfided CCI catalyst C-20-6, Cobalt Molybdenum on silica activated alumina. A hydrogen flow rate of 5000 scf/bbl of feed was used.

Product 1 gave a small improvement in cracking in the lower range of distillation. The slope of the curve, however, is not as steep and gives an endpoint of 53%. This shows improvement in the higher boiling fractions and is a step in the right direction.

The run was ended before more variables could be tested due to plugging of the back pressure regulator valve with tar. It was theorized that uncracked SYNTHOIL tar was causing the plugging. So the run was repeated using a higher pressure and lower LHSV to try to increase conversion.

Run 2 was made using the same Co-Mo catalyst as in Run 1. Run conditions were 450°C and 1000 psig hydrogen pressure. A hydrogen

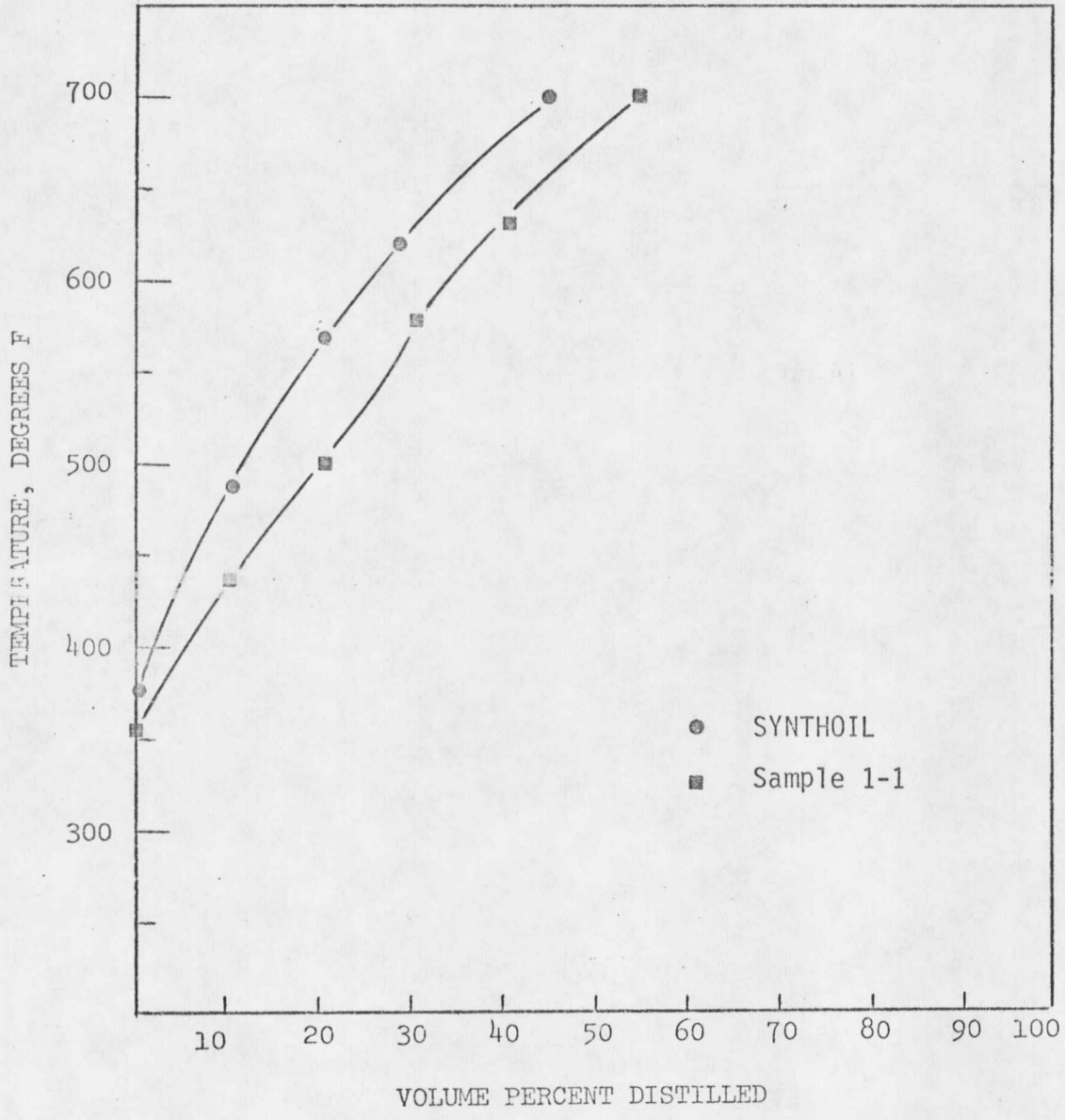

FIGURE 5. ASTM Distillation, Run 1
Catalyst: CCI C-20-6; 4% CoO, 15% MoO_3 on Alumina

flow rate of 10,000 scf/bbl was used.

Products 2-1 and 2-2 are graphed in Figure 6. For product 2-1, SYNTHOIL was fed at a LHSV of 1.4. This product was very noticeably liquid compared to SYNTHOIL and the product from Run 1. Distillate started coming off at 250°F and 70% distilled off by the end point 700°F. This is a good improvement over SYNTHOIL. Percent desulfurization was 70%, while 24% of the nitrogen was removed.

Product 2-2 is under the same conditions only with an increase in LHSV from 1.4 to 3.0. The graph shows no improvement over the SYNTHOIL. No denitrogenation was noted, but sulfur was reduced 43%.

Again the run was ended due to plugging of the back pressure valve. Since conversion seemed to drop off with time during the run, the unreacted SYNTHOIL that was plugging the valve might be due to carboning up of the reactor. To test this theory, a temperature decrease from 450°C to 400°C was decided on for the next run.

Run 3 was made using sulfided Harshaw catalyst Ni-4401, Nickel-Tungsten on silica alumina. Run conditions were a temperature of 400°C and a pressure of 800 psig. Hydrogen flow rate was 10,000 scf/bbl. SYNTHOIL was fed at a LHSV of 1. The product from Run 3 and the feed are plotted on Figure 7. Distillate started coming off at about the same temperature as SYNTHOIL. End point gave 62 volume percent distilled. Heteroatom removal was negligible.

Plugging of the back pressure regulator valve ended the run.

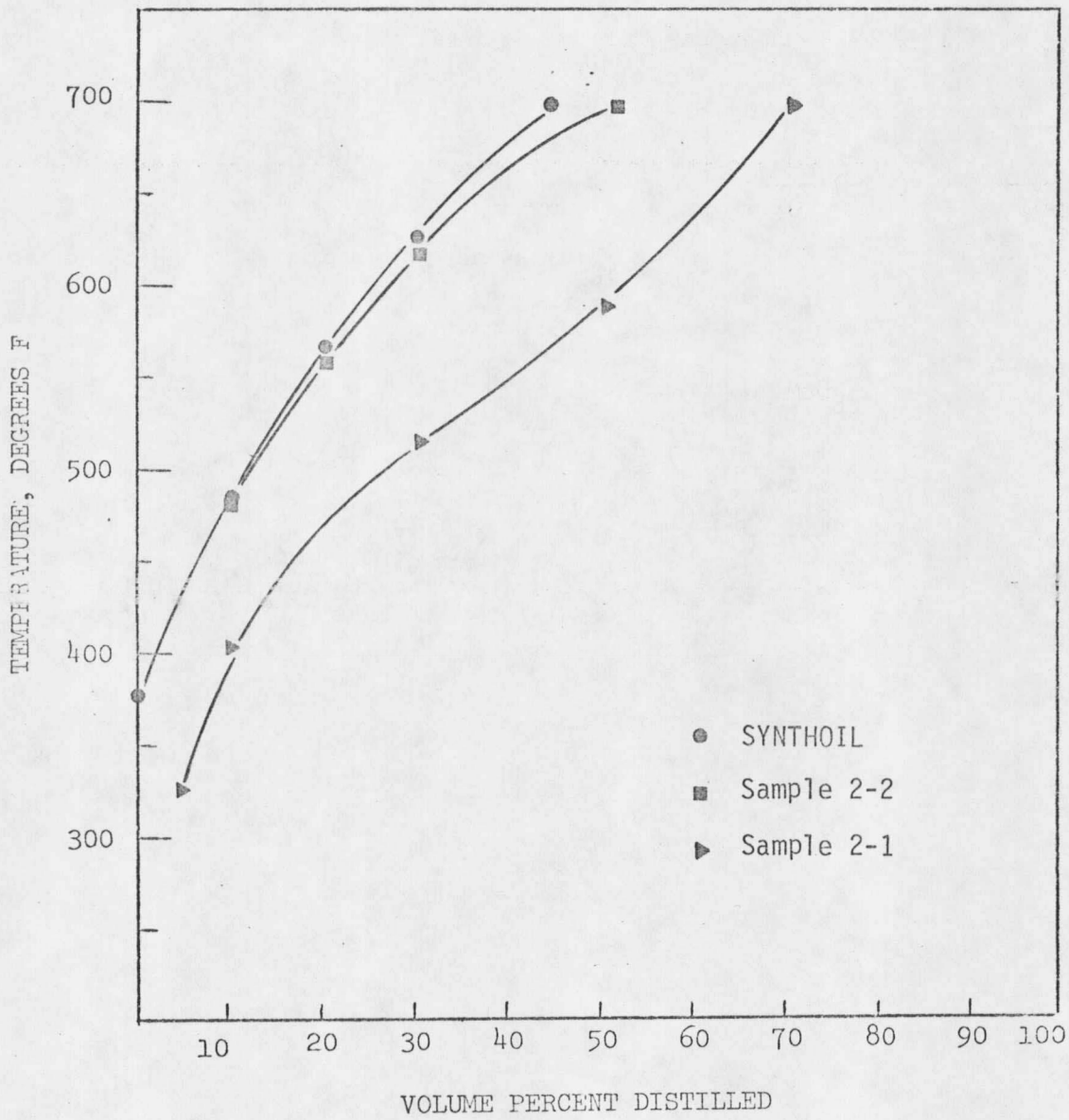

FIGURE 6. ASTM Distillation, Run 2
Catalyst: CCI C-20-6; 4% CoO, 15% MoO_3 on Alumina

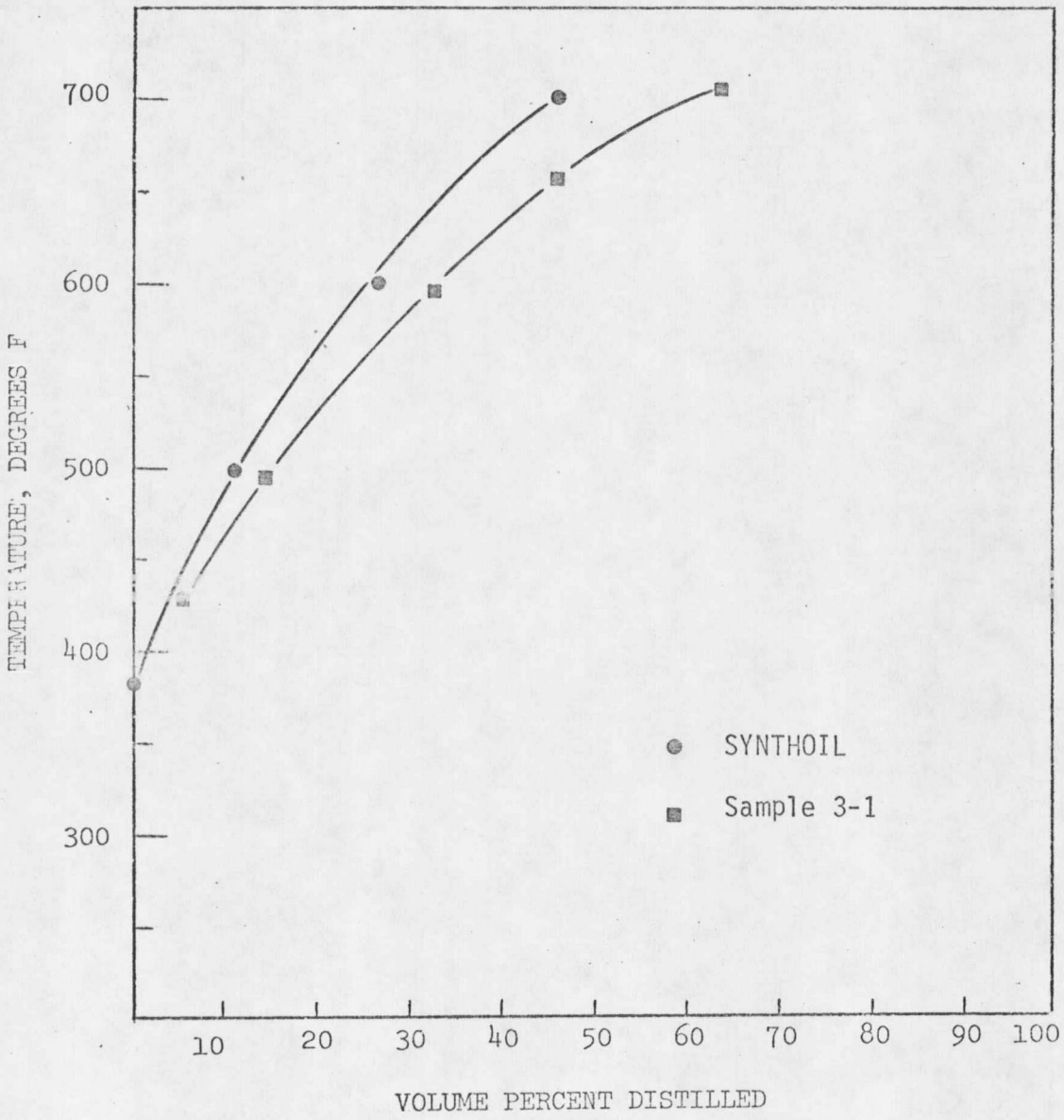

FIGURE 7. ASTM Distillation, Run 3
Catalyst: Harshaw Ni-4401; 6% Ni, 19% W on Silica Alumina

In these preliminary runs, the number one problem was plugging of the back pressure valve three to four hours into the run. This prevented any changing of parameters during the run, which would have supplied more data. Down time between runs to clean and recharge the reactor and to sulfide the catalyst was time consuming and cuts down on the number of runs that can be made.

