



Catalytic hydrogenation of solvent refined coal
by Gary Richard Hass

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

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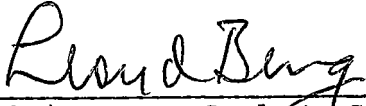
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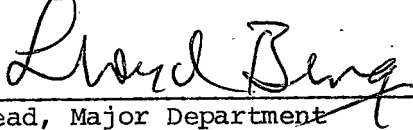
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Approved:



Chairperson, Graduate Committee



Head, Major Department



Graduate Dean

MONTANA STATE UNIVERSITY
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ABSTRACT

Catalytic hydrogenation of Pittsburg and Midway Coal Mining Company's Solvent Refined Coal was accomplished using commercial hydrotreating catalysts and hydrotreating catalysts fabricated at Montana State University. Forty-four batch autoclave tests and thirty-nine trickle bed reactor tests were performed.

Liquid products from the catalyst tests were analyzed for sulfur content, nitrogen content, and distillate yields.

Harshaw HT-400 E 1/16" (Co-Mo) catalyst gave the best nitrogen removal at 450°C of all commercial catalysts tested in the trickle bed reactor. Cyanamid HDS-20A 1/16" Trilobe (Co-Mo) gave the best sulfur removal at 450°C of all catalysts tested in the trickle bed reactor. MSU STK-5-2-2-1.5E (Ni-Co-Mo) gave the best nitrogen removal at 450°C of all catalysts tested. MSU STK-5-2-6-1.5E (Ni-Co-Mo) gave the best sulfur removal at 450°C of all catalysts tested.

A metal loading study was performed to determine the effects of nickel oxide, cobalt oxide, and molybdenum trioxide concentrations on heteroatom removal. Increased molybdenum trioxide concentration significantly improved nitrogen removal. Increased nickel oxide and cobalt oxide concentrations also improved nitrogen removal.

INTRODUCTION AND BACKGROUND

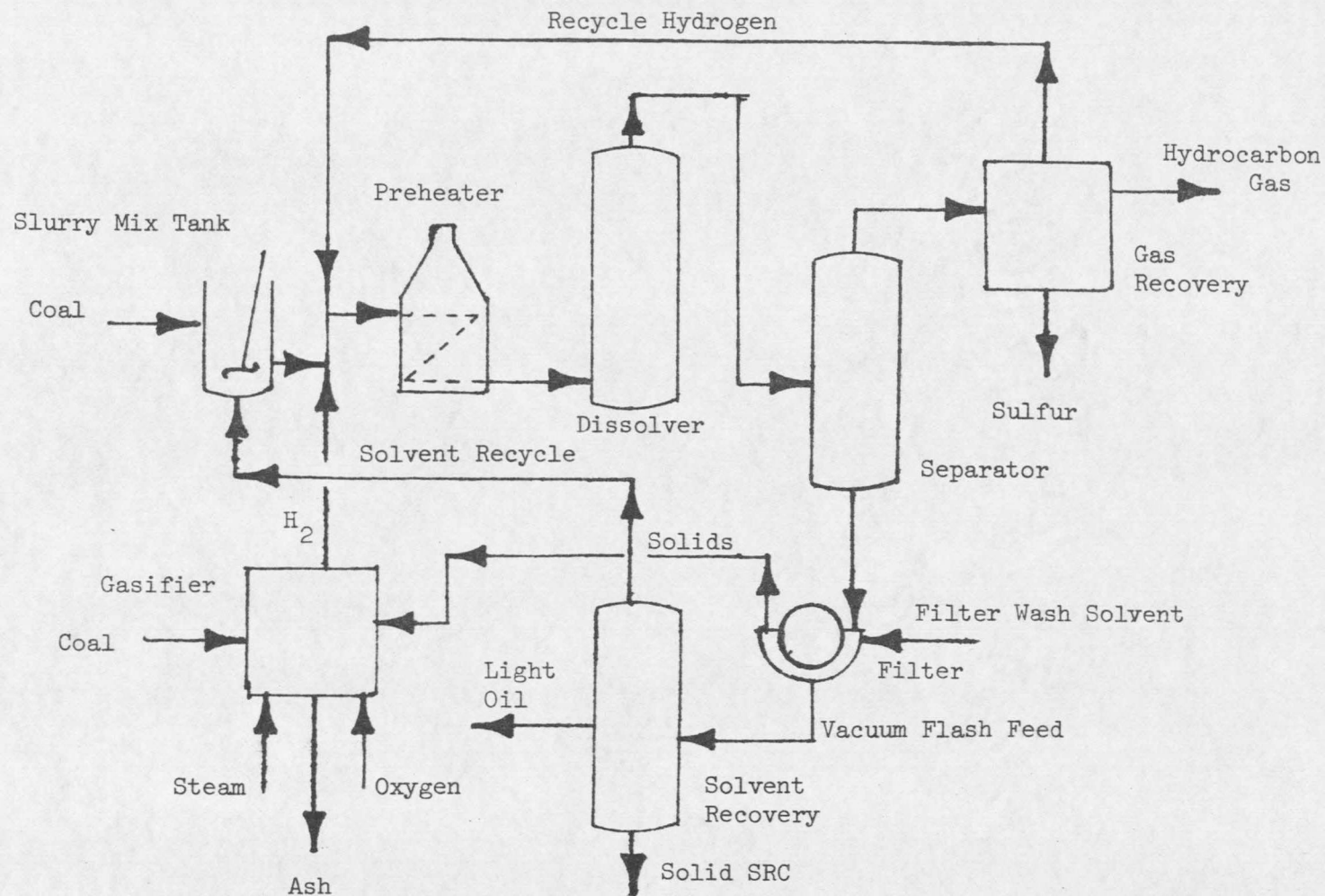
The growing shortage and increased costs of crude oil and natural gas coupled with increased demand for energy in our country has launched an intense effort to find alternative energy sources. Of the many proposed solutions to our energy crisis, coal seems to have the most promising immediate value. Of the 780 billion tons of coal recoverable from reserves determined by mapping and exploration, 226 billion tons are in relatively thick beds and under less than 1000 feet of overburden (1). These deposits are mineable at or near present costs. The American Gas Association reports that there is sufficient coal with available water to support 175 synthetic gas plants of 250 million ft³/day capacity (1,2). A million tons of coal per day could yield 10% of the current daily U.S. needs at 50% conversion to synthetic crude (1).

There are three major driving forces for the production of synthetic fuels. First, because of the diminishing supply of natural gas, the difficulty in shipping natural gas from abroad, and the large costs invested in existing pipeline systems mean gasified coal could supply much needed pipeline quality gas. Secondly, coal can be used for steam and electricity generation. Thirdly, because of limited supplies of crude oil and the glaring fact that the U.S. is overwhelmingly dependent on gasoline- and diesel-powered vehicles means liquified coal products could help as transportation fuels (3).

Coal liquefaction processes do have their drawbacks, however, including tremendous capital investment requirements, water availability, and social and environmental problems (4). Coal liquefaction processes for the production of synthetic crudes are varied depending upon the quality or rank of the coal to be processed. U.S. coals range in increasing carbon content from lignite, through sub-bituminous and bituminous, to anthracite, each of which has unique chemical and physical properties. Coal liquefaction processes include pyrolysis, indirect hydrogenation, direct hydrogenation, and solvent extraction. Pyrolysis (destructive distillation) consists of heating a pulverized coal at successively higher temperatures for the production of coke, coal gas, liquids, tars, and ammonia. In principle, pyrolysis is one of the simplest methods. Examples of recent pyrolysis processes are the FMC COED Process (5,6), Oil Shale Corporation's TOSCOAL Process (7), and Garret Research's Pyrolysis Process (8). Indirect hydrogenation of coal is exemplified by the Fischer-Tropsch synthesis. In 1933, Franz Fischer and Hans Tropsch showed that in the presence of certain catalysts, carbon monoxide is hydrogenated to aliphatic hydrocarbons. Current indirect hydrogenation processes are operated by the South African Coal, Oil and Gas Corporation (SASOL) (9), and Fluor Corporation (10). The direct hydrogenation process was developed in 1913 by Friedrich Berguis. Direct hydrogenation involves the reaction of coal slurried in a recycle oil with hydrogen gas and a

catalyst either in a fixed bed or ebullating bed configuration. Current processes being operated are Exxon's donor solvent process (11,12), Hydrocarbon Research, Inc.'s H-Coal process (13,14,15) and the Bureau of Mines Synthoil Process (16). Solvent extraction processes are really a modified direct hydrogenation for the production of synthetic fuels. A high boiling donor or non-donor solvent and hydrogen are used to dissolve coal at high temperature and pressure. This solution can then be filtered thus removing large amounts of sulfur and ash. Current solvent extraction processes in operation are Pittsburg and Midway Coal Mining Company's Solvent Refined Coal (SRC) process (11,17,18,19) and Consolidation Coal Company's CSF process (11,20,21,22).

Of major concern to this thesis work is the Solvent Refined Coal (SRC) process operated by Pittsburg and Midway Coal Mining Company. A fifty ton/day pilot plant was operated at Fort Lewis, Washington, in the SRC I mode shown in Figure I. The coal (Kentucky #9) is mixed with a solvent in a slurry tank. This slurry is mixed with hydrogen, preheated and fed to a high pressure dissolver. Dissolver effluent passes to a gas-liquid separator. The off-gas from the separator is hydrotreated and recovered hydrogen is recycled. The liquid from the separator is filtered removing much of the sulfur and ash. The filtrate is fed to the solvent recovery steps producing a solid "solvent refined coal." In principle, filter cake is fed to a gasifier for



4

FIGURE 1. SRC I Process Schematic

production of in-plant fuel gas and hydrogen (23,24). More recently, the Pittsburgh and Midway pilot plant has been modified to produce a liquid product in the SRC II mode. Major changes include using the dissolver product as the slurry solvent which is mixed with feed coal and the concentrating of mineral ash in the dissolver stream which is believed favorable to the liquefaction (24).

The SRC process should not be defined as a single product process aimed only at producing a clean solid boiler fuel. Table I shows typical product streams on a weight basis. Table II shows that gas and liquid yields are far from insignificant (25).

Table I. Typical SRC Process Yields

Coal Properties, wt%	
Organic sulfur	1.7%
Pyritic sulfur	1.2%
Ash	11.1%
Product wt% MAF coal feed	
Solvent Refined Coal	63*
Undissolved coal	7
C ₁ - C ₄ gas	6
C ₅ - 350°F	6
350-750°F Distillate	10
H ₂ S	2
CO - CO ₂	2
Water	6

*Solvent Refined Coal Properties: Sulfur content < .9 wt%; Ash content < .1%.