Observations were made of the product collection and cleaning of the back pressure regulator valve and piping from the reactor to the valve. The first product that comes from the reactor was small continuous drops of oil. Gradually the drops change into spurts as the product surges out, then stops, then surges again. These spurts increase in intensity as they decrease in frequency. At the same time an increase in reactor pressure was noted from 10-50 psig between surges and then drops back to operating pressure with each surge of the product. The run is ended when the reactor pressure increases 100-200 psig above the back pressure without any product coming off. When the reactor was taken apart for cleaning, the back pressure valve and piping from the reactor were full of tar which had to be drilled out because it had solidified.

It was theorized that the plugging problem was because the lighter fractions from the SYNTHOIL feedstock are easily driven off and hydrotreated. Some of the heavier fractions are also cracked and hydrotreated, but the tar residue that was left was too thick and

viscous to flow through the back pressure regulator valve. The tar accumulates during the run until it blocks the flow of even the lighter oils.

To get around this problem the piping coming from the reactor was changed. Instead of running the gases and liquid product through the back pressure valve and collecting them, only the gases flowed through the valve. The gases and liquids were separated before the back pressure valve. The liquid product was collected at the bottom of the separator and the product drawn off in batches. No plugging problems were encountered in subsequent continuous runs using this modification.

Due to the time involved in setting up for a continuous run and cleaning up after, bomb autoclave tests were performed on several catalysts. The results from the bomb runs showed promise in predicting catalyst success, so it was decided that a bomb run should be made for each new catalyst tested. Data from the bomb runs would indicate if any improvement in cracking SYNTHOIL or heteroatom removal were made, and at what temperature reaction starts.

Bomb Runs

The twenty-five catalysts tested in bomb runs are listed in Appendix A. All catalysts tested except $SnCl_2$ (Run B11) are commercial catalysts. Most catalysts were dried and sulfided before

being loaded in the bomb. Non-sulfided catalysts will be pointed out in the discussion.

The bomb runs were operated at the same run conditions. An initial hydrogen pressure of 2000 ± 100 psig was used. The bomb was loaded in a rocking heater, heated to 450 ± 5°C, and held at this temperature for one hour. Runs B21, B23, and B24 were operated at lower temperatures.

Comparisons of the catalysts is a difficult problem. Each catalyst must be looked at in its entirety. The type, weight percent, and composition of promoters varies with each catalyst. The type and composition of the supports are also important, along with the physical properties of the support: form, surface area, and pore size. Looking at Appendix A, it can be seen how much the catalysts vary from each other. When one catalyst is said to be better than another, it must be remembered that these are specific catalysts so there may be problems in extrapolating the results to general classes of catalysts. This discussion will look at similarities among catalysts and try to draw some general conclusions where applicable.

The data for the bomb runs is presented in Appendix B. The hydrocracking results for each catalyst are listed as distillate yields in Table IV. The ASTM distillation results are broken down into four products as follows: (1) % Naphtha (IBP - 425°F), (2) % Fuel oil (425-600°F), (3) % Gas Oil (600-700°F), and (4) % Residue

TABLE IV. BOMB RUN DISTILLATE YIELDS

Run #	Catalyst	% Naphtha IBP-425°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F+	Total Vol. % Distilled
	SYNTHOIL	4	20	20	56	44
B8	Ni-1600	5	17	19	59	41
B17	Cr-0103	6	18	19	57	43
B18	Cr-0105	5	20	19	56	44
B13	W-0801	6	22	18	54	46
B23	Ni-4301	7	21	19	53	47
B19	Ni-3210	5	23	19	53	47
B14	Mo-1201	10	22	17	51	49
B27	HC-5-1.5E	6	20	23	51	49
B1	Ni-4401	6	23	20	51	49
B9	Ni-3250	8	20	21	51	49
B12	HT-100	10	22	18	50	50
B29	Shell 344	8	21	21	50	50
B3	Ni-1800	4	23	24	49	51
B21	W-0101	6	25	20	49	51
B2	Ni-1601	7	22	22	49	51
B11	$SnCl_2$	8	24	21	59	51
B28	Shell 324	10	21	21	48	52
B24	Ni-4301	7	22	23	48	52
B7	Ni-4303	12	22	20	46	54
B26	330-3E	12	22	20	46	54
B10	Ni-0104	9	23	22	46	54
B6	C-20-6	10	21	25	44	56
B15	W-0101	23	25	9	43	57
B20	CoMo-0603	9	25	27	39	61
B5	Ni-4301	9	24	28	39	61
B22	HT-400	10	24	30	36	64

TABLE IV (Cont). BOMB RUN DISTILLATE YIELDS

Run #	Catalyst	% Naphtha IBP-420°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F+	Total Vol. % Distilled
B4	CoMo-0401	11	23	31	35	65
B25	HT-500	11	25	29	35	65

Note: Catalysts listed by run numbers and manufacturers identification numbers. Catalyst descriptions given in Appendix A.

(700°F+). The catalysts are arranged in increasing order of total volume percent distilled. The first line is the SYNTHOIL feed distillation results.

Looking at Table IV, no general trends as to what makes a good catalyst are obvious. Of the six best hydrocracking catalysts, all are made by Harshaw. Three are CoMo catalysts (CoMo-0603, HT-400, CoMo-0401) and there are one each of W (W-0101), Ni-W (Ni-4301) and Ni-Mo (HT-500). Two catalysts have supports of silica alumina (CoMo-0401 and Ni-4301). The other four supports are alumina. The products from these catalysts were liquid at room temperature and flowed easily.

Cracking shows about the same trend for all the "best" hydrocracking catalysts except W-0101. Good yields in Naphtha and gas oil ranges were obtained, with a small increase in fuel oil. W-0101 gives more than twice the yield of Naphtha and less than half the yield of gas oil.

The two best hydrocracking catalysts, Harshaw catalysts CoMo-0401 and HT-500, are graphed in Figure 8. The distillation graph for W-0101 is shown in Figure 9.

Harshaw Ni-W catalysts were tested in Runs B5 (Ni-4301) and B7 (Ni-4303). Both catalysts contain 6% Ni and 19% W. Ni-4301 on silica alumina support gives better hydrocracking than Ni-4401 on alumina support. The same trend can be seen for Ketjen catalysts

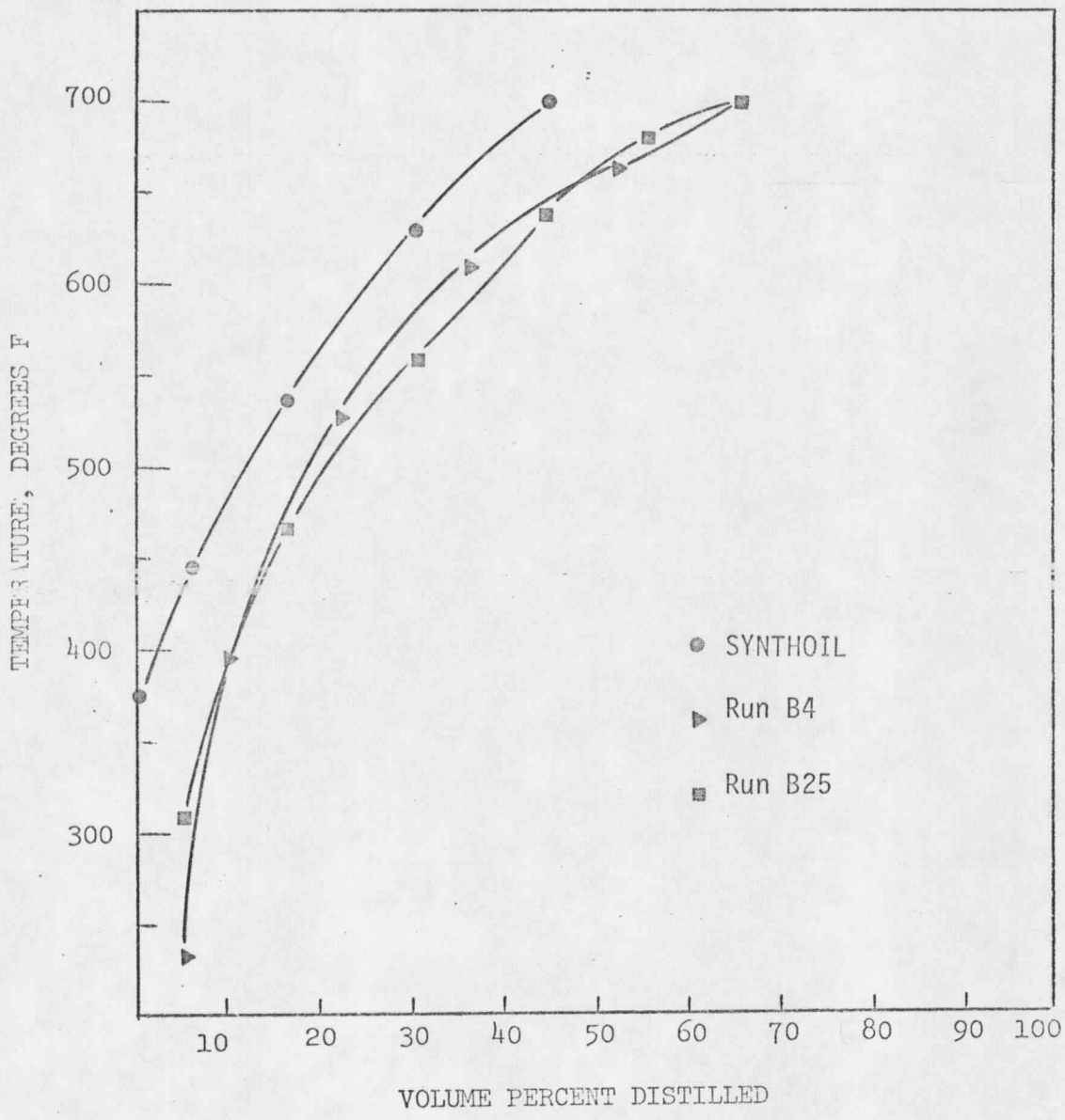

FIGURE 8. ASTM Distillation, Run B4 and Run B25
Run B4 Catalyst: Harshaw CoMo-0401
Run B25 Catalyst: Harshaw HT-500

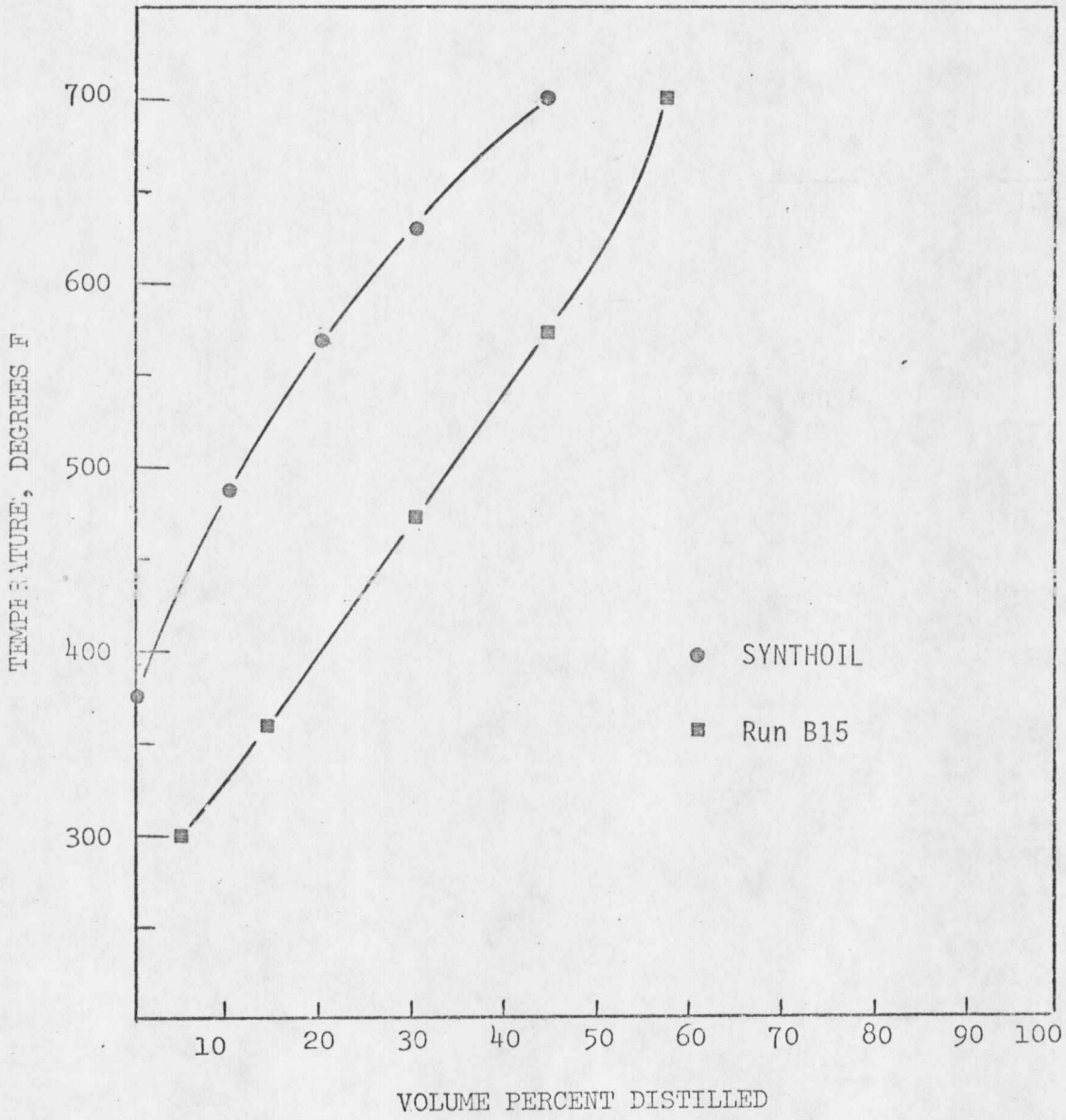

FIGURE 9. ASTM Distillation, Run B15
Catalyst: Harshaw W-0101; 10% WO_3 on Alumina

330-3E (6.2% NiO, 20% WO_3 on silica alumina) and HC-5-1.5E (6.5% NiO, 21% WO_3 on alumina). The silica alumina support did a better job of hydrocracking.