Table II. SRC Process Gas and Liquid Yields*

$C_1 - C_4$ gas, scf [†]	3130
CH_4 gas	2100
$C_5 - 350^\circ F$ gal	32
bbl	0.762
350-750°F distillate, gal	38
bbl	0.904
Total liquid, gal	70
bbl	1.666

*Per ton solvent refined coal

†Approximate analysis of $C_1 - C_4$ gas cut:

	<u>Vol %</u>	<u>BTU value/ft³</u>
CH_4	67.0	680
C_2H_6	19.3	340
C_3H_8	10.0	260
C_4H_{10}	3.7	120
	<u>100.0</u>	<u>1400</u>

The major objective of this thesis research was to catalytically hydrotreat and hydrocrack products from the SRC I process.

Chemistry of Catalytic Hydrotreating

Catalytic hydrotreating of synthetic crudes consists of two main parts: the hydrogenation of unsaturated hydrocarbons, and the hydrogenolysis of heteromolecules. Depending upon the final use of the syncrude products, various degrees of hydrotreating are acceptable.

If liquid SRC products are used as boiler fuels the requirements would be a hydrogen to carbon mole ratio about 1.6; and nitrogen, sulfur, and mineral levels below .5 wt %. The sulfur level is determined from the current EPA standards. Products from SRC can easily meet the sulfur and mineral standard, therefore the major steps in producing a liquid boiler fuel are to reduce nitrogen levels below 0.5 wt % and to increase the hydrogen content of the fuel. Some emphasis must be placed on hydrosulfurization because of possible future changes in EPA standards (26). However, if liquid SRC products are to be used as a catalytic cracker feedstock, the nitrogen requirements are more stringent. Catalysts used in catalytic cracking operations provide acid sites which facilitate cracking of hydrocarbon feeds. These acid sites are neutralized by nitrogen which acts as a poison. Deactivation of the catalysts progresses in direct proportion to the duration of operation and in proportion to the amount of nitrogen in the cat cracker feed. In cat cracking operations it is common practice to maintain activity of the catalyst at desired yield levels by a progressive increase in the severity of the reaction conditions to the extent that this is economically feasible, after which time the catalyst is replaced by fresh or regenerated catalyst. The preferred nitrogen level for catalytic cracker feed is in the range of 100-400 ppm (27). Various hydrocracking processes can tolerate more nitrogen in the feedstock. Examples of these processes are Standard Oil of

Indiana's Ultracracking process and Union Oil's Unicracking process which can tolerate nitrogen concentrations up to .3 wt % (28,29).

Petroleum hydrotreating processes use efficient technologies and are governed by fairly well established kinetics. The most important factor for further progress in this field is the catalyst. The choice of hydrotreating catalyst components depends upon the type of reaction they are meant to activate, i.e., pure hydrogenation, heteromolecule hydrogenolysis, or isomerization. It must be kept in mind that these reactions must be carried out in the presence of large amounts of sulfur containing hydrogen (30).

Specific reactions to be carried out by a hydrotreating catalyst are: (a) Polyaromatic hydrogenation in which polyaromatics are hydrogenated to monoaromatics or saturates which are easier to crack and give less tendency toward coke formation; (b) denitrogenation in which nitrogen compounds are removed thus preventing inhibition of the acid function of cracking catalysts resulting in higher conversion and less severe operating conditions in cracker units; (c) desulfurization providing lower sulfur content in cat cracker gasoline which allows for better lead susceptibility; and (d) heavy metals removal--catalysts act as absorbents for heavy metals which are severe poisons for cracking catalysts and usually limit the end boiling point in cracker feeds (31). Data in the literature show that these reactions can be performed satisfactorily by the use of catalysts made of metallic

sulfides from Group VIB and VIII of the Periodic Table, usually produced by the sulfiding of corresponding metal oxides deposited on a refractory oxide (SiO_2 , Al_2O_3 or $\text{SiO}_2\text{-Al}_2\text{O}_3$) (30).

Solvent Refined Coal has a high asphaltene content (32). In synthetic crude hydrotreating, one of the main problems with catalyst activity is the rapid initial deactivation due to the deposition of carbonaceous materials (33). This is accompanied by the deposition of mineral matter, which continues throughout the reaction. The relationship between the structure of the syncrude and initial carbon deposition is not clear. It is believed to be due to large asphaltene molecules present in syncrude. The average size of these molecules, 40 to 50 Å, is in the range of the diameters of the micropores in conventional alumina supported catalysts. This leads to plugging of small pores which represent a large fraction of the total catalyst surface area. Optimization of the pore size distribution becomes very significant. Similarly, the mineral content of SRC causes problems. The analysis of SRC performed by Mobil Oil Company show high iron (140 ppm), titanium (130 ppm), and sodium (100 ppm) content. Total mineral content can be as high as .25 wt %. This is a large amount of ash. For instance, a pilot plant processes 100 tons of SRC per day would have to handle up to 500 pounds/day ash. This could have considerable effect on catalyst activity. The presence of large molecules causes the additional problem of pore diffusion limitations.

Furthermore, the three phases present lead to film diffusion limitations in the reactor fluid stream (32,34).

Hydrotreating studies performed in microreactors using small concentrations of model compounds such as benzothiophene, acridine, pyridine, and quinoline have given some insight into the mechanism by which sulfur and nitrogen are removed from feedstocks. In studies of the desulfurization of dibenzothiophene and methyl-substituted dibenzothiophenes, data show good fits with first order kinetics with respect to the sulfur containing compound. The mechanism seems to have three steps: (a) Absorption of the reactant molecules on the catalyst surface presumably as the sulfur atom interacts with an anion vacancy; (b) hydrogen donation to the carbon atom contiguous to the sulfur with breaking of the carbon-sulfur bonds (c) desorption of the sulfur by addition of another pair of hydrogen atoms. Methyl substitution near the sulfur atom in dibenzothiophene greatly reduce the reactivity, believed to be caused by steric effects which restrict the interaction of the sulfur atom and the surface of the catalyst (35-42).

In studies involving denitrogenation of acridine, data show that before the nitrogen atom is removed, large amounts of ring hydrogenation takes place. The breaking of the carbon-nitrogen bond has been shown to be the rate determining step (41). This has also been shown to be the case with single ring heterocyclics such as pyridine (42).

Other hydrotreating studies yield data on the interactions of metal sulfides and supports. For a series of tests using pairs of metal sulfides (Co-Mo, Ni-Mo, Co-W, Ni-W) impregnated on alumina and silica supports, maximum hydrogenation activity was obtained using a ratio of Group VIII metal/Group VIB metal in the range of .25 to .33. For the desulfurization of thiophene, which involves simultaneous hydrogenating and hydrogenolysis activity of the metallic sulfides coupled with the acid function of the support, the same metal ratios provided maximum activity. However, the differences in desulfurization activity is less pronounced for metals impregnated on alumina than for those impregnated on silica. This means the acidity of alumina is greater than that of silica. Different deposits of metal on supports also affect the overall acidity of the catalyst. Silica-alumina supports show even more acidity than do pure alumina supports. Nickel oxides deposited on silica alumina reduce the overall acidity of the catalyst. Nickel-tungsten deposits also reduce the overall acidity, whereas molybdenum oxides increase the overall acidity. Metallic sulfides improve the stability of the acid function of the catalyst by improving hydrogenation which eliminates certain unstable compounds which by polymerization on acid sites could cause coke formation. By careful choice of combinations of metals and supports, these catalyst types can lend themselves to varied hydrotreatment processes (30).

Operational Considerations of Trickle Bed Reactors

Trickle bed reactors are fixed bed reactors where the feed consists of both a gas and a liquid. The liquid flows down over the bed of catalyst and the gas either flows concurrent or countercurrent to the liquid. Cocurrent operations allows for better distribution of the liquid over the catalyst and allows for higher liquid flow rates without flooding problems. Commercial trickle bed reactors have been in operation for the last twenty-five years for hydrodesulfurization, hydrocracking, and hydrotreating high boiling petroleum feeds. Reaction conditions allow hydrocarbon feeds to react as a vapor-liquid mixture at liquid hourly space velocities ($LHSV = \text{volume of liquid feed} / (\text{volume of catalyst} \times \text{hr})$) in the range of .5 to 10. Direct and capital costs of trickle bed reactors are claimed to be twenty percent lower than hydrotreating units that are operated completely in the vapor phase. Also, high boiling feedstocks can be treated in trickle bed reactors that would undergo too excessive cracking if treated entirely in the vapor phase.

The principal alternative to the trickle bed reactor is the fluidized bed reactor in which the catalyst is in motion. Fluidized bed reactors have the advantages of easier temperature control, easy heat recovery, adaptability to either batch or flow processing, easy catalyst removal and regeneration, and ability to operate at high

catalyst effectiveness factors because of the use of finely powdered catalyst. Disadvantages of a fluidized bed reactor include a residence time distribution that approaches that of a continuous stirred tank reactor (CSTR) which makes it difficult to obtain high conversion; the high ratio of liquid to solid which allows homogeneous side reactions to become important, and the high cost of catalyst removal equipment.

In a trickle bed reactor the catalyst bed is fixed, the flow pattern is closer to plug flow, and the liquid to catalyst ratio is much lower thus limiting side reactions. If heat effects are substantial, they can be controlled by recycle of the product liquids or by varying the gas flow rates. Recycle, however, may not be feasible if the product is unstable at reaction conditions or if high conversion is desired, since high recycle rates make the system approach that of a CSTR. When complete vapor phase operation is feasible, trickle bed operation can save energy costs of feedstock vaporization.

Trickle bed reactors in the petroleum industry are operated over a wide variety of conditions depending on the properties of the feedstock and the nature of the reaction. Typically less reactive, higher boiling, viscous feeds are operated at low liquid flow rates. Representative superficial velocities are 10 to 100 ft/hr for heavy gas oils or residual fractions and 100 to 300 ft/hr for naphthas, calculated assuming the feed is all liquid. Hydrogen flow to liquid flow is commonly expressed (at standard conditions) as the volume of

hydrogen per barrel of feed. Representative values are 2000 to 3000 scf/bbl for desulfurization of heavy gas oils, 5000 scf/bbl for desulfurization of resids, and 5000 to 10,000 scf/bbl for a hydrocracker. Mild hydrofinishing reactors may use considerably less hydrogen. Representative operating condition for commercial reactors are a pressure range of 500-2500 psig; temperature range from 345°C to 425°C, and catalyst particle sizes from 1/32 inch to 1/8 inch. Present day units are multiple bed systems three to six meters high and up to two meters in diameter. In multiple bed systems, hydrogen is injected between beds for temperature control. The quantity of hydrogen used far exceeds stoichiometric proportions and is usually determined by requirements of temperature control, better liquid distribution, or to extend catalyst life. Bed height is determined by the need for certain gas or liquid distribution or by the crush strength of the catalyst. In both chemical and petroleum processing, reactors are designed to run essentially adiabatically. Of particular interest to this research is that bench scale reactors can be operated at the same liquid hourly space velocities that are used commercially. The fact that conditions for commercial and bench scale studies operate under different hydrodynamic flow conditions means contacting efficiencies might be somewhat different. Most laboratory studies involving highly exothermic reactions and low liquid flow rates may exhibit significant heat effects which can cause temperature instability and vaporization

which may cause only partial wetting of the catalyst. Another problem encountered with syncrude processing is that the number of compounds of varying reactivities present in coal liquids leads one to be fairly arbitrary in interpreting kinetic data (43,44,45,46,47).