Heteroatom removal is also important in upgrading SYNTHOIL. Table V lists the heteroatom removal for bomb runs in order of increasing hydrocracking. No trends are obvious from the table.

The best desulfurization catalyst is Ni-0104, which is a powder containing 60% Ni on Kieselguhr. This catalyst was not presulfided. At the end of the run, the powder catalyst had to be chipped out of the bomb. A serious plugging problem would probably be encountered if a powder catalyst were tried in the continuous fixed bed reactor.

One other catalyst that was not presulfided Ni-3250, also gave good desulfurization results. This catalyst is very interesting because it has an alkaline support while most catalysts are slightly acidic.

Sulfided catalysts Shell 324 (NiMo) and Harshaw CoMo-0603 gave better than 50% desulfurization.

Denitrogenation is much more difficult than desulfurization. The two best hydrocracking catalysts gave the best denitrogenation results. The catalysts are CoMo-0401 and HT-500 (NiMo).

Shell catalyst 344 (CoMo on alumina) gave the best heteroatom removal (48% deS and 32% deN). However, hydrocracking results with this catalyst were not very good.

TABLE B. BOMB RUN HETEROATOM REMOVAL

Run #	Catalyst	Vol. % Distilled	% DeS	% DeN
B8	Ni-1600	41	07	10
B17	Cr-0103	43	00	05
B18	Cr-0105	44	05+	00
B13	W-0801	46	27	04
B23	Ni-4301	47	41	17
B19	Ni-3210	47	05	25
B14	Mo-1201	49	36	19
B27	HC-5-1.5E	49	25	23
B1	Ni-4401	49	41	18
B9	Ni-3250	49	50+	17
B29	Shell 344	50	48	32
B12	HT-100	50	36	18
B3	Ni-1800	51	16	00
B21	W-0101	51	09	00
B2	Ni-1601	51	07+	06
B11	$SnCl_2$	51	20+	10
B28	Shell 324	52	55	21
B24	Ni-4301	52	23	28
B7	Ni-4303	54	45	18
B26	330-3E	54	30	12
B10	Ni-0104	54	57+	16

TABLE V (Cont.) BOMB RUN HETEROATOM REMOVAL

Run #	Catalyst	Vol. % Distilled	% DeS	% DeN
B6	C-20-6	56	18	25
B15	W-0101	57	25	03
B20	CoMo-0603	61	52	25
B5	Ni-4301	61	32	29
B22	HT-400	64	34	13
B4	CoMo-0401	65	16	33
B25	HT-500	65	32	33

+ Catalysts not sulfided

Note: Catalysts listed by run numbers and manufacturers identification numbers. Catalyst descriptions given in Appendix A.

% DeS based on SYNTHOIL containing .44% S

% DeN based on SYNTHOIL containing 1.06% N

Bom runs also supply data on temperature effects. ASTM distillation curves of Runs B5, B23, and B24 are graphed in Figure 10. These runs were made using the same Harshaw Ni-4301 catalyst and keeping all run conditions the same except the reaction temperature. Run B5 was operated at 450°C which is the usual reaction temperature. A decrease in hydrocracking is noted in going from 450°C to 418°C and finally to 400°C.

The heteroatom removal vs. temperature is also given in Figure 10. The percent denitrogenation decreases with decreasing temperature. The sulfur removal starts to show this trend, but the highest percent desulfurization is at the lowest temperature.

The bomb runs do a good job of screening catalysts to be tested in the continuous reactor.

Continuous Runs

Catalysts were tested in the continuous reactor to determine the effects of varying the LHSV, temperature, and hydrogen flow. The catalysts, data, and results for these runs are given in Appendix C.

Preliminary continuous reactor runs were plagued with plugging problems that caused the runs to end after only a short time on stream. A gas-liquid separator was installed after the reactor to alleviate the problem.

Comparing the bomb runs, Appendix B, to the "best" continuous

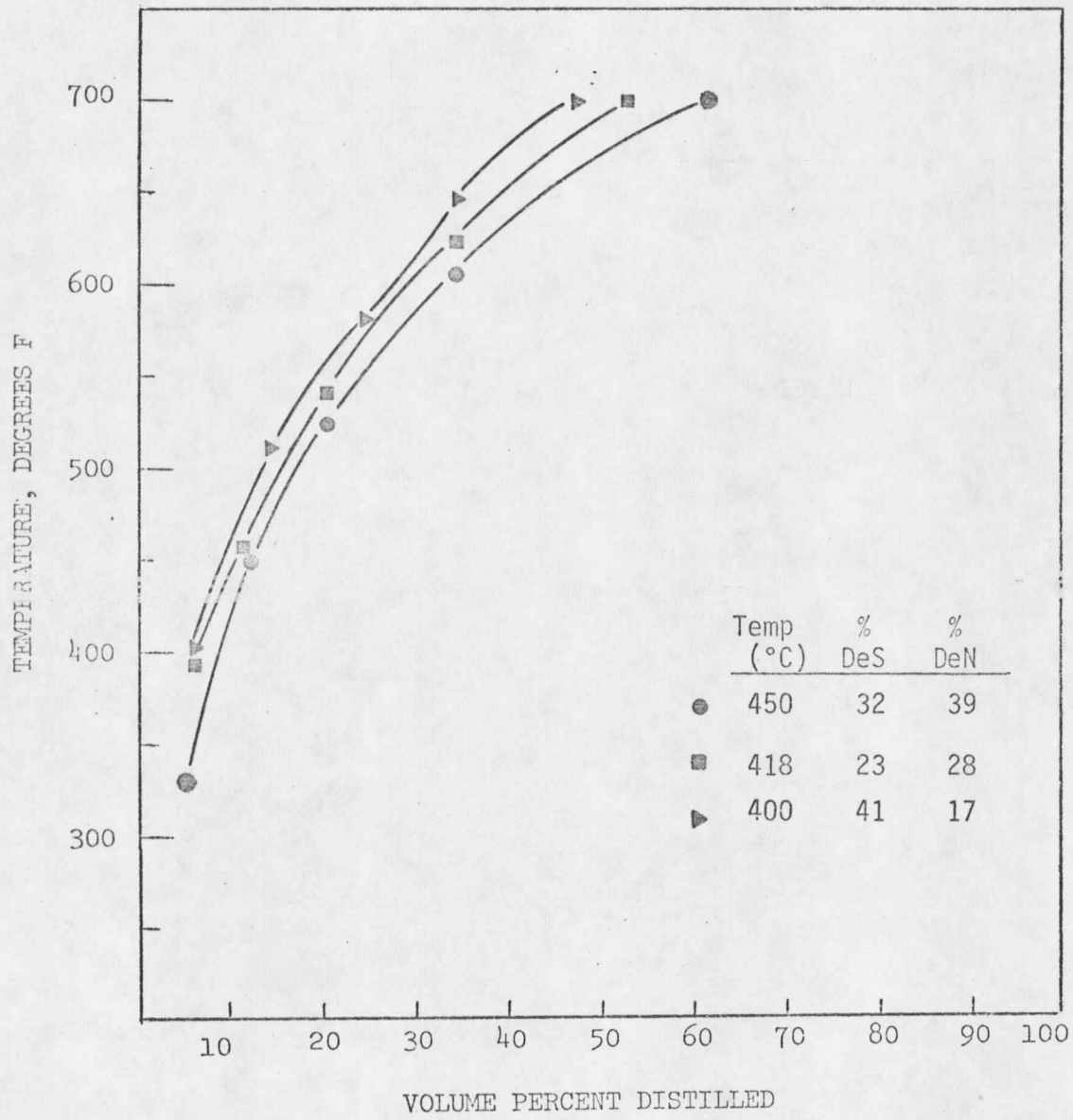

FIGURE 10. Temperature Effects on Bomb Runs
Catalyst: Harshaw Ni-4301; 6% Ni, 19% W on Silica Alumina

products from Runs 4 through 9, Appendix C, for the same catalysts shows an improvement in hydrocracking and desulfurization for the continuous runs. Denitrogenation did not increase and in some cases decreased. The "best" continuous products were usually at LHSV around one.

Figures 11 and 12 are graphs of two of the "best" catalysts, in both the bomb and continuous runs.

Looking at Figure 11 for CoMo-0401 shows an increase in cracking in the middle fractions. Desulfurzation more than doubled from 16% to 50%. Denitrogenation decreased from 33% to an insignificant 4%.

Figure 12, for HT-500, indicates an increase in hydrocracking all along the curve. Again desulfurization more than doubled from 32% to 70%. The percent denitrogenation stayed approximately the same at 33% compared to 32%.

Four samples from Run 4 with the same hydrogen flow rate and varying LHSV are plotted in Figure 13. The graph shows that as LHSV is increased there is a trend of decreasing cracking. Sample 4-2 and 4-5 contradict, but the distillations are close together and so are LHSV's.

Figure 14 is a plot of the three samples from Run 5, at different LHSV with constant hydrogen flow rate. The trend of a decrease in cracking with an increase in LHSV is not observed for all samples. Sample 5-1 with a LHSV of 2.17 gives a better distillate than