In its physical form the trickle bed reactor is hydrodynamically similar to the absorption tower and much information on matters such as flow patterns, pressure drop, holdup, and liquid distribution can be obtained from studies directed towards absorbers. Absorption occurs entirely between a gas and a liquid and the function of the solid is to provide good contacting. In comparing packed bed absorbers and trickle bed reactors several things should be kept in mind.

1. Absorption towers are operated at higher gas and liquid flow rates, which approach flooding.
2. In order to achieve high flow rates absorption towers use large packing materials such as Berl saddles, whereas trickle bed catalysts are small extrusions, spheres, or pellets.
3. In bench scale absorption towers a considerable portion of the absorption may occur in the liquid trickling down the wall. In a trickle bed reactor the wall contributes nothing to the reaction, but wall flow is a means of bypass channeling.

4. Gas flow is usually cocurrent for trickle bed reaction and countercurrent for absorbers.
5. Catalyst particles are usually highly porous whereas absorber packings are nonporous. Liquid held in catalyst pores may be a major fraction of the holdup which give very different wetting characteristics for trickle bed reactors.

At sufficiently low liquid and gas flow rates liquid trickles over the catalyst in rivulets and the gas flows continuously through the voids. As gas and/or liquid rates are increased one encounters rippling, slugging, or pulsing flow characteristic of commercial trickle bed reactors. At high liquid flow rates and low gas rates, the liquid phase becomes continuous and the gas phase passes in the form of bubbles (43,44,48,49).

One topic that is still under discussion is the effect of the ratios of reactor diameter to catalyst particle diameter. Porter et al. (50,51,52) reports that in bench scale trickle bed reactors, liquid migrates to the wall and that the fraction flowing down the wall increases to a steady state value at about one foot down the bed. The steady state wall fraction corresponds to as much as 30 to 60% of total liquid at ratios of reactor diameter to particle diameter of as high as 10, and drops at higher ratios. This thesis used a ratio between 5.65 (1/8" catalyst particles) and 11.3 (1/16" catalyst particles).

Also important is particle shape. Acres observed that cylindrical catalyst particles tend to pack together end to end causing liquid to channel through the bed and spherical catalyst particles tend to channel liquid to the wall (53).

In all heterogeneous catalytic reactions, the understanding of transport phenomena become important. To insure that data obtained from trickle bed reactors is a true measure of catalyst performance a conscious effort to eliminate mass and heat transfer effects is needed. There are three domains in which concentration and temperature gradients should be minimized. These are intraparticle--within individual catalyst particles; interphase--between the external surface of the catalyst particles and the fluids adjacent to them; and interparticle between local fluid regions (43,44,45,54,55).

For intraparticle effects the general solution is to test catalysts at their highest value of effectiveness factor. Effectiveness factor is defined as the ratio of the actual rate of reaction to that which would occur if the temperature and concentration were constant throughout the catalyst particle. Unfortunately, to calculate the effectiveness factor directly, a knowledge of the reaction kinetics and intrinsic rate constants is required. This becomes difficult with a complex feedstock such as a synthetic crude. Some basic considerations are helpful. Effectiveness factors become inversely proportional to the characteristic dimension of the catalyst. Therefore,

highest effectiveness factors are obtained by use of smaller particles. Also important in pore diffusion is the viscosity of the feedstock, making the use of a diluent advantageous. When the molecular size of the reactant becomes significant with respect to pore size, as is the case with the asphaltene components of syncrudes, the concentration of the reactant in the pores becomes less than that in the bulk phase by mere geometrical exclusion. Therefore, large pore dimensions become important. If the reactant is present in both the liquid and vapor phase, some unusual effects can develop if heat and/or mass transfer limitations are significant. Even with a highly exothermic reaction, it is unlikely that intraparticle temperature differences will exceed more than a few degrees especially with a gas as insoluble as hydrogen. However, if pores become filled with vapor, temperature gradients of hundreds of degrees are possible because of large increases in effective diffusivities. These increases in effective diffusivities can also cause marked increase in reaction rates. (43,44,45,54,55,56).

A major conclusion about interphase transport was that mass transfer through the liquid film around a catalyst particle will not be significant unless the catalyst particles themselves are operating at very low effectiveness factors. This results because the effective diffusivity within a particle does not usually exceed a value of about twenty percent of the diffusivity in the boundary layer or film adjacent to the pellet, and the film thickness is usually substantially

less than the catalyst radius. If gas-liquid mass transfer is appreciable as will occur at high reaction rates and high liquid flow rates, a higher rate of reaction per unit quantity of catalyst can be obtained by mixing inert material with the catalyst. These inert zones allow enhanced opportunity for gas to dissolve in the liquid. Dissolved hydrogen in the liquid in contact with the solid catalyst also decreases carbon laydown. Dilution of the catalyst bed also helps minimize hot spots in highly exothermic reactions (43,46,54,55).

Interparticle transport effects, both radial and axial, are difficult to evaluate and control. One common approach is to use a differential reactor which operates at low conversions. The recycle reactor provides a means of operating at finite low conversion. Flow rates past the catalyst can be varied to eliminate interphase and interparticle gradients. The well-stirred catalytic reactor (Berty Reactor), in which pellets are suspended in wire cages offers still another alternative (57).

In this thesis work all catalysts were diluted 1:1 by volume with inert material. Ketjen Catalyst Company reports that in small single pass trickle bed reactors that contain a thermowell tube, conversion data correlate very well with scaled up reactors if the catalyst is diluted (58).

A very important factor in heterogeneous catalysis is the temperature at which the reactions are carried out. As the temperature of

the reaction increases, the rate controlling the overall rate of reaction will pass from the surface chemical kinetic step to control by a combination of the surface kinetic step and pore diffusion, and at higher temperatures to control by film diffusion. It is necessary to operate at sufficiently low enough temperatures to be in the region controlled by pore diffusion and chemical kinetics in order to determine differences that can be attributed to the chemical and physical properties of the catalyst (44).

The pressure of operation can have significant effects on diffusion rates and also reaction rates. All too often in laboratory experiments pressure is limited by the working pressure of available equipment (44).

Research Objective

The objective of this research was to catalytically upgrade Solvent Refined Coal products to clean distillate fuels. This means to decrease sulfur and nitrogen content of the feedstock and to increase the amount of product recovered in the ASTM D-86 distillation.

The research plan consisted of testing commercial hydrotreating catalysts in both batch autoclave tests and in trickle-bed tests. From these data on commercial catalysts, new hydrotreating catalysts were prepared and also tested for their hydrotreating ability. It was hoped that this work would lead to a greater insight for future catalyst development.

MATERIALS, EQUIPMENT AND PROCEDURES

Feedstock Analysis

A five gallon drum of solid Solvent Refined Coal (SRC) granules, a five gallon drum of SRC Light Oil, and fifty-five gallon barrel of SRC Vacuum Flash Feed were received from Pittsburgh and Midway Coal Mining Company's pilot plant operation in Fort Lewis, Washington.

These SRC products were made from Kentucky #9 coal from the Colonial Mine. Analysis of the feed coal is listed in Table III. Analyses of the SRC Light Oil, Recycle Solvent, and Filter Wash Solvent are listed in Table IV. An analysis of solid SRC granules is listed in Table V. An analysis of SRC Vacuum Flash Feed is listed in Table VI (59).

Catalyst Pretreatment

All catalysts tested were pretreated by sulfiding by the following procedure. The catalyst was supported in a 2-1/2 foot piece of Inconel pipe by use of 1/4-inch Denstone (64) inert support material. The catalyst was treated with a 10% hydrogen-sulfide in hydrogen mixture for twelve hours. Temperature was maintained at $340^{\circ}\text{C} \pm 10^{\circ}\text{C}$ by use of a powerstat on the electric pipe heater. Exit gases from the sulfider were scrubbed with water and 20% sodium hydroxide-water solution before venting to the hood.

Extreme caution should be taken whenever using hydrogen sulfide because it can cause collapse, coma and death within a few seconds

Table III

SRC Feed Coal Analysis, January 1977 wt %Kentucky #9 Coal

Carbon	71.35%
Hydrogen	5.07%
Nitrogen	1.44%
Sulfur	3.50%
O ₂ (diff)	7.55%
Ash	10.12%
Moisture	0.97%

Sulfur Forms (wt % on coal)

Pyritic Sulfur	1.63%
Sulfate Sulfur	0.09%
Organic Sulfur	1.76%
Total	3.48%

Average Mineral Residue Analysis (wt %)

Carbon	27.61%
Hydrogen	1.39%
Nitrogen	0.54%
Sulfur	7.29%
Ash	63.17%
Pyridine Insol	96.98%

(59)

Table IV

SRC Process Solvent Analysis

Distillation Product	<380°F	380-480°F	480-850°F
Light Oil	45%	47%	8%
Filter Wash Solvent	24	75	1
Recycle Solvent	0	11	89

Elemental Analysis of Plant Solvents

<u>Description</u>	<u>Light Oil</u>	<u>Filter Wash Solvent</u>	<u>Recycle Solvent</u>
% Carbon	82.25	83.17	87.81
% Hydrogen	9.62	8.82	7.66
% Nitrogen	0.45	0.67	0.66
% Sulfur	0.39	0.14	0.45
% Oxygen (diff)	7.29	7.20	3.42
% Dow therm	--		1.52

(59)

Table V

SRC Analyses

<u>SRC Granules</u>		<u>SRC Light Oil</u>	
Sampled 6-13-75		Sampled 6-22-75	
% Carbon	87.33		82.25
% Hydrogen	5.60		9.62
% Nitrogen	2.28		0.45
% Sulfur	0.68		0.39
% Oxygen	4.11		7.29
% Ash	.33		--

Flash Pt 325°FDistillation D-86

Bar = 744 mm Hg

1BP 210 F

5% 321

10% 332

20% 339

30% 342

40% 346

50% 348

60% 354

70% 358

80% 363

90% 370

95% 377

End Pt 408

Recovery 98%

Table VI

SRC Vacuum Flash Feed as Received

 Sampled 1-24-77

% Carbon	87.43	
% Hydrogen	7.15	
% Nitrogen	1.17	reanalyzed periodically as per data tables
% Sulfur	0.72	
% Oxygen	3.72	
% Ash	.249%	

ASTM D-86 Distillation @ 640 mmHg

<u>Vol</u>	<u>Temp</u>	<u>Vol %</u>
IBP	408	
5 ml	445	10.4
10	485	20.8
15	544	31.2
20	598	41.6
25	642	52.0
30	684	62.4
33.5	Final	69.7

Wt % recovered 69.2 wt%

 (59)

after one or two inspirations. Hydrogen sulfide is extremely hazardous because it fatigues the sense of smell in high concentrations, therefore giving no warning (60).

Batch Autoclave Tests

Batch autoclave tests were made in a Parr Series 4000 pressure reaction apparatus (61). The Parr autoclave and heater-rocker are shown in Figure 2.

Initial hydrotreating studies (runs prior to #26B) were made with a mixture of 75 grams of solid Solvent Refined Coal and 150 grams of SRC Light Oil. Twenty-five milliliters of catalyst were also charged to the Parr autoclave. The copper head gasket and autoclave head were secured using a torque wrench. New copper head gaskets were torqued to 60 ft-lbs. Subsequent runs with the same head gasket were torqued higher in 10 ft-lb increments until reaching 100 ft-lbs, upon which a new copper head gasket was installed. The pressure gauge and gauge block were attached to the autoclave head. The autoclave was pressurized to 2500 ± 50 psig with hydrogen gas using a Haskel gas booster air-driven compressor (62). If no hydrogen leaks were detected, the autoclave was secured in the heater-rocker (61). Silver Goop (63) was used on all threaded autoclave connections to prevent bolt seizure at high temperature. The autoclave was heated to $415-420^{\circ}\text{C}$, which usually took about fifty minutes. An iron constantan thermocouple, placed in the base of the autoclave, connected to a single point

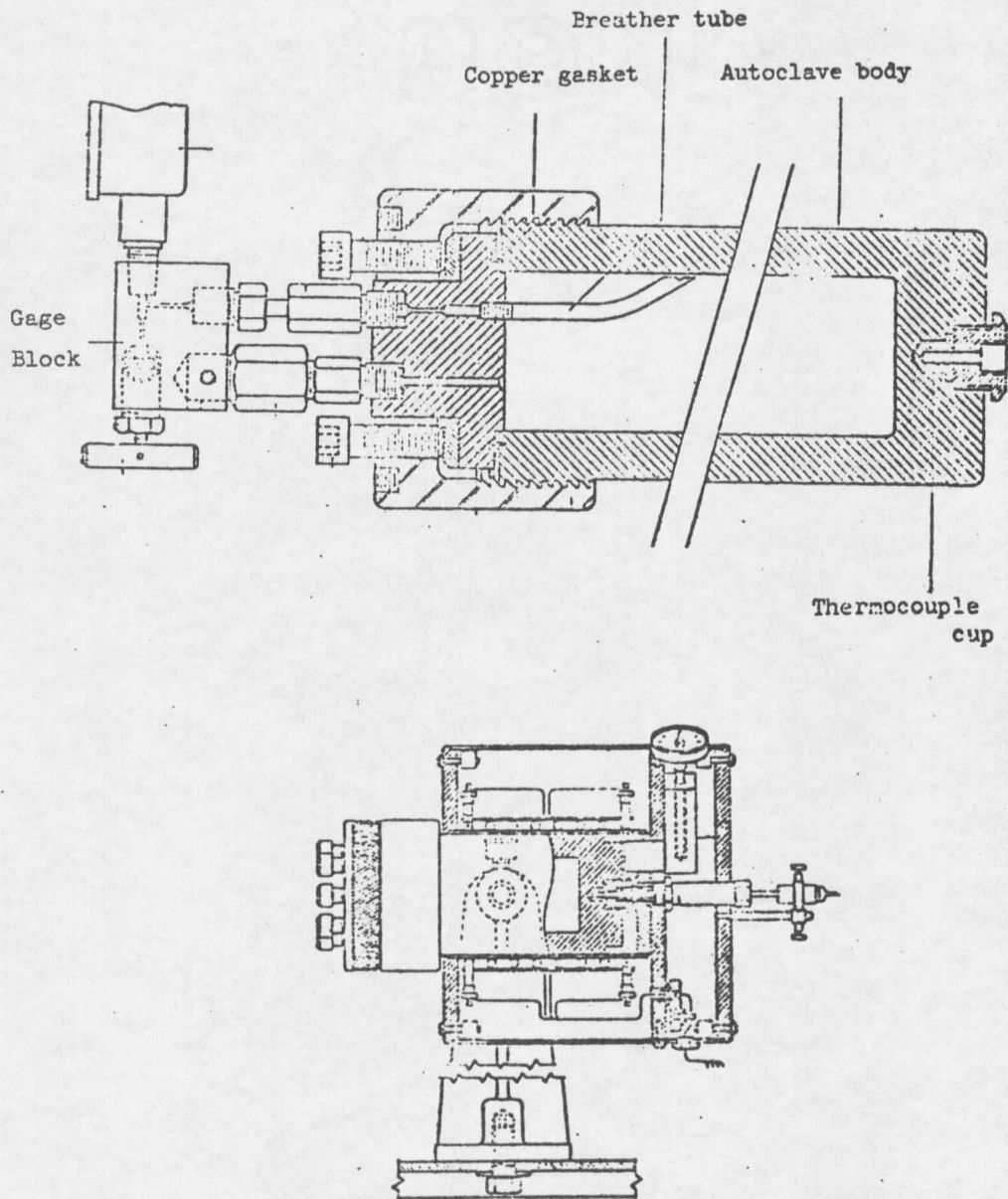


FIGURE 2. Rocking Autoclave Assembly Details

Honeywell recorder monitored the temperature of the reaction mixture. Reaction temperature was controlled by manual adjustment of a Powerstat variable transformer. Pressures were recorded at fifteen minute intervals during each test. The residence at run temperature was either 30 min or one hour. Upon completion of the run, the autoclave was removed from the heater rocker and allowed to cool to room temperature. (Note: autoclave should never be quenched in a liquid to speed cooling, as this could cause structural failure of the autoclave body.) After the autoclave reached room temperature, the hydrogen consumption (measured by the difference in cold loading pressure and the final room temperature pressure) was recorded. The gases in the autoclave were vented slowly in a hood by opening of the needle valve in the autoclave gauge block. The autoclave head and gauge block were removed and the reaction products were filtered to remove catalyst and decanted for analysis. For Runs #26B-44B, 200 grams of SRC Vacuum Flash Feed was substituted for the solid SRC and SRC Light Oil as feedstock.

Continuous Trickle Bed Reactor

The continuous trickle bed reactor was designed and constructed by the Chemical Engineering Department at Montana State University (MSU). A schematic of the trickle bed reactor is shown in Figure 3.

Temperature
Recorder

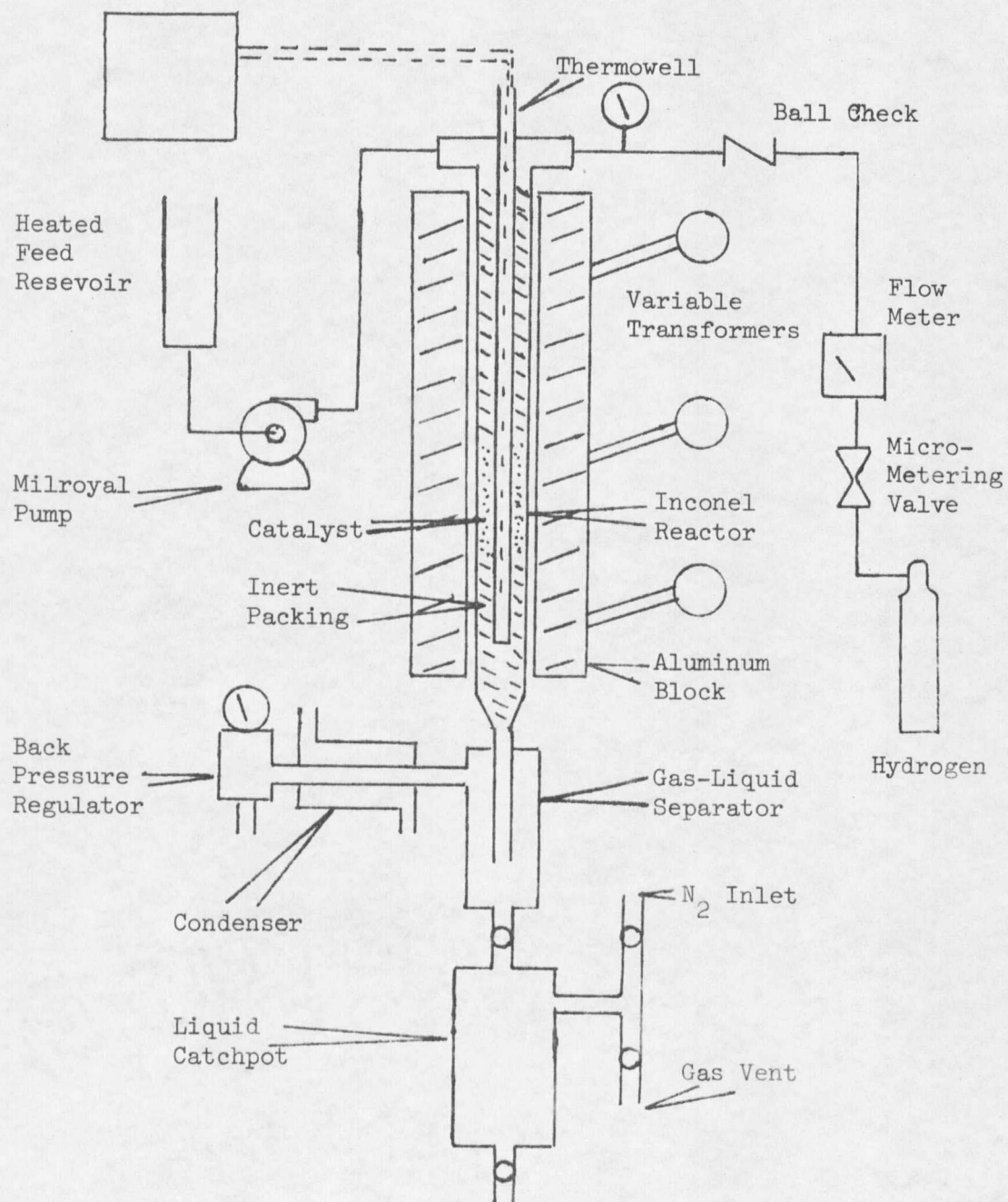


FIGURE 3. Trickle Bed Reactor(not to scale)

The reactor consisted of a 1-inch I.D. schedule-80 Inconel pipe forty inches long. The top of the reactor was fitted with 1/4-inch stainless steel cross which allowed the fitting of a 36-inch piece of stainless steel tubing, which served as a thermowell, and the fitting of two feed ports, one for the syncrude and one for the hydrogen. The reactor was fitted into the bore of a 6-inch O.D. aluminum block which was about three feet long. The aluminum block was wrapped with three sets of nichrome wire heating coils encased in ceramic beads. Each heating coil was connected to a Powerstat variable transformer which was manually operated for temperature control. Four iron-constantan thermocouples were placed in the 1/4-inch stainless steel thermowell at eight inch intervals. The thermocouples were connected to a Leeds and Northrup multipoint recorder. These four thermocouples allowed the monitoring of two temperatures in the preheat section of the reactor and two temperatures in the catalyst section of the bed.