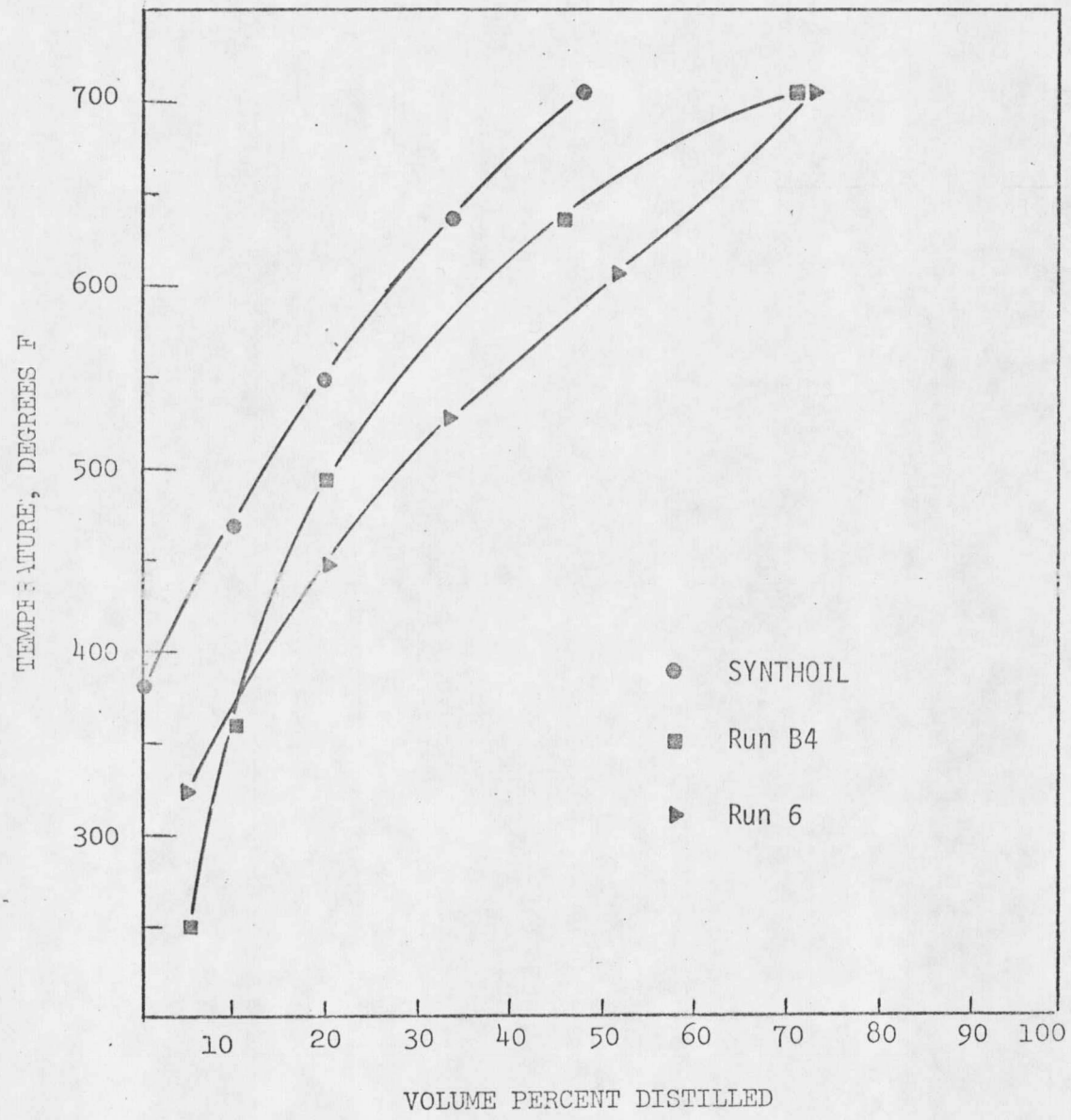

FIGURE 11. ASTM Distillation, CoMo-0401
Catalyst: 3% CoO, 9% MoO_3 on Alumina

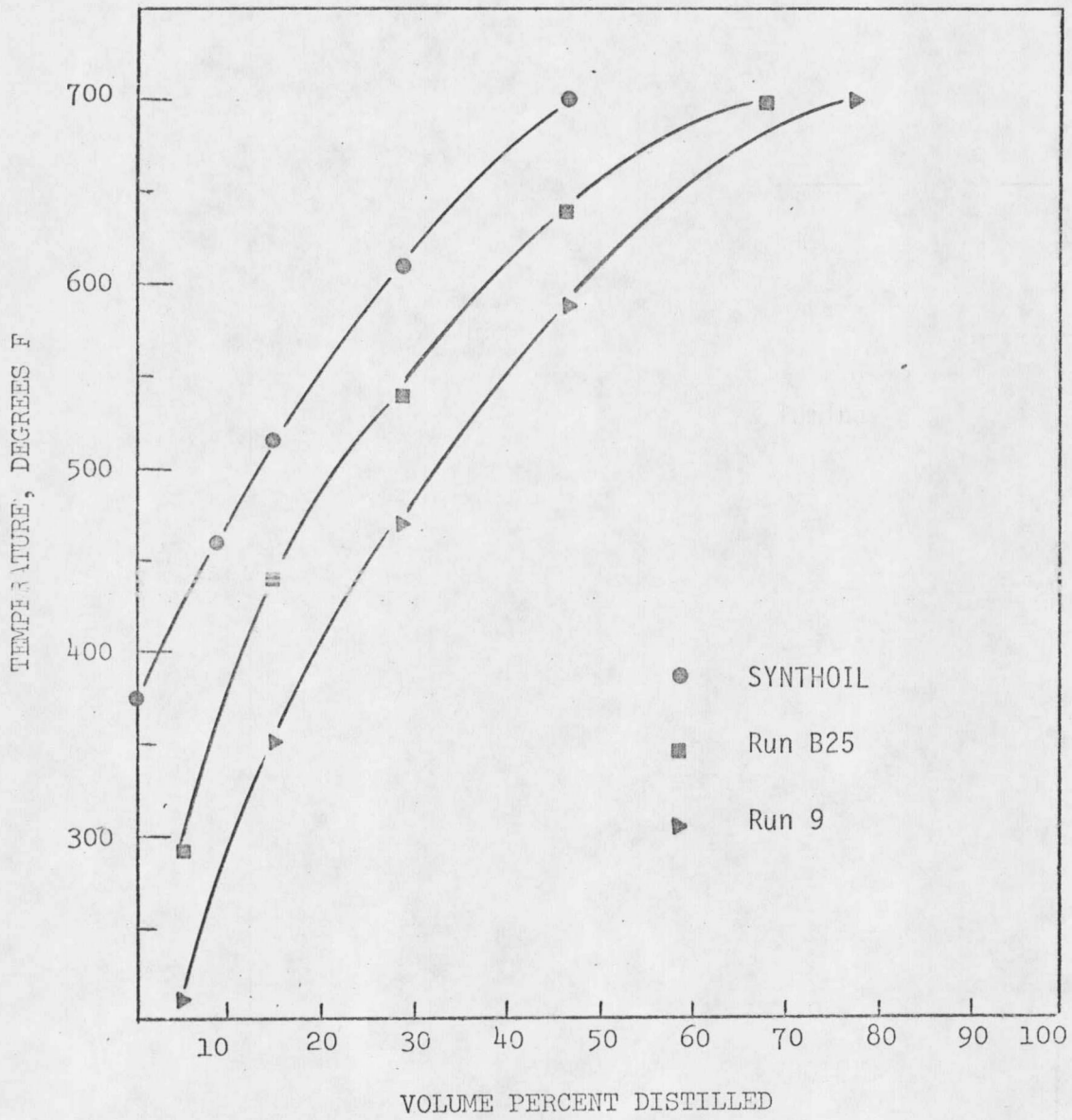

FIGURE 12. ASTM Distillation, HT-500
Catalyst: 3% NiO, 15.5% MoO_3 on Alumina

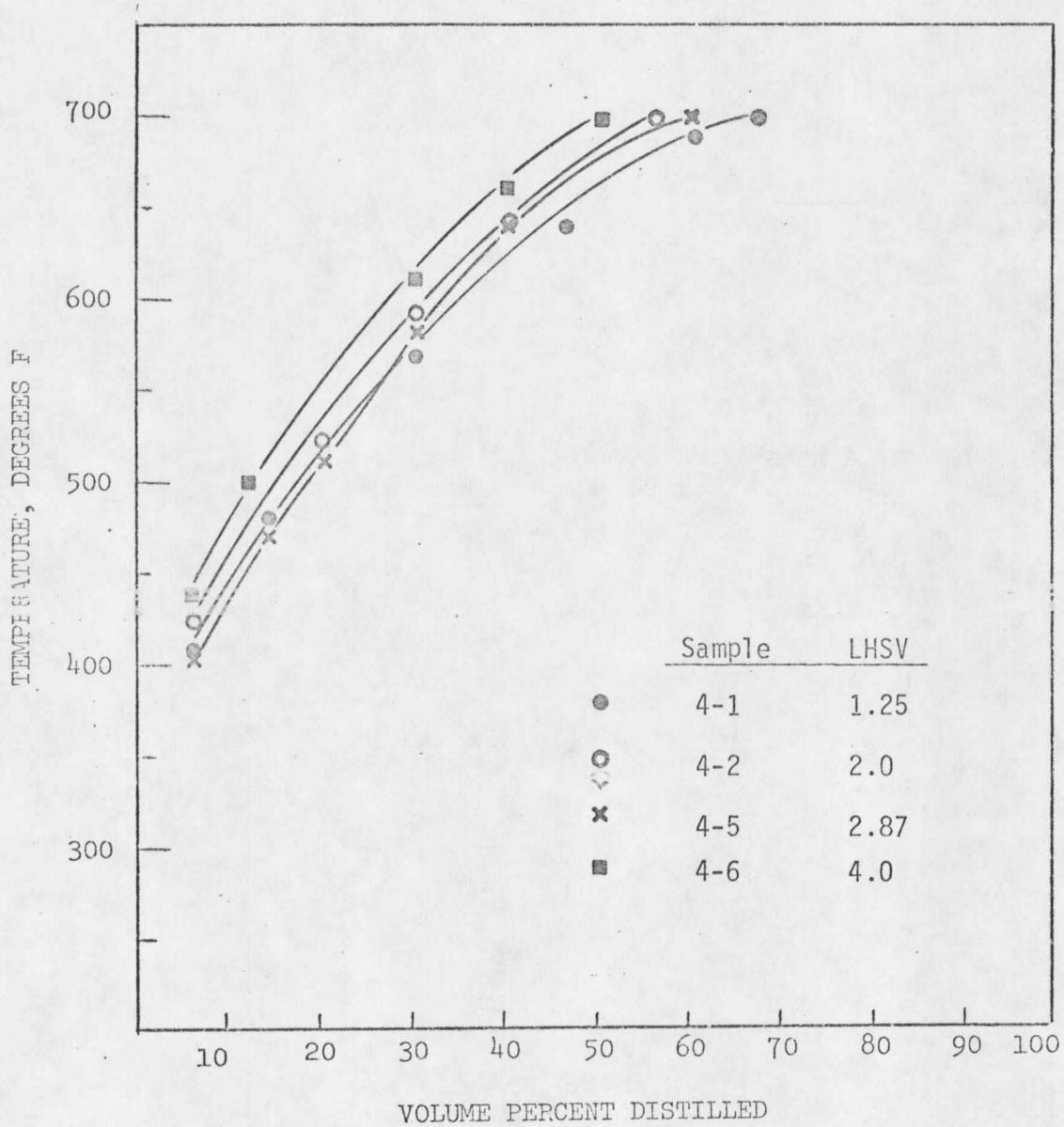

FIGURE 13. ASTM Distillation, Run 4
Catalyst: Harshaw Ni-1601
3% Ni, 3% Co, 3% Fe on Alumina

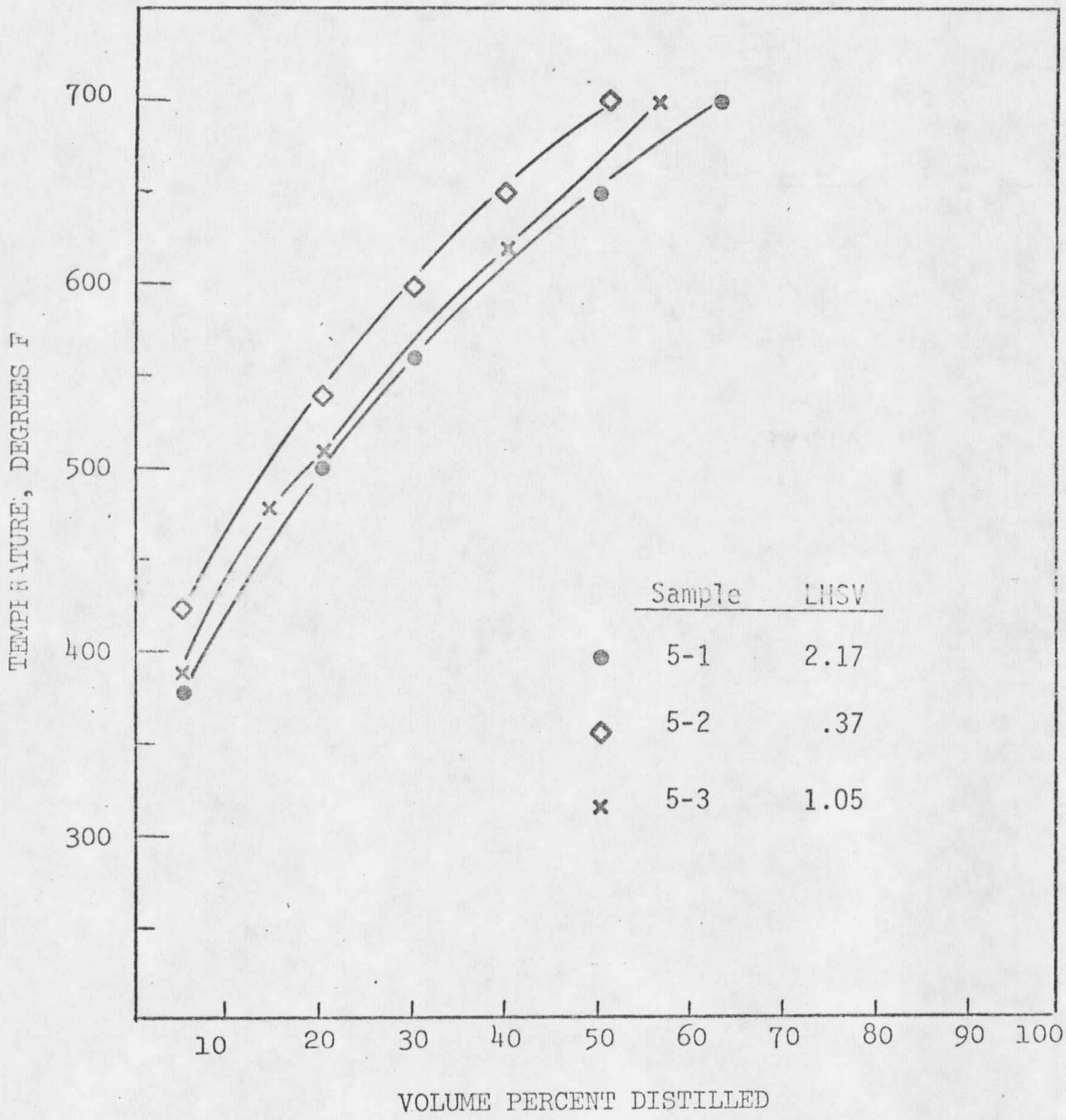

FIGURE 15. ASTM Distillation, Run 5
Catalyst: Harshaw Ni-3210
35% Ni on Proprietary Support

sample 5-3 with a LHSV of 1.05. No explanation is readily obvious. Looking at sample 5-2 with a LHSV of 0.37, its distillation curve is not very much improved over sample 5-1 as would be expected with the difference in LHSV. Some other phenomenum such as deactivity of the catalyst with time or possibly a decrease in hydrogen flow rate with time could produce these results. Hydrogen flow is controlled by a very fine micro-metering valve. This valve is calibrated before each run with a wet test meter and a calibration curve is drawn. Some variable could change during the run changing this calibration. For example, a restriction in the reactor which produces a larger back pressure than indicated on the back pressure regulator valve, would cause a decrease in hydrogen flow.