The reactor was loaded at the top with 200 cc of 1/4" Denstone (64) inert support and followed by 25 cc of 1/8" Denstone inert support to serve as the preheat section. Sixty cc of catalyst diluted with 60 cc of 1/8" inert support were loaded as the catalyst section. More 1/8" Denstone inert support material filled the bottom section of the reactor. A cone of stainless steel screen, used as a plug-support, was placed in the bottom of the reactor before the 1/4-inch I.D. reactor closure was threaded into the pipe.

SRC Vacuum Flash Feed was pumped into the top of the reactor by use of a Milton Roy Model MR-1-49 Simplex packed piston pump equipped with a 5/16-inch piston. The pump was equipped with a manually controlled micrometer adjustment for feed rate control. The pump check valves were encased in a steam jacket which was kept at 200°F. All feed lines and reservoirs were wrapped with Cole-Parmer flexible heating cords (65) to prevent feed from freezing up.

Technical grade hydrogen was fed through a regulator, a micrometer valve, and a ball check valve to the top of the reactor. During the last ten trickle bed reactor runs, a Brooks Thermal Mass Flowmeter (66) was installed downstream from the micrometer valve to monitor hydrogen flow rates.

Gases and liquids were passed through the trickle bed reactor to a gas-liquid high pressure separator. The gases passed through a condenser and through a Grove back pressure regulator. The Grove back pressure regulator was equipped with a Teflon diaphragm which can handle the corrosive gases. Exit gases were scrubbed with a 20% sodium hydroxide water solution and vented. The liquids passed from the gas-liquid separator into a pressurized catchpot. When liquid samples were taken, the 1/8-inch ball valve between the separator and the catchpot was closed and pressure was released from the catchpot. The liquid sample was then drained from the bottom of the catchpot. The catchpot

was repressurized with nitrogen and the valve between the separator and the catchpot was reopened putting the catchpot back on stream.

Continuous Trickle Bed Catalyst Tests

After the reactor was loaded, as previously discussed, it was placed in the aluminum block. The catchpot system and the liquid and hydrogen feed lines were attached and thermocouples were placed in the thermowell. All pipe fittings were sealed using Teflon tape and Silver Goop. The system, excluding the pump, was pressurized and checked for leaks. A wet test meter was attached to the gas exit and the micrometer valve was calibrated. In later runs when the Brooks Thermal Mass Flowmeter was used, it was also calibrated using a wet test meter. If everything calibrated satisfactorily, the reactor was depressurized and the pump line reopened. The variable Powerstats were turned on to initiate preheat which usually took eight hours. After the reactor reached temperature, the SRC Vacuum Flash Feed, all liquid feed lines, reservoirs, and the pump jacket were preheated. The feed reservoirs were filled and the pump was started to fill the feed lines before pressurizing the reactor. If the reactor was pressurized before the liquid line was filled the pump would tend to cavitate. The liquid rates were then set to desired value and temperature adjustments were made. The liquid flow rates were measured by using a stop watch and timing the flow from a graduate side arm attached to

the main feed reservoir. Samples for all runs, unless specifically noted, were taken as follows:

Sample 1 - 3 hours - 90 ml/hr - unsteady state

Sample 2 - 2 hours - 90 ml/hr - LHSV = 1.5

Sample 3 - 2.5 hours - 60 ml/hr - unsteady state

Sample 4 - 3 hours - 60 ml/hr - LHSV = 1.0

Sample 5 - 1 hour - 120 ml/hr - unsteady state

Sample 6 - 1.5 hours - 120 ml/hr - LHSV = 2.0

Samples 2, 4, and 6 were decanted for analysis. The intermediate samples were saved but not analyzed.

After the final sample was taken, the pump, hydrogen flow, and heaters were shut off, and the reactor depressurized. The catchpot system was removed and rinsed thoroughly with acetone, which cleaned it sufficiently for the next run. The hydrogen inlet valve at the top of the reactor was closed and all SRC Vacuum Flash Feed remaining in the pump and reservoir was drained. The reservoirs were filled with 30 W motor oil, which was pumped through the reactor while it was still hot. This loosened catalyst particles and flushed the system of reactants. (Caution: the smoke from hot motor oil is very hard to tolerate and the room must be vented thoroughly during cleaning.) After pumping the motor oil, the reactor was removed from the aluminum block using asbestos gloves. This allowed the reactor to cool quicker, facilitating easier cleaning.

Analytical Procedures

The products from all runs were analyzed for nitrogen content, sulfur content, and the extent of cracking.

Sulfur analyses were performed by the quartz tube method using a Bico-Brown Shell design sulfur apparatus (67,68,69). Feed sulfur which was analyzed periodically varied from .64 wt% to .72 wt% as noted in the data tables.

Nitrogen content was determined by Macro-Kjeldahl method (67,70,71,72). Temperature of digestion was very important in obtaining good reproducible results with Kjeldahl analysis. To insure high enough digestion temperatures, the use of 0.5 gram product samples and 40 grams of potassium sulfate were the only modification made to standard Kjeldahl procedures in this thesis work. Nitrogen content of the feedstock varied from 1.06 wt% to 1.22 wt% as noted in the data tables.

The amount of cracking was determined by ASTM D-86 atmospheric distillation (73) which measures the cumulative amount of product which boils below 700°F.

Catalyst Preparation

Many catalysts were prepared in MSU laboratories. These catalysts were prepared by impregnating commercial supports with various combinations of chromium, molybdenum, nickel, and tungsten oxides. Supports were impregnated using water solutions of chromium nitrate,

ammonium molybdate, nickel nitrate, and ammonium tungstate, respectively. Metal oxides were impregnated one at a time and percentages impregnated were determined gravimetrically. The general procedure for impregnation was as follows:

1. Oven dry supports at 110°C for 8 hrs.
2. Calcine supports at 450°C for 8 hrs.
3. Record weight of support after cooling.
4. Impregnate support in tumbler with specific metal solution.
5. Air dry in tumbler.
6. Oven dry impregnated support at 110°C for 8 hours.
7. Calcine impregnated support at 450°C for 8 hours.
8. Record weight after calcination after cooling.
9. Calculate weight percent of metal oxide impregnated.

This procedure was repeated as needed to obtain the projected percentages of metal oxides.

RESULTS AND DISCUSSION

Forty-four batch autoclave tests were performed testing twenty-three commercial catalysts and ten catalysts that were fabricated at Montana State University. Thirty-nine trickle bed reactor tests were performed testing seventeen commercial catalysts and eighteen catalysts that were fabricated at Montana State University. The products from these runs were analyzed for sulfur content, nitrogen content, and the amount of distillable liquids.

The data from these runs are presented in the appendices. Appendix A contains all obtainable catalyst description data. Appendix B contains the data from the batch autoclave tests. Appendix C contains the data from the trickle bed reactor tests. Appendix D contains statistical data of the metal loading study performed on catalysts prepared at Montana State University. All catalysts fabricated at Montana State University are designated by the prefix MSU.

Batch Autoclave Tests

Batch autoclave tests were performed on two different feedstocks. The original feedstock was a 1:2 weight ratio mixture of solid SRC granules and SRC Light Oil. Heteroatom removal data and final distillate yields for these runs (Run #4B through 25B) are listed in Table VII. Complete run data are listed in Appendix B. The second feedstock used for Runs #26B-#44B was SRC Vacuum Flash Feed, which is a cut from the SRC I process sampled just downstream from the filters

(Figure 1). Heteroatom removal data and final distillate yields are tabulated in Table VIII. Complete run data are listed in Appendix B. Figure 4 shows the difference in the ASTM distillations of these two feedstocks. The SRC Light Oil solvent used in the original batch runs all boils below 425°F. This led to difficulty in discerning cracking abilities of various catalysts since the solvent accounts for 67% of the volume distilled. There were two major reasons for switching to SRC Vacuum Flash Feed for a feedstock; the first being that the switch eliminated the need to mix SRC with solvent and, secondly, SRC Vacuum Flash Feed was a pourable liquid that when heated was a suitable feedstock for trickle bed reactor tests.

Batch autoclave tests were designed to screen catalysts for heteroatom removal ability, conversion of feed to distillate products, and appropriate temperature of operation. By performing the batch tests, many catalysts were tested in a short period of time. If a catalyst showed little or no activity in a batch test, it was not tested in the trickle bed reactor. No effort was made to predict any trends in batch data.

Batch runs #1B-#3B were a preliminary study to find a suitable solvent to dissolve solid SRC granules so a liquid feed could be prepared for trickle bed reactor tests. Pyridine was deemed unsuitable because of its high nitrogen content although it was a very good

Table VII

Batch Autoclave Data Summary*
(of SRC/SRC Light Oil feed)

Run #	Catalyst	Wt % DS**	Wt % DN***	ASTM Dist. Vol % at 700°F
4B	Girder T-368-C	2.0	13.0	74.0
5B	Harshaw Co-Mo-0401T 1/8"	42.2	35.8	73.2
8B	Harshaw Co-Mo-0401T 1/8"	44.0	45.4	74.1
9B	Harshaw Ni-4303E 1/12"	46.0	0.0	76.3
10B	Harshaw Ni-4303E 1/12"	54.0	23.6	75.8
11B	Harshaw HT-100E 1/12"	53.0	31.1	74.4
13B	Harshaw Ni-4404E 1/10"	44.0	29.7	75.3
14B	Harshaw CR-0304T 1/8"	0.0	19.0	75.6
15B	Harshaw Mo-1201T 1/8"	10.0	1.0	74.9
16B	Harshaw CR-0103T 1/8"	0.0	2.0	73.1
18B	Harshaw Co-Mo-0603T 1/8"	0.0	36.0	78.0
19B	Harshaw Ni-3250T 1/8"	0.0	12.0	76.6
20B	Harshaw Ni-3210T 3/16"	0.0	8.0	73.8
21B	Harshaw W-0801T 1/8"	0.0	5.0	74.6
22B	Harshaw CR-0105T 1/8"	0.0	0.0	76.7
23B	Harshaw W-0101T 1/8"	0.0	21.0	73.4
24B	Harshaw HT-400E 1/16"	57.0	16.0	79.5
25B	Harshaw V-0601T 1/8"	0.0	15.1	74.5

*Feedstock: SRC/SRC light oil 1:2 wt ratio: Feed Nitrogen = 1.06 wt%,
Feed sulfur = .50 wt%.

**Weight percent desulfurization

***Weight percent denitrogenation

Table VIII

Batch Autoclave Data Summary Using SRC Vacuum Flash Feed*

Run #	Catalyst	Wt % DS	Wt % DN	ASTM Dist. Vol % at 700°F
26B	Harshaw HT-400E 1/16"	34.8	25.4	68.4
27B	Harshaw HT-500E 1/18"	32.2	16.9	64.5
28B	Ketjen HC-5-1.5E	5.8	27.0	61.9
29B	Ketjen 330-3E	37.3	12.3	66.2
30B	Harshaw Co-Mo-0401T 1/8"	36.0	29.5	67.9
31B	MSU-STK-6-E 1/16"	17.7	1.5	65.1
32B	Shell 324E 1/16"	75.3	27.5	75.7
33B	Shell 344E 1/16"	52.5	18.8	76.0
34B	MSU STK-5-E 1/16"	44.1	20.2	73.7
35B	Harshaw Ni-4401T 1/8"	35.7	20.4	65.9
36B	MSU STK-8-2E 1/16"	47.7	21.5	77.1
37B	MSU STK-10-E 1/16"	28.3	12.0	69.1
38B	MSU STK-11-E 1/16"	38.9	12.0	69.5
39B	Harshaw Ni-4303E 1/12"	42.1	19.4	66.1
40B	MSU STK-14-E 1/16"	58.8	10.2	76.2
41B	MSU STK-9-E 1/16"	8.7	14.9	64.6
42B	MSU STK-12-E 1/16"	46.7	16.1	61.7
43B	MSU STK-13-E 1/16"	21.0	21.7	66.2
44B	MSU STK-8-1-E 1/16"	15.7	29.4	70.5

*Feedstock: SRC Vacuum Flash Feed: Feed Nitrogen = 1.30 wt%;
Feed Sulfur = .664 wt%.

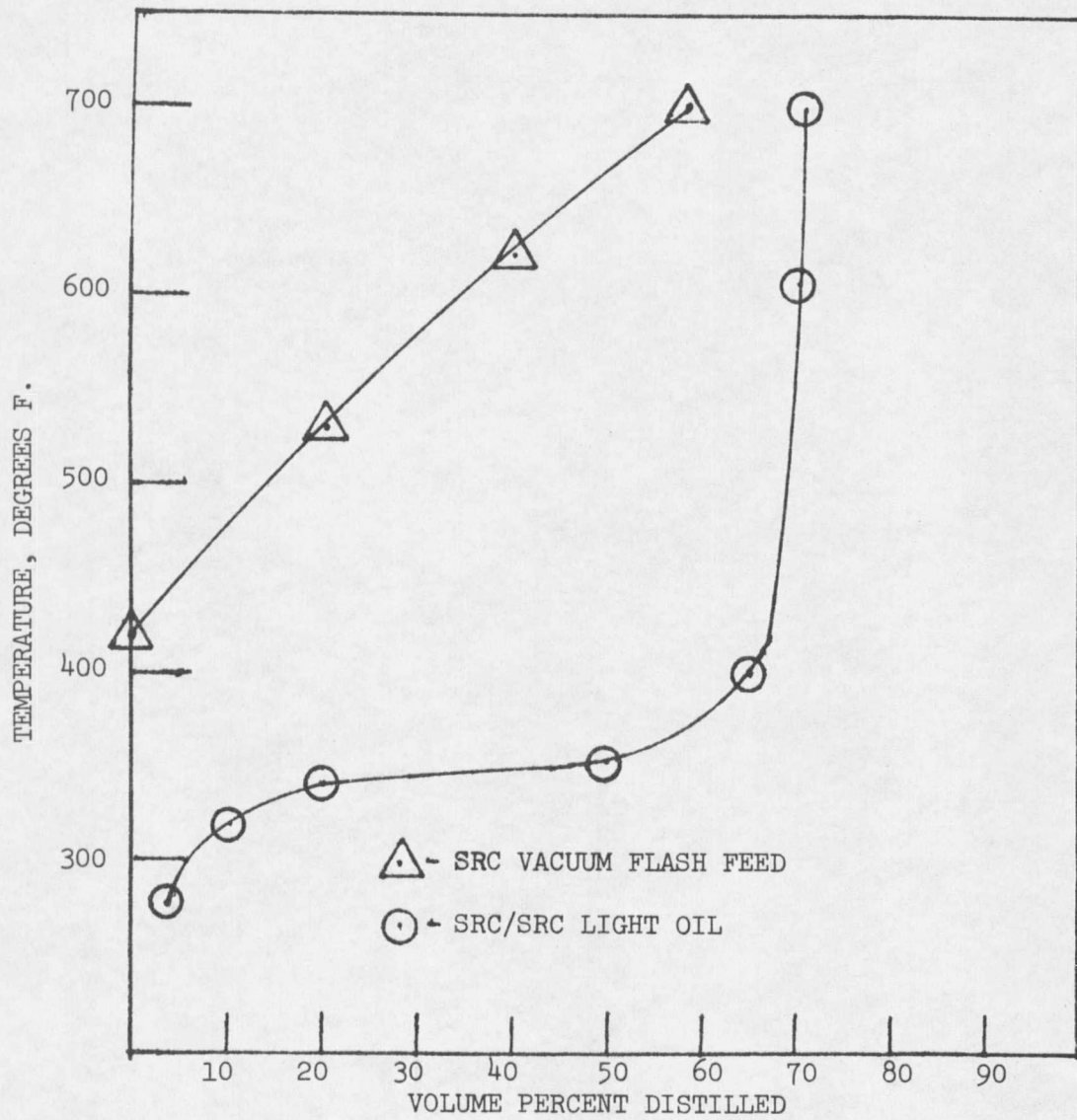


FIGURE 4. ASTM DISTILLATIONS OF SRC/SRC LIGHT OIL AND SRC VACUUM FLASH FEED

solvent. The decision was made to use the native solvent, i.e., SRC Light Oil.

From the batch tests performed on commercial catalysts, it was concluded that many metal combinations such as those contained in Shell 324 (Ni-Mo), Harshaw HT-400 (Co-Mo), and also Harshaw Ni-4401 (Ni-W) gave respectable desulfurization and denitrogenation. From these data it was decided to make a series of nickel oxide-molybdenum trioxide catalysts on Norton 6176 Al_2O_3 support. Added to several of these catalysts was one additional promoter. These catalysts were tested in the batch autoclave to see if any specific combination of metals would be particularly suitable for the hydrotreating of synthetic crudes. These catalysts are listed in Table IX. The data from these tests are listed in the latter part of Table VIII, with complete run data in Appendix B. Data from these runs show that Ni-Co-Mo, Ni-Co-W, and Ni-Mo-Zn combinations show good potential for syncrude hydrotreating catalysts. From the data obtained in these catalysts, it was decided to make a series of NiO , CoO , MoO_3 catalysts on various commercial support materials to see if there were any gross support effects on syncrude hydrotreating. These catalysts are listed in Table X. Each support was impregnated using the same concentrations of metal solutions to determine the affinity of the supports for metal oxides. These catalysts were not tested in the batch autoclave but rather in the trickle bed reactor. Batch autoclave testing was

Table IX

MSU Promoted Nickel-Molybdenum Catalysts

Catalyst	Wt % NiO	Wt % MoO ₃	Wt % Promoter
MSU STK-10	2.6	18.9	1.7% Co, .9% Fe ₂ O ₃
MSU STK-8-2	1.4	8.5	11.2% WO ₃
MSU STK-11	1.2	11.0	3.7% Cr ₂ O ₃
MSU STK-14	2.3	17.4	1.8% Cu ₂ O
MSU STK-9	0	21.0	2.0 ZnO
MSU STK-12	2.7	17.8	1.7 ZnO
MSU STK-13	3.0	11.0	0.5 Fe ₂ O ₃
MSU STK-8-1	1.4	8.6	11.0 WO ₃
MSU STK-5	0.4	18.0	1.2 CoO
MSU STK-1	6.5	15.0	-0-
MSU STK-6	1.5	17.1	1.2 CoO
MSU STK-5-2-1	0.48	23.9	0.75 CoO

Support Norton 6176 1/16" Alumina Extrusions

Table X

Ni-Co-Mo Catalysts

Catalyst	Support	% MoO ₃	% NiO	% CoO
MSU STK-5-2-1	Norton 6176	23.9	.48	.75
MSU STK-5-2-2	Ketjen 003-1.5E	13.1	.26	1.15
MSU STK-5-2-3	Ketjen 000-3E	16.4	.5	1.1
MSU STK-5-2-5	Ketjen 005-2E	14.0	.5	.8
MSU STK-5-2-6	Ketjen 007-1.5E	15.5	.2	1.1

Support Properties

Support	% Al ₂ O ₃	% SiO ₂	% Na ₂ O	S.A. m ² /g	P.V. cc/g	P.D. ¹ Å
Norton 6178	99.85	.12	.014	250	.9	152
Ketjen 003-1.5E	bal.	1.33	.01	240	.7	117
Ketjen 006-1.5E	bal.	.37	.10	200	.73	146
Ketjen 005-2E	bal.	.55	.06	150	.64	171
Ketjen 000-3E	bal.	1.5	.13	230	.64	111

¹ Average Pore Diameter = $40,000 \times \text{P.V.} / \text{S.A.}$ in Å

discontinued because more data was available from the trickle bed reactor.

Trickle Bed Reactor Tests

Catalysts were tested in the trickle bed reactor to determine the effects of LHSV, temperature, and the effects of specific chemical and physical catalyst properties on the hydrotreating of SRC Vacuum Flash Feed. Heteroatom removal data and final distillate yields for all trickle bed runs are listed in Table XIII. Complete trickle bed run data are contained in Appendix C.

Trickle bed reactor tests C-1 through C-17 were made on the most promising commercial tests from the batch autoclave tests. All trickle bed reactor tests were made at 1000 psig and 450°C except for the temperature study runs. Work reported by others used higher pressure and obtained good results, but 1000 psig was the limiting working pressure of our equipment (74,75).