Run 6 looked at one of the better catalysts CoMo-0401. With constant hydrogen flow rates, the feed was varied to give different LHSV. The results are presented in Figure 15. It is quite evident that distillation results are inversely proportional to LHSV.

Figures 16-19 try to show some trends in heteroatom removal. Figure 16 is a plot of percent desulfurization vs. LHSV for three different catalysts. As can be seen the percent desulfurization decreases as the LHSV increases. The percent denitrogenation graphed in Figure 17 vs. the LHSV shows a general trend of increasing with increasing LHSV. Two data points contradict this statement, however.

Heteroatom removal vs. hydrogen flow rate is graphed in Figures

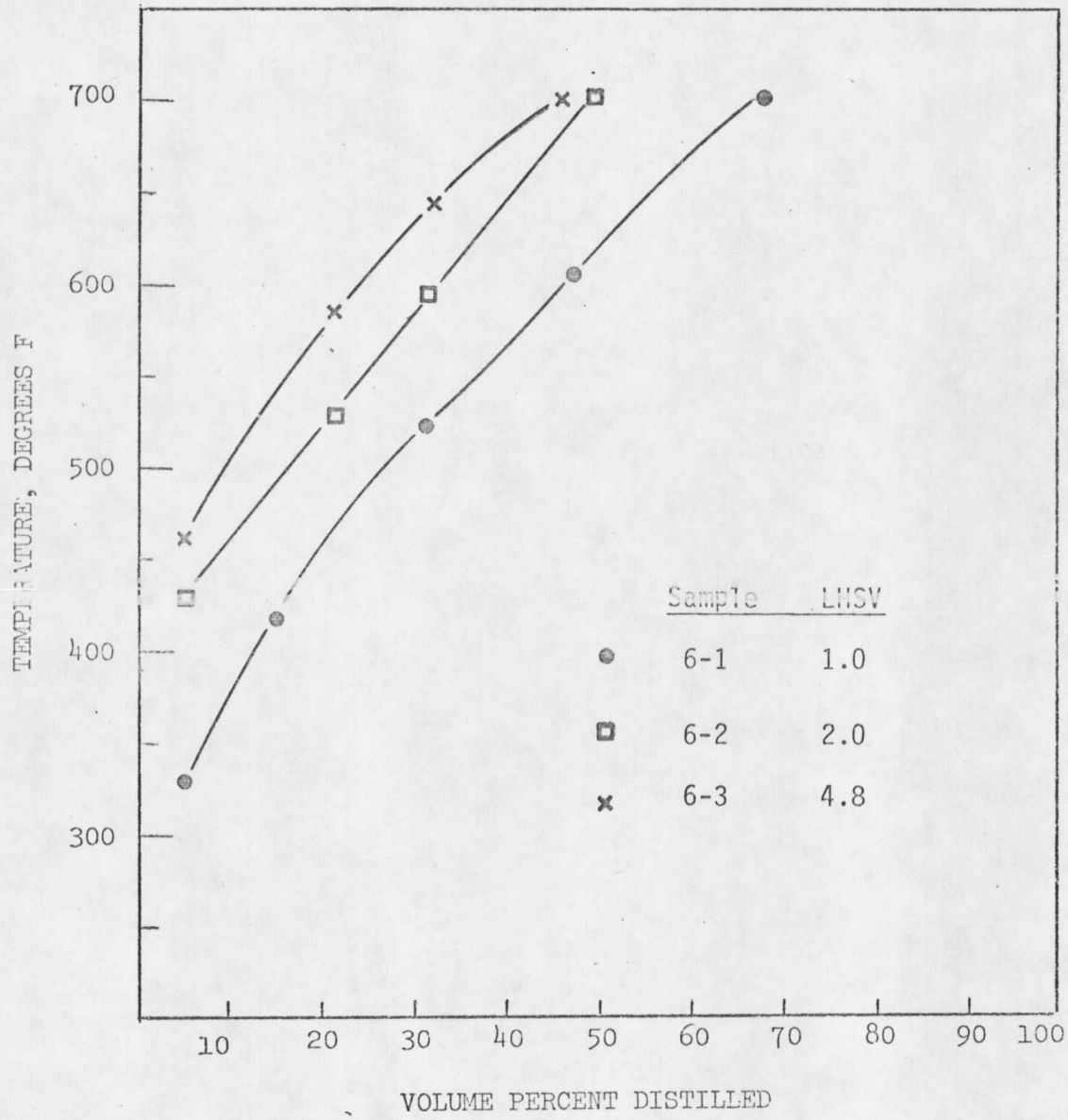

FIGURE 15. ASTM Distillation, Run 6
Catalyst: Harshaw CoMo-0401
3% CoO, 9% MoO_3 on Silica Alumina

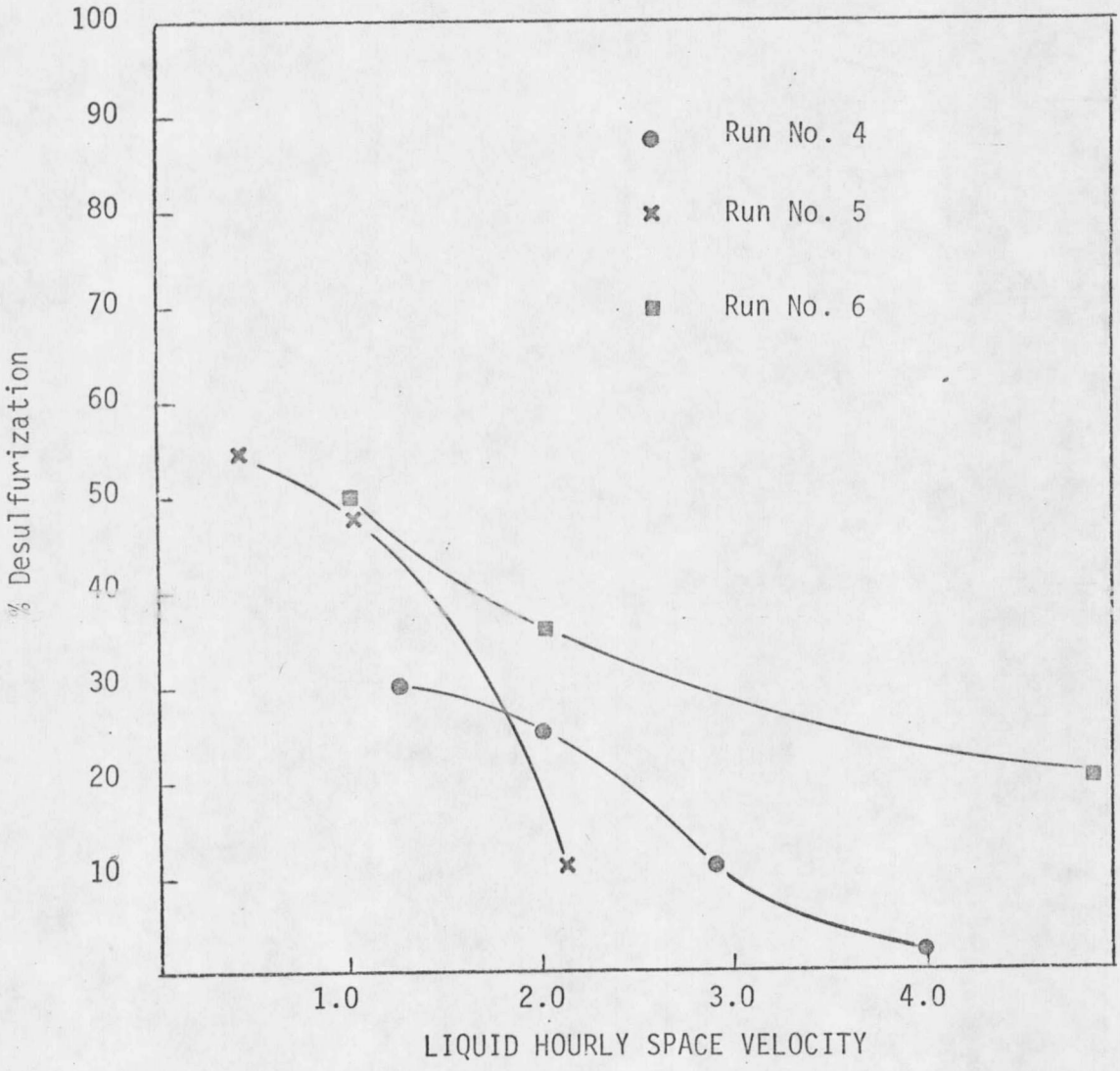

FIGURE 16. Percent Desulfurization vs. LHSV

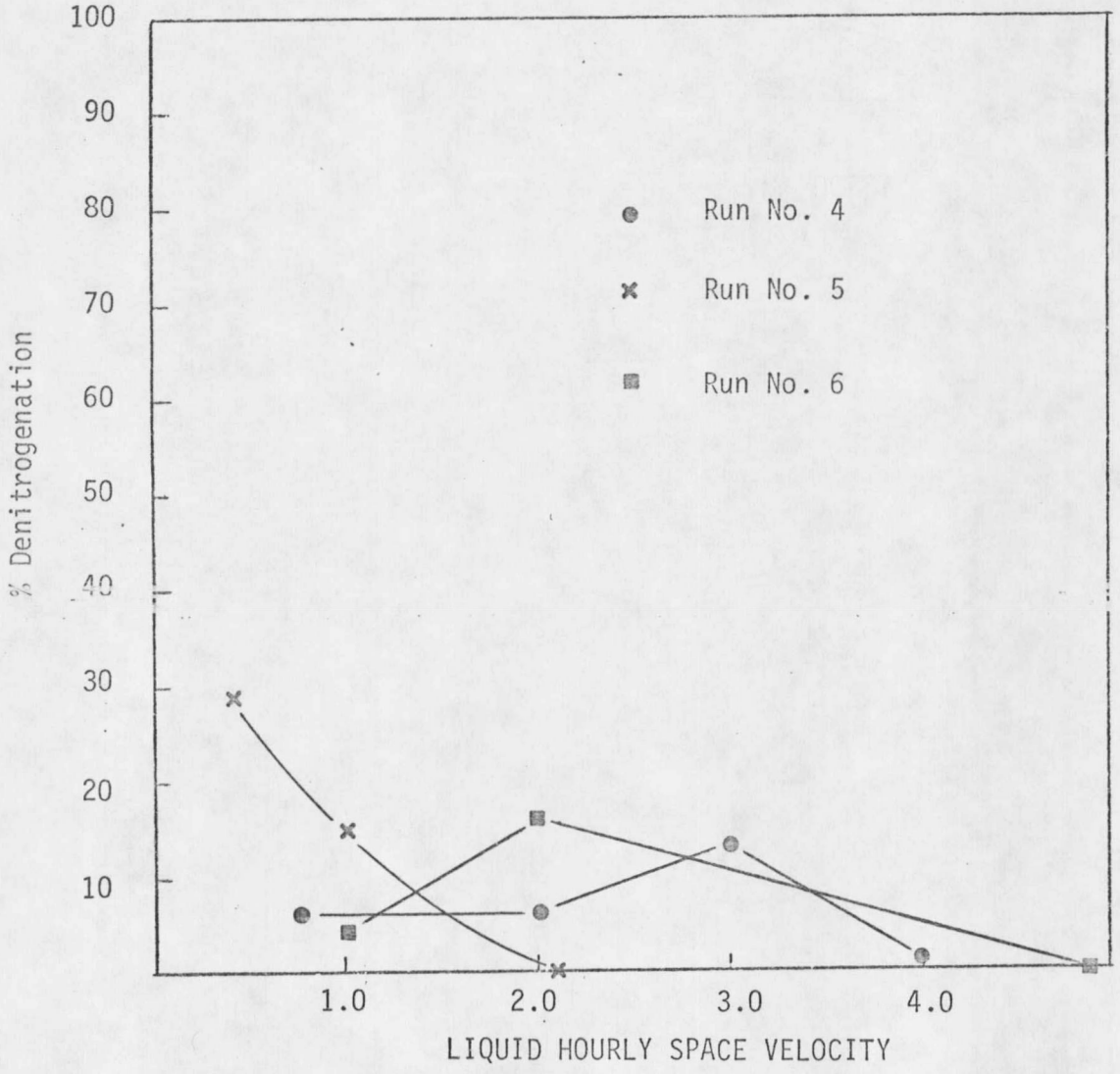

FIGURE 17. Percent Denitrogenation vs. LHSV

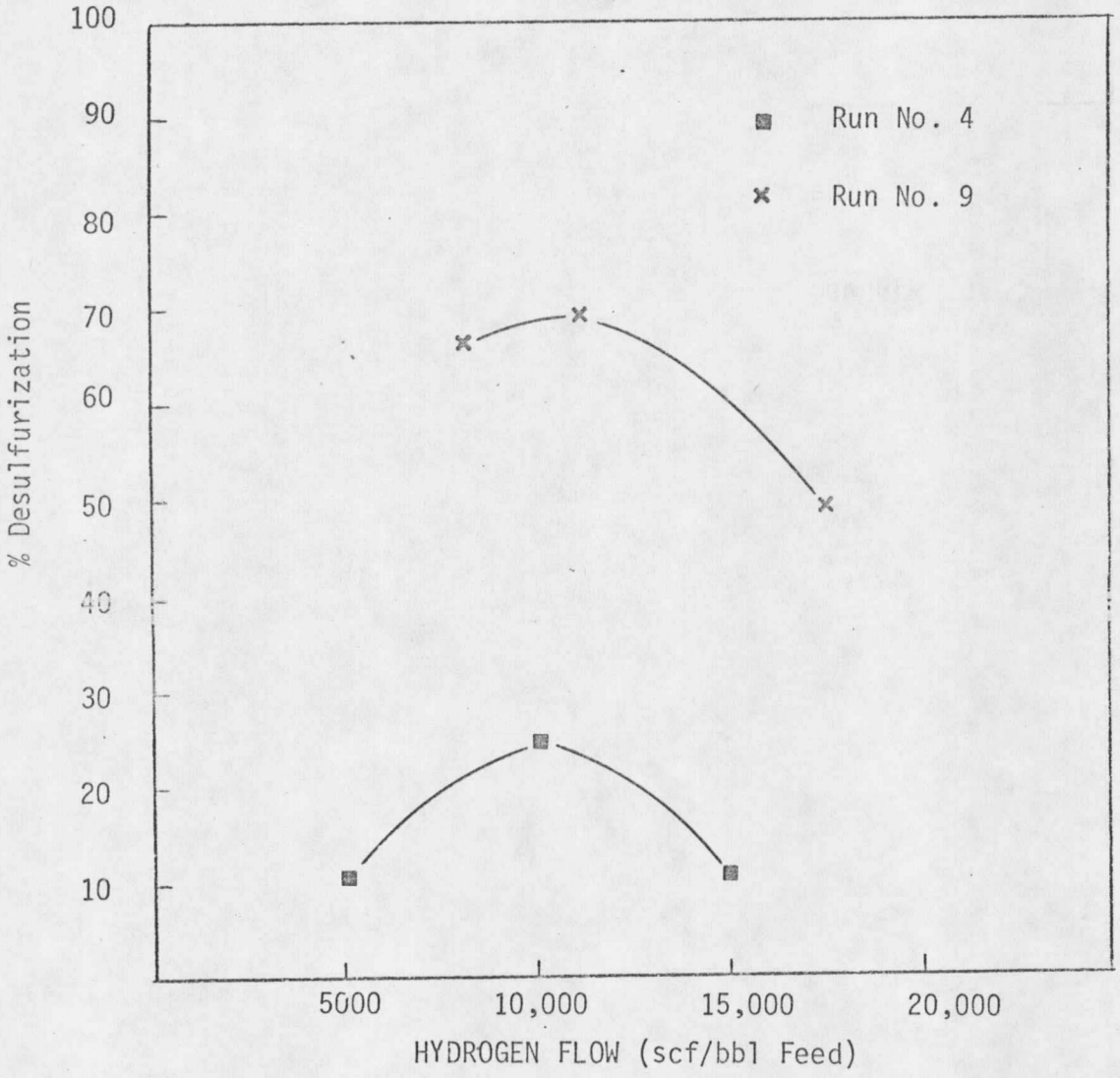

FIGURE 18. Percent Desulfurization vs. Hydrogen Flow

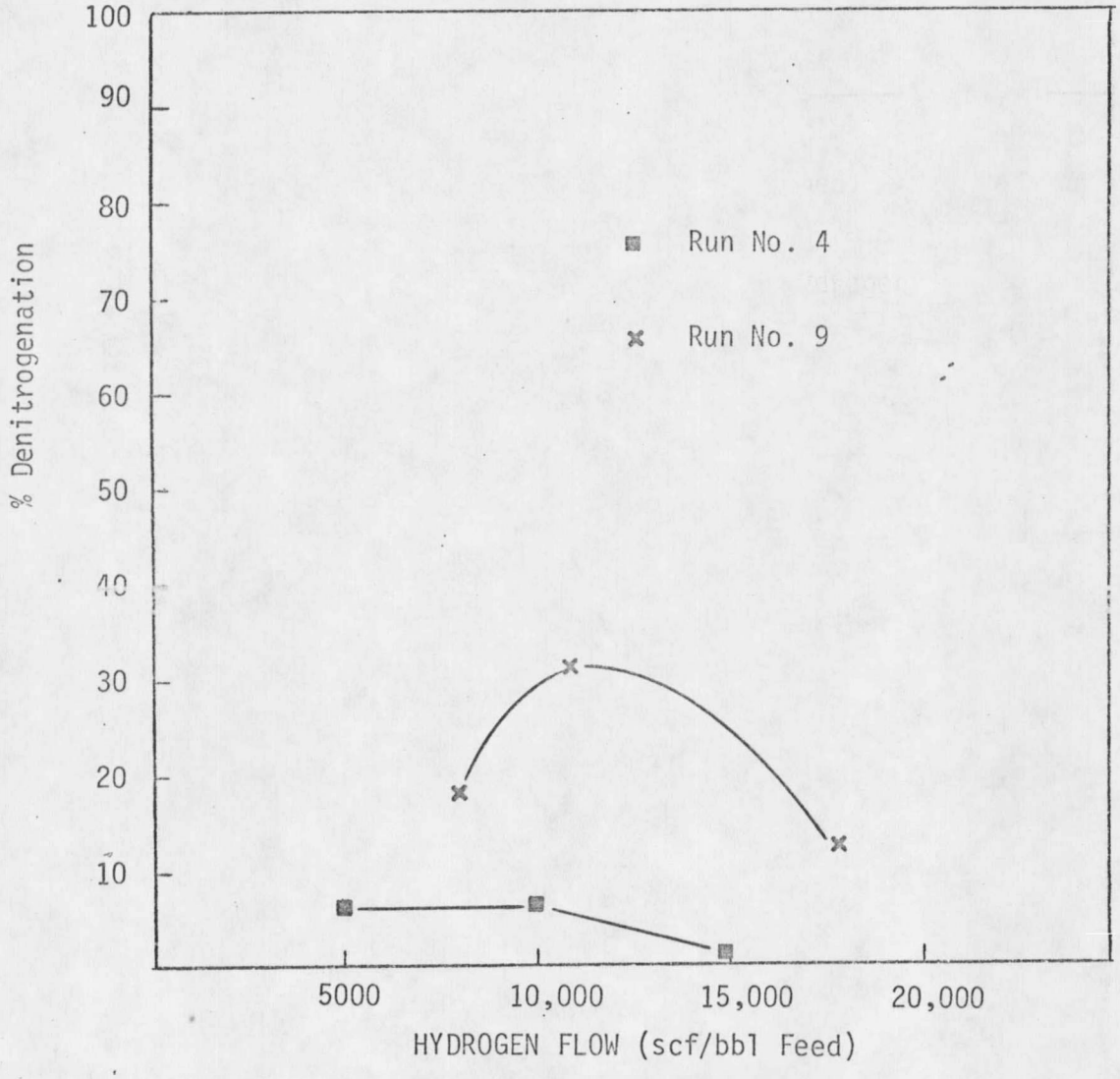

FIGURE 19. Percent Denitrogenation vs. Hydrogen Flow

18 and 19 for Run 4 (Ni-1601) and Run 9 (HT-500). The LHSV was approximately constant. In Figures 18 and 19 the percent desufluriza-tion and percent denitrogenation, respectively, reach a maximum at approximately 10,000 scf/bbl and then decrase. The worst results were at hydrogen flow rates greater than 15,000 scf/bbl. At these high flow rates the hydrogen must blow the SYNTHOIL through the catalyst bed so fast that good contacting and reaction do not occur.

Run 9, catalyst HT-500, was made to determine the effect of hydrogen flow rate. Figure 20 shows that a hydrogen flow rate of 11,000 scf/bbl gives the best hydrocracking results. This agrees with the flow rate for heteroatom removal given above.

Run 7 was made using a Ni-W catalyst Ni-4301. Four different temperatures were tested. The ASTM distillation results are graphed in Figure 21. It is noted that hydrocracking decreases with a decrease in temperature.

Figure 22 is the heteroatom removal for the continuous run. In this graph percent desulfurization and percent denitrogenation show the same general trend of decrease with a decrease in temperature.

The data from Run 8 (Ni-4303) is given in Appendix C. The object of the run was to determine if there was any deactivation of the catalyst during a 12 hour run (normal one day run). Samples 8-1, 8-2, and 8-3 were taken the first day of the run. All operating parameters were kept as consistent as possible for the 12 hour run.

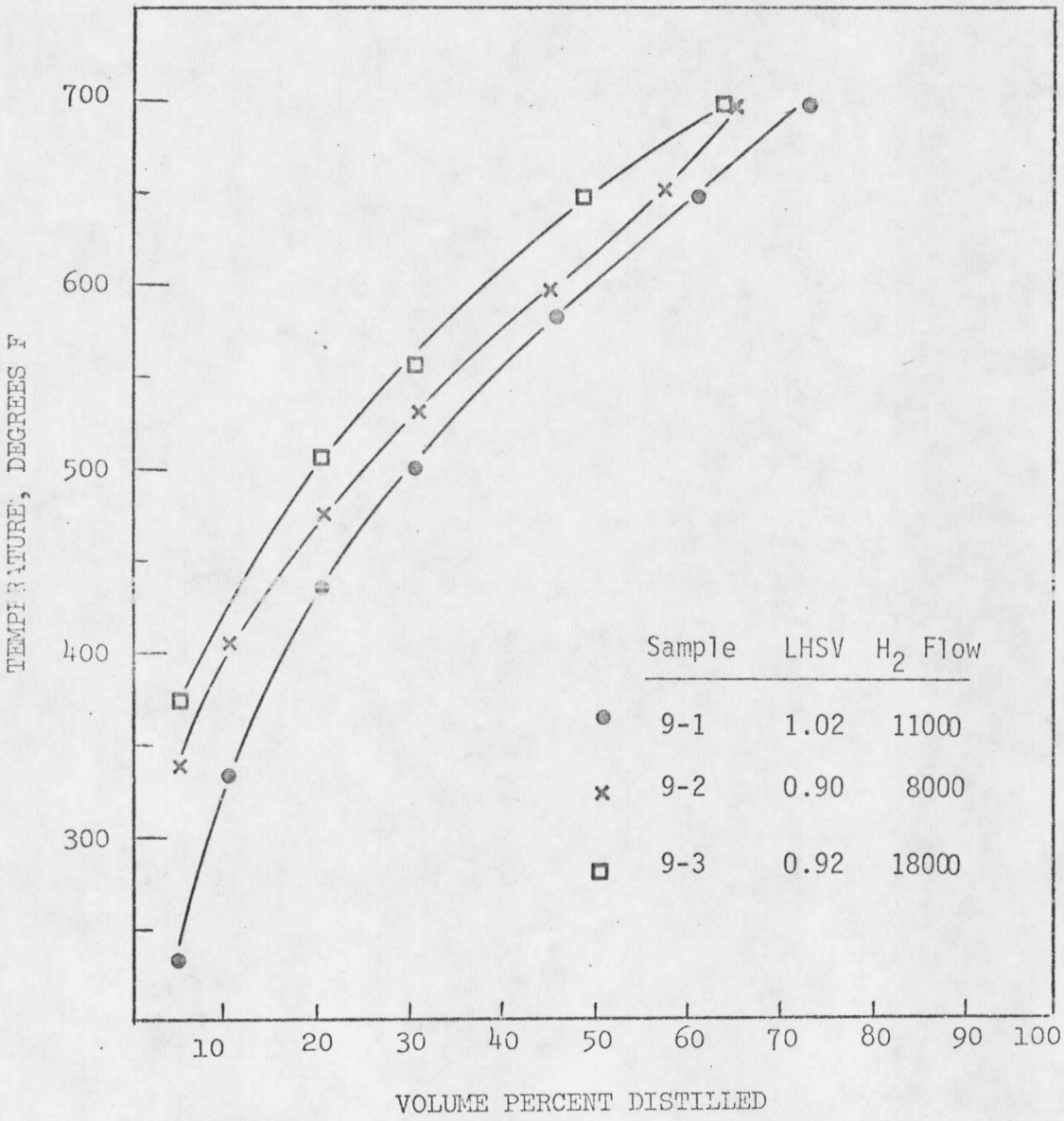

FIGURE 20. ASTM Distillation, Run 9
Catalyst: Harshaw HT-500; 3% NiO, 15.5% MoO_3 on Alumina