Early in the use of the trickle bed reactor, tests were made to determine what types of diffusion were affecting trickle bed reactor tests. Runs C-4 and C-5 were made with the same catalyst (Harshaw HT-400 Co-Mo) with the only difference being the particle size of the catalyst extrusion. As seen from the data in Table XIII, denitrogenation was increased by as much as 15% and desulfurization by as much as 21% when the smaller extrusion was used. This indicates that pore diffusion is very much present in our reactors. Work of Kujawa

(76) showed that film diffusion was also present in the hydrotreating of COED Pyrolysis Oil in an identical reactor as used for this thesis work. Also important in hydrotreating was the hydrogen flow rate. Work reported by Runnion (77) showed that a flow rate of 10,000 scf/bbl seemed to be optimum. This flow rate was used in all catalyst tests for this thesis work. From this preliminary work, it was decided to use, whenever possible, 1/16-inch extrusions to help eliminate pore diffusion effects. Some problems arose when catalyst manufacturers were unable to supply the small extrusions.

After testing commercial catalysts, the five Ni-Co-Mo catalysts listed in Table X were tested in the trickle bed reactor to determine support effects. The heteroatom removal data and distillate yields for these five catalysts are listed in Table XIII, Runs C-18 through C-22. Figure 5 shows the weight percent denitrogenation vs LHSV for these five catalysts. MSU STK-5-2-2-1.5E gave the best denitrogenation with MSU STK-5-2-6-1.5E giving the second best performance. These catalysts were made on similar supports having 1.3-1.5% SiO_2 and 230-240 m^2/gr surface area. MSU STK-5-2-1E 1/16" was made on Norton 6176 support which is high surface area alumina. The impregnation of this support with MoO_3 seemed to coat and cake up the outside surface of the support. Possible reason for poor performance was that many of the small pores were plugged, which physically excludes large asphaltene molecules. MSU STK-5-2-3-3E and MSU STK-5-2-5-2E are larger

extrusions which could increase pore diffusion in trickle bed reactions. Figure 6 shows the weight percent desulfurization vs. LHSV for these five catalysts. MSU STK-5-2-6-1.5E gave the best overall desulfurization for the group. Figure 7 shows the ASTM D-86 distillation for MSU STK-5-2-2-1.5E. At a space velocity of 1.0, 86 volume percent of the products were recovered. Figure 8 shows the ASTM D-86 distillation for MSU STK-5-2-6-1.5E. At a space velocity of 1.0, 85 volume percent of the products were recovered.

On the basis of this data it was decided to further investigate the Ni-Co-Mo metal combinations. Since nitrogen proved to be the harder heteroatom to remove from syncrude, it was decided to prepare a series of Ni-Co-Mo catalysts on Ketjen-003-1.5E support which was the support used for MSU STK-5-2-2 catalyst. Eight catalysts were prepared with target values of 0.5 and 1.5 wt% NiO, 1.5 and 3.0 wt% CoO, and 12 and 18 wt% MoO₃. These catalysts are listed in Table XI. These catalysts were all tested at 450°C in the trickle bed reactor. Heteroatom removal data and distillate yields are listed in Table XIII, runs C-30 through C-37. Complete run data are listed in Appendix C. The prime interest of this series of runs was to obtain enough data so that a statistical analysis could be applied to determine the effects of the various concentrations of metals. The data obtained from these runs is repeated in Table D-I of Appendix D. The data was used in a 2⁴ factorial design experiment (78). A design experiment