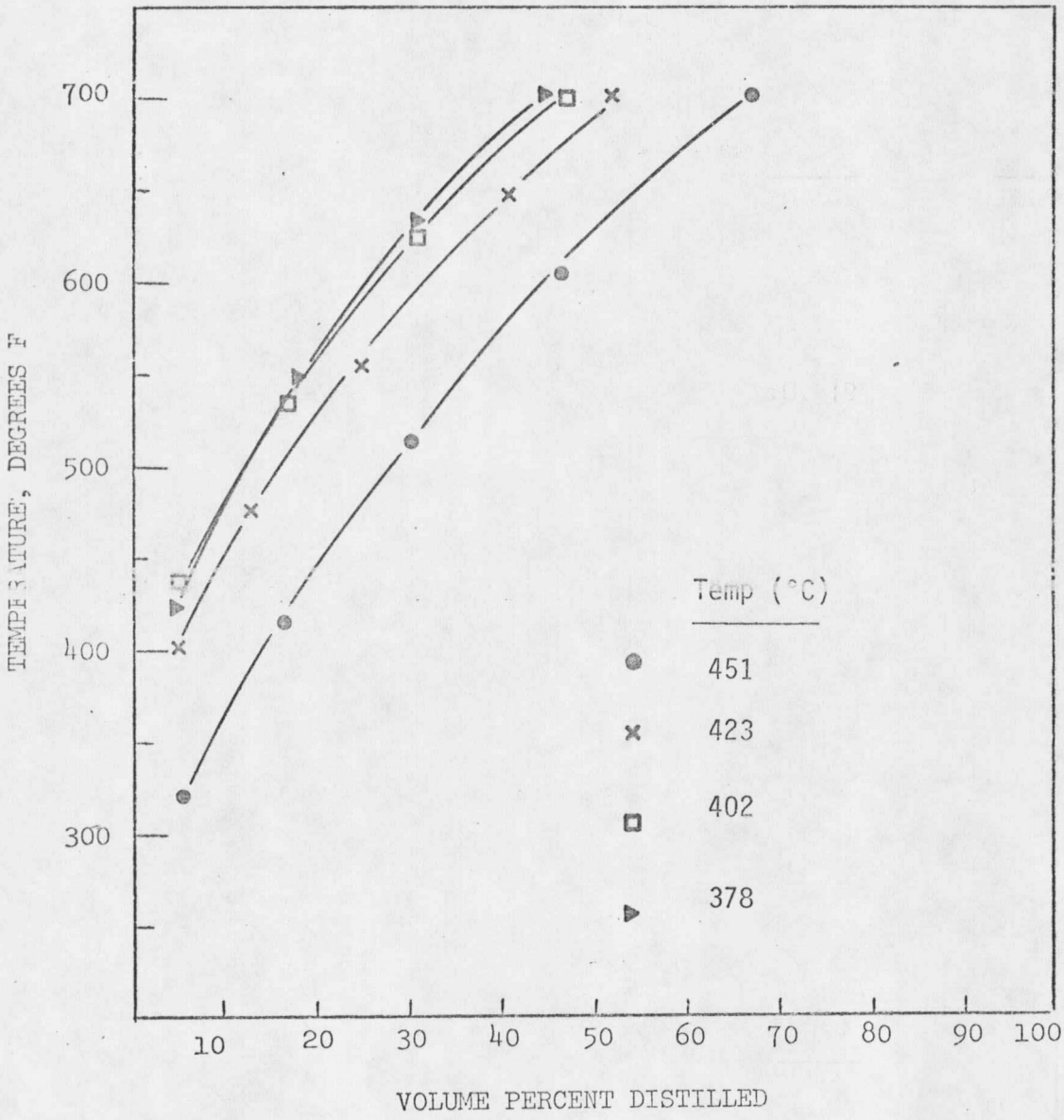

FIGURE 21. ASTM Distillation, Run 7
Catalyst: Harshaw Ni=4301; 6% NiO, 19% WO_3
on Silica Alumina

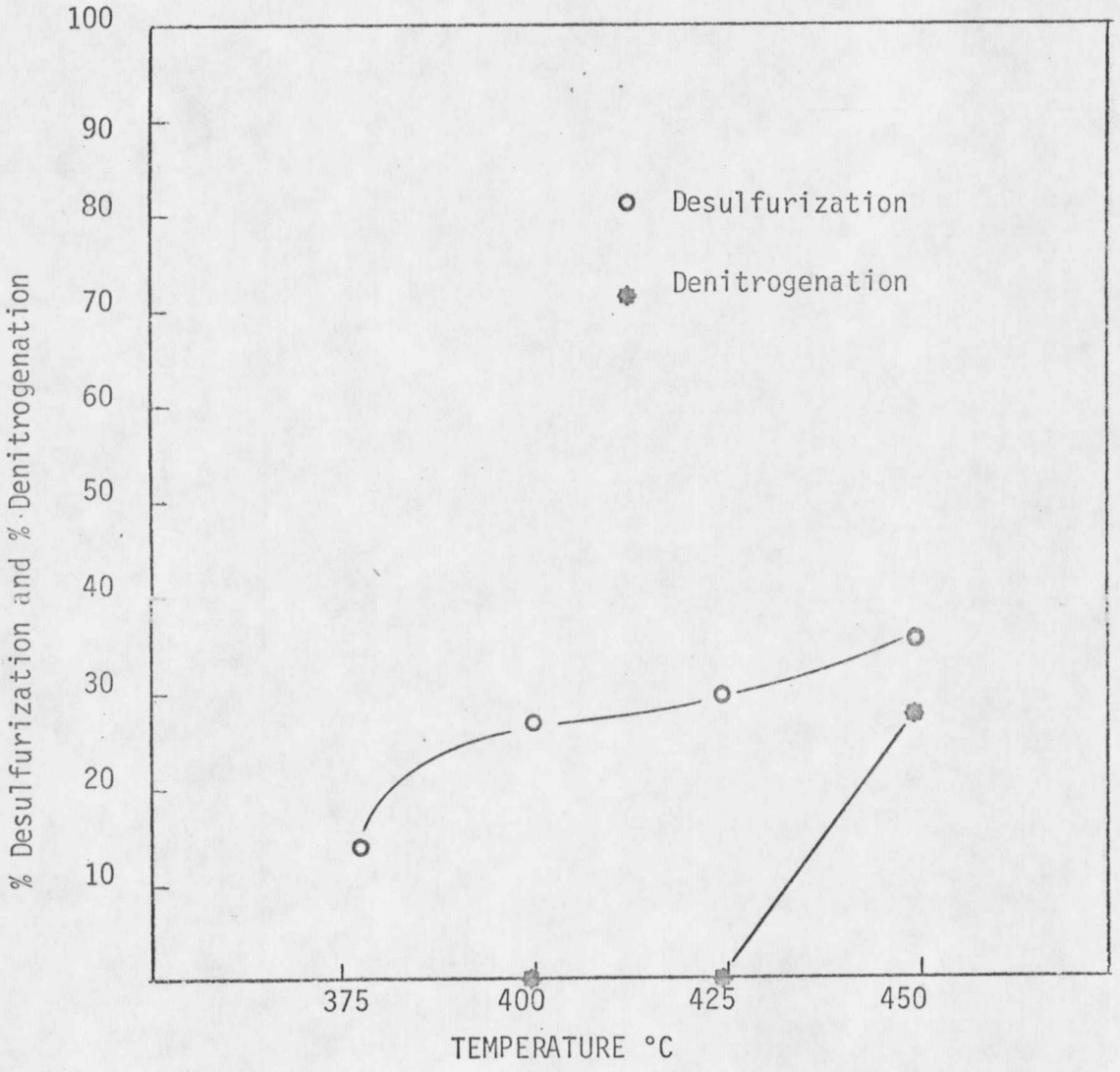

FIGURE 22. Percent Desulfurization and Denitrogenation vs. Temperature

Run No. 7
Catalyst: Harshaw Ni-4301

No deactivation of the catalyst was noted in hydrocracking, desulfurization, or denitrogenation during the 12 hours. The SYNTHOIL feed to the reactor was then stopped and a stream of hydrogen was trickled through the reactor overnight. Samples 8-4 and 8-5 were taken the second day. The hydrogen flow rate was doubled from 5000 to 10,000 scf/bbl. All other operating parameters remained the same. A decrease was noted from the first day in hydrocracking, desulfurization and denitrogenation. It was hoped that this test would allow runs to be made on consecutive days with no deactivation of the catalyst. But while no deactivation of the catalyst seems to occur in a 12 hour run, the catalyst does see degradation from SYNTHOIL residue in sitting overnight.

The discrepancies in the data show a need to get a better fix on the flow rates through the reactor. The Hills-McCanna chemical proportioning pump was unreliable. Flow varied for no apparent reason. Repeatability was difficult due to the inaccuracy in setting the pump stroke.

Hydrogen flow was even more of a problem to measure and control. Changing any pressure in the system would affect the hydrogen flow. As an example the back pressure increased due to plugging and also due to increased pressure drop across the reactor once SYNTHOIL was pumped through the reactor. A wet test meter was connected to the gas outlet after the scrubber in runs 8 and 9. By assuming that 90%

of the gases coming off were hydrogen, relative changes in hydrogen flow could be determine. A hydrogen flow meter is necessary to give accurate quantitative numbers for hydrogen flow.

No material balances were made on the system because of the problems with the hydrogen and SYNTHOIL feeds as mentioned above. Sensitive chromatograph analysis of the exit gases is also necessary.

CONCLUSIONS

1. Hydrocracking, desulfurization, and denitrogenation of SYNTHOIL can be accomplished to some degree using commercial hydrotreating catalysts.
2. No general statements can be made as to what makes a "good" catalyst.
3. Harshaw catalyst HT-500 (Ni-Mo on alumina) gave the best hydrocracking and denitrogenation results in both the bomb and continuous run.
4. Shell catalyst 344 (CoMo on alumina) gave the best heteroatom removal in a bomb (48% desulfurization and 32% denitrogenation).
5. Nitrogen is the more difficult heteroatom to remove.
6. Continuous runs at LHSV $\simeq$ 1 give better hydrogenation and desulfurization results than the bomb run for the same catalyst.
7. Hydrocracking and heteroatom removal decrease as the LHSV increases.
8. A hydrogen flow rate of approximately 10,000 scf/bbl showed the best hydrocracking and heteroatom removal.
9. A reaction temperature of 450°C and a pressure of 800 psig gives the best results in hydrocracking and heteroatom removal.

FUTURE WORK

1. Hydrogen flow meter is needed to control flow rates.
2. Exhaust gases should be sampled with a chromatograph to analyze for light hydrocarbons, hydrogen sulfide and ammonia. Data will allow a material balance to be made on the system.
3. The effects of film and pore diffusion should be tested to determine if they are rate controlling steps in catalysis.
4. Study of catalyst support chemistry, physical properties, and reactivity is necessary to determine the best support. Molecular sieve zeolites need to be looked at in this area.
5. Optimize metal loading. Work should include analysis of catalyst properties of both commercial catalysts and those made at Montana State University.

APPENDICES

APPENDIX A. BATCH RUN CATALYST DESCRIPTION

Run #	Catalyst
B1	Harshaw catalyst Ni-4401 (1/10" extrusions) 6% NiO, 19% WO_3 on Silica Alumina.
B2	Harshaw catalyst Ni-1601 (1/8" tablets) 3% NiO, 3% CoO, 3% FeO on activated Alumina. Surface area = 78 m^2/g Pore volume = .28 cc/g
B3	Harshaw catalyst Ni-1800 (4-8 mesh granules) 10% Ni), 1% CuO on Silica. Surface area = 3 m^2/g
B4	Harshaw catalyst CoMo-0401 (1/8" tablets) 3% CoO, 9% MoO_3 on Silica Alumina. Surface area = 160 m^2/g Pore volume = 0.40 cc/g
B5	Harshaw catalyst Ni-4301 (1/12" extrusions) 6% NiO, 19% WO_3 on Silica Alumina. Surface area = 228 m^2/g Pore volume = .37 cc/g
B6	Catalyst and Chemical Co. catalyst C-20-6 4% CoO, 15% MoO_3 on Alumina.
B7	Harshaw catalyst Ni-4303 (1/12" extrusions) 6% NiO, 19% WO_3 on Alumina. Surface area = 152 m^2/g Pore volume = 0.54 cc/g
B8	Harshaw catalyst Ni-1600 (1/4" spheres) 3% NiO, 3% CoO, 3% FeO on inert Silica Alumina. Surface area = 1 m^2/g

Run #	Catalyst
B9	Harshaw catalyst Ni-3250 (1/8" tablets) 50% Ni on alkaline support. Surface area = 150 m^2/g Pore volume = 0.34 cc/g
B10	Harshaw catalyst Ni-0104 (powder) 60% Ni on Kieselguhr Surface area = 150 m^2/g Pore volume = .2 cc/g
B11	Catalyst impregnated on support in house 26% $SnCl_2$ on Silica. Support: Johns-Manville cellite 408 (5/32" pellets) Surface area = 3 m^2/g Pore volume = 0.65 cc/g Pore diameter (mean) = .98μ
B12	Harshaw catalyst HT-100 (1/12" extrusions) 3.8% NiO, 16.8% MoO_3 on 1.5% Silica promoted Alumina. Surface area = 175 m^2/g Pore volume = 0.54 cc/g
B13	Harshaw catalyst W-0801 (1/8" tablets) 10% WO_3 on high activity Alumina Surface area = 145 m^2/g Pore volume = 0.36 cc/g
B14	Harshaw catalyst Mo-1201 (1/8" tablets) 10% MoO_3 on high activity Alumina. Surface area = 160 m^2/g Pore volume = 0.36 cc/g
B15	Harshaw catalyst W-0101 (1/8" tablets) 10% WO_3 on Alumina. Surface area = 75 m^2/g Pore volume = 0.37 cc/g

B17 Harshaw catalyst Cr-0103 (1/8" tablets) 12% CrO_3 on active Alumina.

Surface area = 63 m^2/g Pore volume = 0.35 cc/g

B18 Harshaw catalyst Cr-0105 (1/8" tablets) 9% Cr_2O_3, 1.5% K_2O on active Alumina.

Surface area = 67 m^2/g Pore volume = 0.34 cc/g

B19 Harshaw catalyst Ni-3210 (3/16" tablets) 35% Ni on proprietary support.

Surface area = 175 m^2/g Pore volume = 0.45 cc/g

B20 Harshaw catalyst CoMo-0603 (1/8" tablets) 3% CoO, 9% MoO_3 on Alumina.

Surface area = 160 m^2/g Pore volume = 0.40 cc/g

B21 Same catalyst as Run #B15

B22 Harshaw catalyst HT-400 (1/16" extrusions) 3% CoO, 15% MoO_3 on Alumina.

Surface area = 220 m^2/g Pore volume = 0.55 cc/g

B23 Same catalyst as Run #B5

B24 Same catalyst as Run #B5

B25 Harshaw catalyst HT-500 (1/8" extrusions) 3% NiO, 15.5% MoO_3 on Alumina.

Surface area = 210 m^2/g Pore volume = .44 cc/g

Run #	Catalyst
B26	Ketjen catalyst Ketjenfine 330-3E, 6.62% NiO, 19.8% WO_3 on Silica Alumina Surface area = 193 m^2/g Pore volume = 0.43 cc/g
B27	Ketjen catalyst HC-5-1.5E; 6.5% NiO, 21% WO_3 on Alumina. Surface area = 200 m^2/g Pore volume = 0.62 cc/g
B28	Shell Catalyst 324 (1/116" extrusions) 2.7% Ni, 13.2% Mo, on Alumina. Surface area = 160 m^2/g Pore volume = 0.5 cc/g
B29	Shell catalyst 344 (1/16" extrusions) 2.4% Co, 9.9% Mo on Alumina. Surface area = 195 m^2/g Pore volume = 0.6 cc/g

APPENDIX B. BATCH RUN DATA

Run #B1

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4401	800	49	49	41	18

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	395	30	608
	10	450	40	662
	20	540	49	700

Run #B2

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1601	150	51	51	07	06

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	410	40	660
	10	450	50	697
	20	540	51	700
	30	610		

Run #B3

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1800	100	51	50	16	20

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	445	30	620
	10	480	40	665
	29	553	51	700

Run #B4

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
CoMo-0401	1300	65	61	16	33

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	200	40	630
	10	410	50	660
	20	510	60	685
	30	580	65	700

Run #B5

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	700	61	59	32	29

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	350	40	630
	10	445	50	668
	20	530	61	700
	30	590		

Run #B6

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
C-20-6	675	56	53	18	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	650
	10	420	50	685
	20	515	56	700
	30	590		

Run #B7

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4303	90	54	49	45	18

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	360	40	642
	10	405	50	685
	20	515	54	700
	30	585		

Run #B8

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-1600	275	41	41	07	10

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	430	30	660
	10	490	41	700
	20	590		

Run #B9

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-3250	700	49	50	50	17

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	390	30	620
	10	440	40	670
	20	540	49	700

Run #B10

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-0104	600	54	53	57	16

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	645
	10	430	50	686
	20	520	53	700
	30	580		

Run #B11

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
$SnCl_2$	775	51	50	20	10

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	390	30	585
	10	445	40	640
	20	522	51	700

Run #B12

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-100	800	50	50	36	18

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	300	30	590
	10	425	40	650
	20	521	50	700

Run #B13

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0801	500	46	47	27	04

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	410	30	615
	10	463	40	670
	20	543	46	700

Run #B14

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Mo-1201	500	49	46	36	19

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	365	30	390
	10	430	40	650
	20	520	49	700

Run # B15

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0101	800	57	55	25	03

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	305	40	620
	10	338	50	680
	20	405	57	700
	30	475		

Run #B17

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Cr-0103	200	43	41	00	05

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	405	30	635
	10	485	40	685
	20	570	43	700

Run #B18

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Cr-0105	250	44	43	05	00

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	425	30	628
	10	480	40	680
	20	560	44	700

Run #B19

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-3210	400	47	45	05	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	425	30	610
	10	470	40	670
	20	540	47	700

Run #B20

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
CoMo-0603	700	61	57	52	25

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	628
	10	432	50	675
	20	504	61	700
	30	570		

Run # B21

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
W-0101	400	51	50	09	00

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	415	30	595
	10	467	40	665
	20	540	51	700

Run #B22

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-400	1000	64	62	34	13

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	355	40	630
	10	418	50	670
	20	510	60	693
	30	580	64	700

Run # B23

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	250	47	45	41	17

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	400	30	618
	10	475	40	675
	20	540	47	700

Run #B24

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Ni-4301	400	52	51	23	28

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	395	30	605
	10	470	40	665
	20	540	52	700

Run #B25

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HT-500	1000	65	64	32	34

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	315	40	622
	10	410	50	668
	20	500	60	692
	30	560	65	700

Run #B26

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
330-3E	700	54	51	30	12

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	340	40	628
	10	405	50	688
	20	512	54	700
	30	573		

Run #B27

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
HC-5	500	49	48	25	23

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	415	30	623
	10	468	40	675
	20	560	49	700

Run #B28

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Shell 324	700	51	52	55	21

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	325	30	592
	10	422	40	660
	20	435	51	700

Run #B29

Catalyst	H_2 take-up Psig	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
Shell 344	800	50	47	48	32

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	5	330	30	610
	10	450	40	670
	20	540	50	700

NOTES:

1. SYNTHOIL Feed Analysis

Distillate Yield Vol. %	Wt. %	Weight % S	Weight % N
44	43	.44	1.06

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	0	380	30	632
	5	440	40	682
	10	490	44	700
	20	570		

2. Catalysts listed by run numbers and manufacturuers identification numbers. Catalyst descriptions given in Appendix A.
3. H_2 take-up is calculated by taking the difference between the charge pressure ≈2000 psig of hydrogen and the pressure upon cooling the bomb to room temperature after the run.
4. ASTM Distillation data can be graphed with volume percent as the abscissa and the temperature as the ordinate. Use a volume percent of 5 as start because distillate started coming off all samples at <200°F. End point for distillation is 700°F.

5. Bomb run conditions: 450°C for 1 hour.

Except - Run #B21 run at 427°C

Run #B23 run at 400°C

Run #B24 run at 418°C

APPENDIX C. CONTINUOUS RUN DATA

Run #1

Catalyst and Chemical Company catalyst C-20-6
4% CoO, 15% MoO_3 on Alumina

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
1-1	4	5000	54	51	27	19

ASTM Distillation:

Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	360	30	582
5	404	40	631
10	440	50	680
20	502	54	700

Run #2

Same catalyst as in Run #1

Temperature: 450°C Pressure: 1000 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
2-1	1.4	10,000	70	67	70	24
2-2	3.0	10,000	51	50	43	01

ASTM Distillation:

Sample #2-1 Vol. %	Sample #2-1 Temp (°F)	Sample #2-2 Vol. %	Sample #2-2 Temp (°F)
0	252	0	370
5	332	5	444
10	441	10	494
20	460	20	556
30	520	30	628
40	565	40	682
50	594	50	698
60	657	51	700
70	700		

Run #3

Harshaw Catalyst Ni-4401 (1/10" extrusions)
6% NiO, 19% WO_3 on Silica Alumina

Temperature: 400°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
3-1	1.0	10,000	62	61	09	13

ASTM Distillation:	Vol. %	Temp (°F)	Vol. %	Temp (°F)
	0	301	30	576
	5	429	40	633
	10	471	50	670
	20	532	62	700

Run #4

Harshaw catalyst Ni-1601 (1/8" tablets)
3% NiO, 3% CoO, 3% FeO on active Alumina
Surface area = 78 m^2/g Pore volume = 0.28 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
4-1	1.25	10,000	67	65	30	06
4-2	2.00	10,000	55	52	25	06
4-3	2.24	5,000	54	52	11	06
4-4	2.14	15,000	60	57	11	01
4-5	2.87	10,000	59	57	11	13
4-6	4.00	10,000	54	52	02	01

Run #4 (cont)

ASTM Distillation:

4-1		4-2		4-3	
Vol.%	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	215	0	300	0	218
5	415	5	410	5	428
10	453	10	466	10	464
20	525	20	531	20	531
30	575	30	594	30	606
40	620	40	645	40	650
50	657	50	685	50	692
60	683	55	700	54	700
67	700				

4-4		4-5		4-6	
Vol.%	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	216	0	218	0	250
5	428	5	420	5	425
11	458	10	458	10	454
20	522	20	515	20	540
30	579	30	581	30	598
40	630	40	642	40	660
50	670	50	680	50	692
60	700	59	700	54	700

Run #5

Harshaw catalyst Ni-3210 (3/16" tablets)
35% Ni on proprietary support
Surface area = 175 m^2/g Pore voluem = 0.45 cc/gm

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	%DeN
5-1	2.17	10,000	57	54	11	00
5-2	.37	10,000	63	60	55	29
5-3	1.05	10,000	51	50	48	15

ASTM Distillation:

5-1		5-2		5-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	380	0	<200	0	<200
10	462	5	390	5	436
20	508	10	427	10	470
30	564	20	501	20	541
40	615	30	560	30	597
50	679	40	606	40	648
57	700	50	654	50	698
		60	695	51	700
		63	700		

Run #6

Harshaw catalyst CoMo-0401 (1/8" tablets)
3% CoO, 9% MoO_3 on Silica Alumina
Surface Area = 160 m^2/g Pore volume = 0.40 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
6-1	1.00	10,000	65	62	50	04
6-2	2.03	10,000	48	51	36	16
6-3	4.80	10,000	43	50	20	00

ASTM Distillation:

6-1		6-2		6-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	<200	0	220	0	360
5	336	5	440	5	468
10	399	10	466	10	510
20	466	20	540	20	580
30	530	30	595	30	642
40	574	40	654	43	700
50	620	48	700		
60	688				
65	700				

Run #7

Harshaw Catalyst Ni-4301 (1/12" extrusions)
6% NiO, 19% WO_3 on Silica Alumina
Surface area = 228 m^2/g Pore volume = 0.37 cc/g

Temperature: varies Pressure: 800 psig

Sample #	Temp (°C)	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol.%	Wt. %	%DeS	%DeN
7-1	451	1.71	10,000	65	65	36	28
7-2	423	1.70	10,000	51	48	30	00
7-3	402	2.0	10,000	45	45	27	00
7-4	378	1.67	10,000	46	44	16	18

ASTM Distillation:

7-1 Vol.%	7-1 Temp. (°F)	7-2 Vol. %	7-2 Temp (°F)	7-3 Vol. %	7-3 Temp (°F)
0	225	0	340	0	330
5	330	5	404	5	437
10	370	10	462	10	476
20	458	20	528	20	560
30	514	30	591	30	614
40	572	40	644	40	680
50	628	51	700	45	700
60	689				
65	700				

7-4 Vol. %	7-4 Temp (°F)
0	370
5	430
10	487
20	570
30	630
40	685
46	700

Run #8

Harshaw catalyst Ni-4303 (1/12" extrusions)
6% NiO, 19% WO_3 on alumina
Surface area = 152 m^2/g Pore volume = 0.54 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	%DeS	%DeN
8-1	1.00	5,000	57	54	68	17
8-2	0.98	5,000	56	54	61	03
8-3	1.00	5,000	62	57	68	17
8-4	1.03	10,000	53	52	50	00
8-5	.96	10,000	48	47	20	12

ASTM Distillation:

8-1		8-2		8-3	
Vol. %	Temp (°F)	Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	190	0	180	0	200
5	254	5	360	5	350
10	410	10	408	10	405
20	500	20	500	20	475
30	552	30	577	30	528
40	629	40	632	40	590
50	680	50	690	50	630
57	700	56	700	62	700

8-4		8-5	
Vol. %	Temp (°F)	Vol. %	Temp (°F)
0	200	0	300
5	410	5	437
10	468	10	480
20	527	20	550
30	576	30	604
40	625	40	680
53	700	48	700

Run #9

Harshaw Catalyst HT-500 (1/8" extrusions)
3% NiO, 15.5% MoO_3 on Alumina
Surface area = 210 m^2/g Pore volume = 0.44 cc/g

Temperature: 450°C Pressure: 800 psig

Sample #	LHSV	H_2 Flow scf/bbl	Distillate Yield Vol. %	Wt. %	% DeS	% DeN
9-1	1.02	11,000	72	69	70	31
9-2	0.90	8,000	64	61	67	18
9-3	0.92	18,000	64	61	50	12

ASTM Distillation:

9-1 Vol. %	9-1 Temp (°F)	9-2 Vol. %	9-2 Temp (°F)	9-3 Vol. %	9-3 Temp (°F)
0	200	0	200	0	200
5	200	5	344	5	380
10	340	10	410	10	430
20	440	20	480	20	510
30	505	30	535	30	554
40	564	40	580	40	595
50	600	50	630	50	557
60	650	60	692	60	690
72	700	64	700	64	700

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