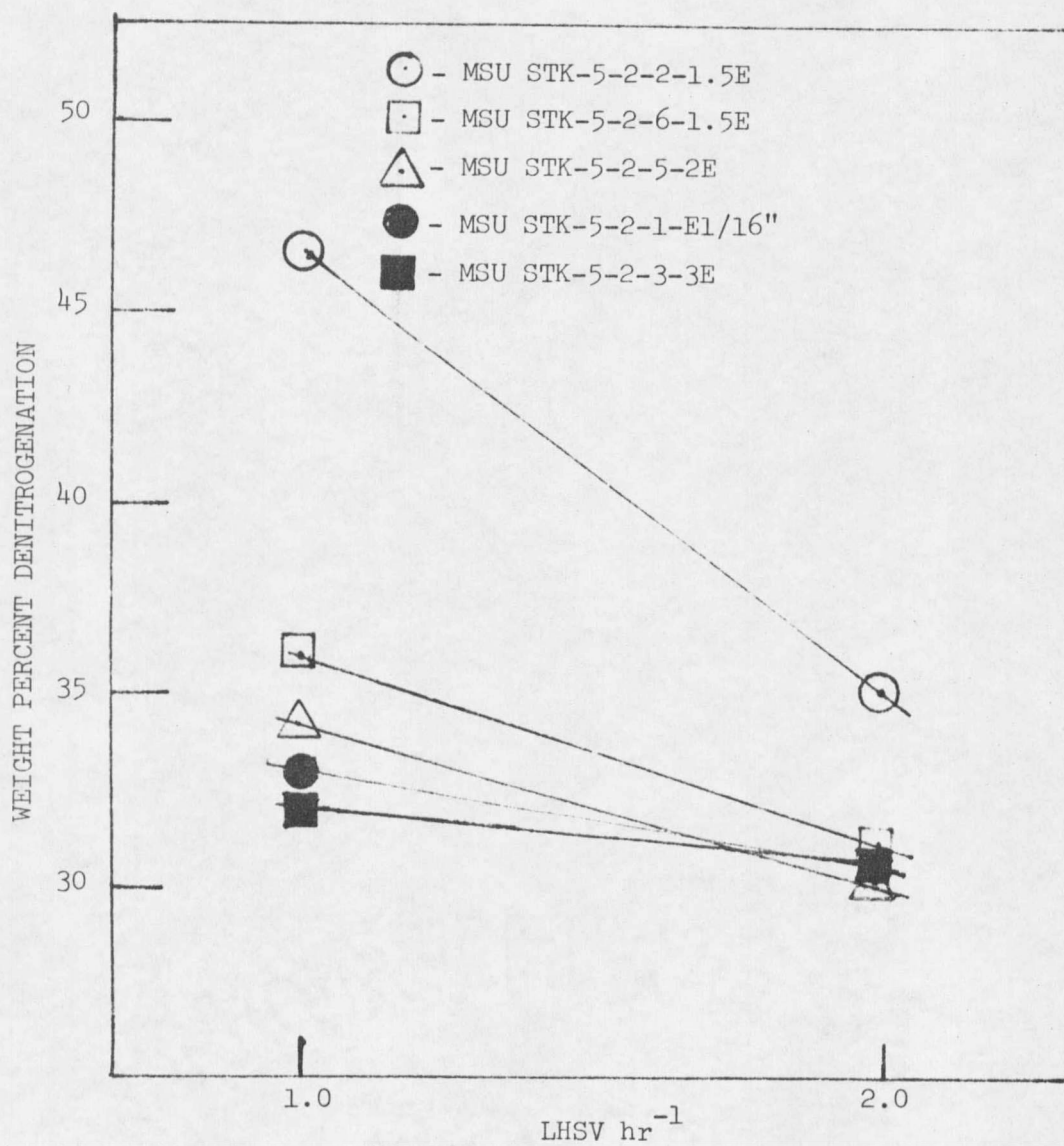


FIGURE 5. PERCENT DENITROGENATION vs. SPACE VELOCITY FOR MSU FABRICATED CATALYSTS

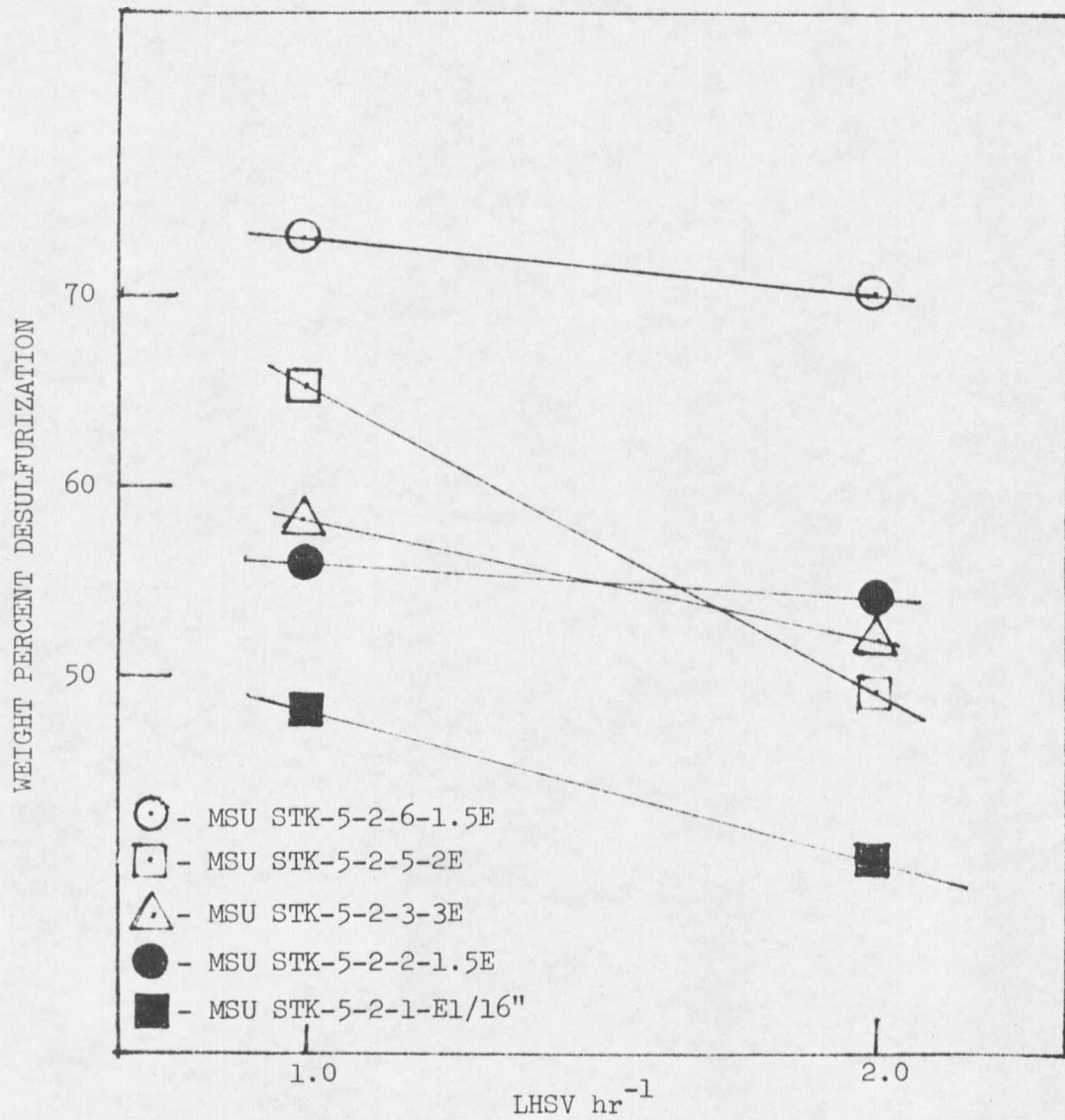


FIGURE 6. PERCENT DESULFURIZATION vs. SPACE VELOCITY FOR MSU FABRICATED CATALYSTS

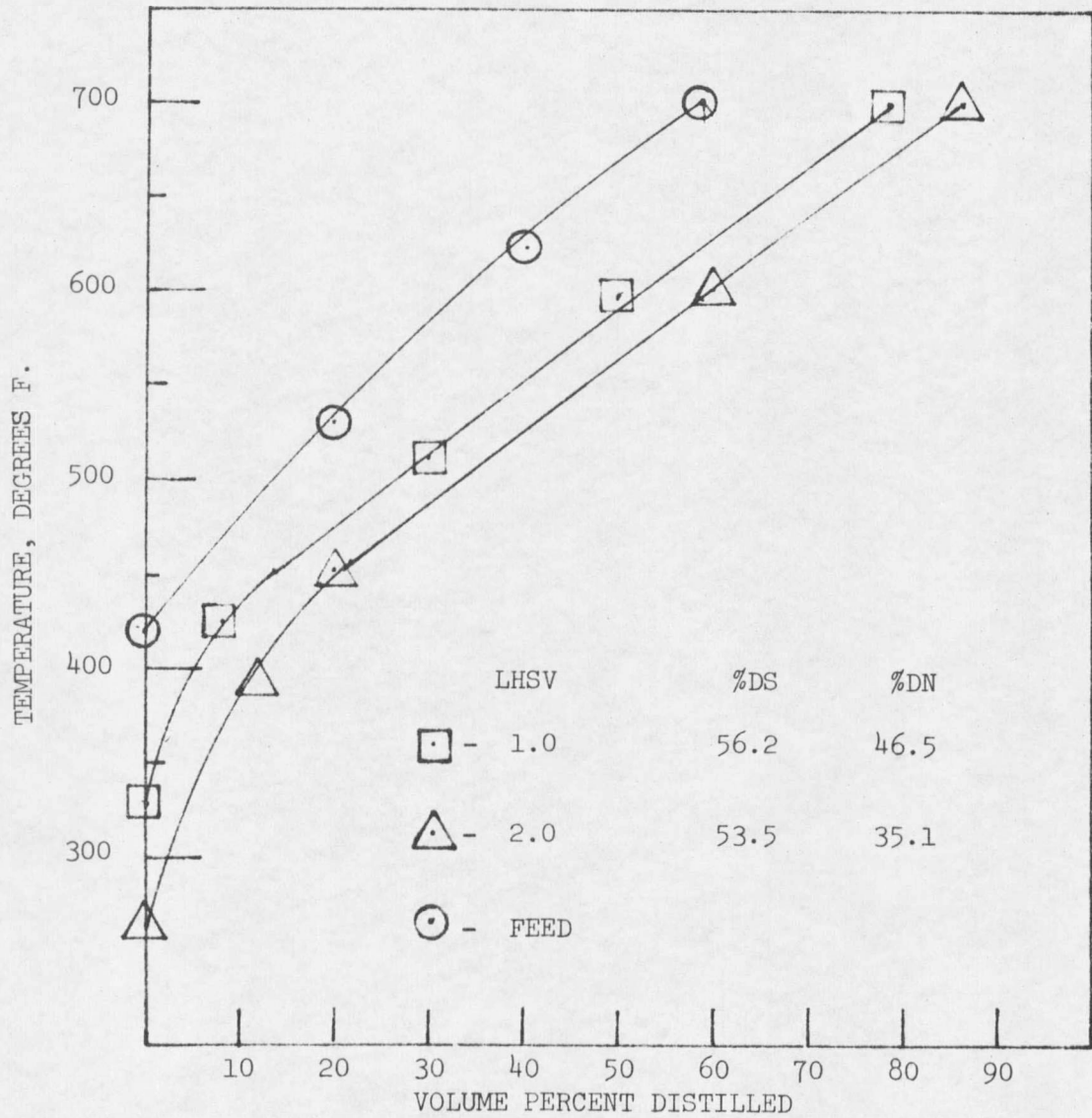


FIGURE 7. MSU-STK-5-2-2-1.5E CATALYST PERFORMANCE
BEST MSU FABRICATED DENITROGENATION CATALYST

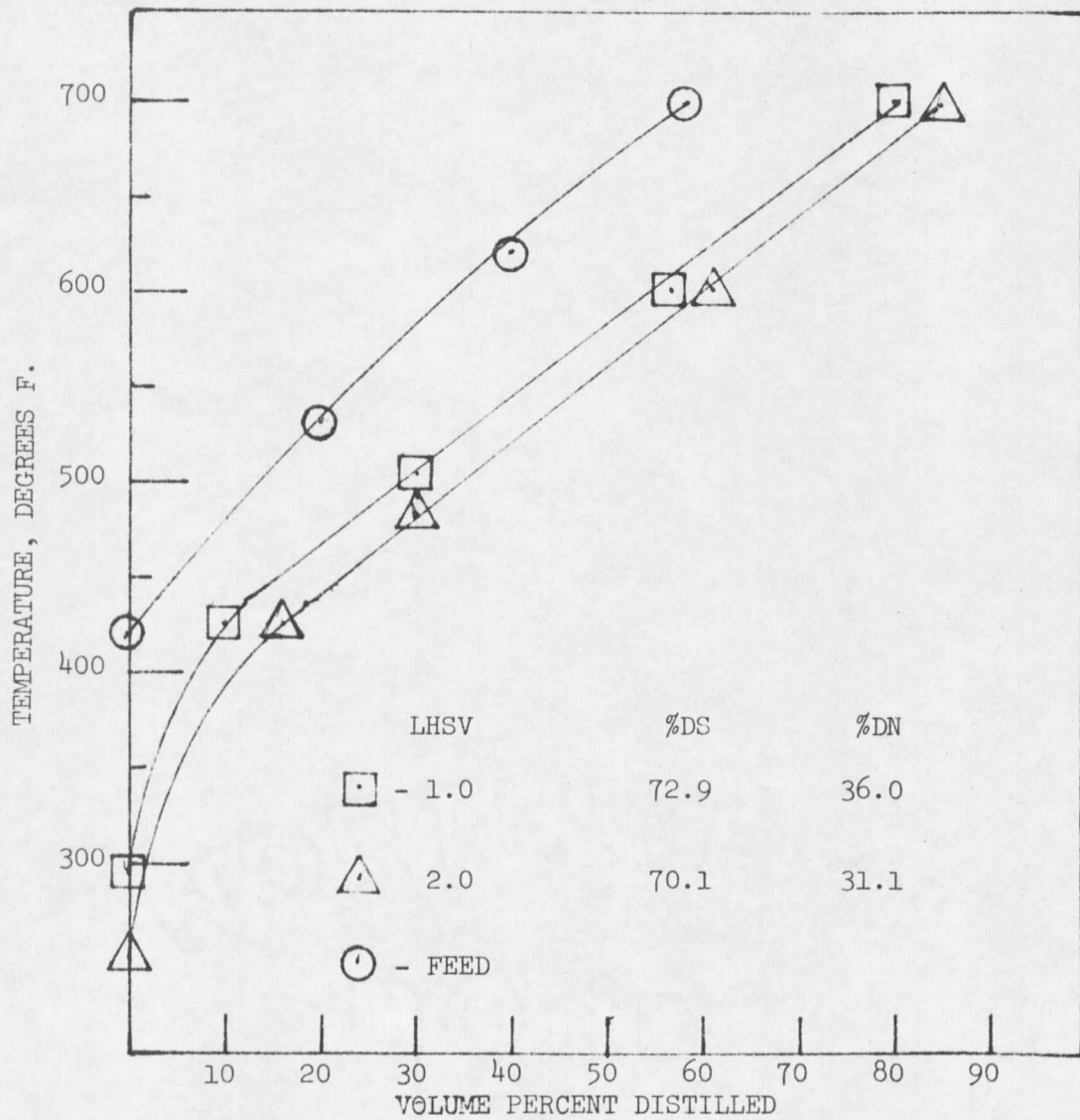


FIGURE 8. MSU STK-5-2-6-1.5E CATALYST PERFORMANCE
BEST MSU FABRICATED DESULFURIZATION CATALYST

Table XI

Catalyst Data
MSU Ni-Co-Mo Optimization

Catalyst	% NiO	% CoO	% MoO ₃
MSU - 1003	1.4	3.0	18.0
MSU - 2003	1.4	1.4	19.1
MSU - 3003	.5	3.6	17.7
MSU - 4003	.5	1.6	17.4
MSU - 5003	1.8	3.1	10.3
MSU - 6003	1.7	1.4	13.2
MSU - 7003	.5	3.0	11.6
MSU - 8003	.5	1.8	11.7

Support Properties: Ketjen 003-1.5E: 98.66% Al₂O₃, 1.33% SiO₂,
.01% Na₂O

S.A. = 240 m²/g, P.V. = 7 cc/g, P.D. = 117Å

was carried out for the nitrogen removal data and also the sulfur removal data. There were four factors to consider: space velocity, nickel oxide concentration, cobalt oxide concentration, and molybdenum trioxide concentration. There were two levels of each factor: space velocities of 1.0 and 2.0, and two concentrations of each metal oxide. The analysis of variance showed that increased space velocity was statistically significant in reducing both nitrogen and sulfur removal as would be expected. The increased MoO_3 concentration caused significant increase in nitrogen removal. The effect of increased MoO_3 concentration is shown graphically in Figure 9. About a 4% increase in nitrogen removal was obtained with increased MoO_3 concentration. The analysis of variance also showed that there was an interaction between NiO and MoO_3 and also between CoO and MoO_3 , both of which favored nitrogen removal. These interactions are shown graphically in Figures 10 and 11. In both cases the higher total metal loadings gave better nitrogen removal. The complete statistical analysis for both sulfur and nitrogen data is presented in Tables D-II through D-VII of Appendix D.

Another series of five catalysts were prepared at MSU to determine interactions between nickel oxides, cobalt oxides, and tungsten trioxide. These catalyst descriptions are presented in Table XII. Heteroatom removal data and distillate yields are listed in Table XIII, Runs C-23 through C-27. These catalysts gave very good cracking

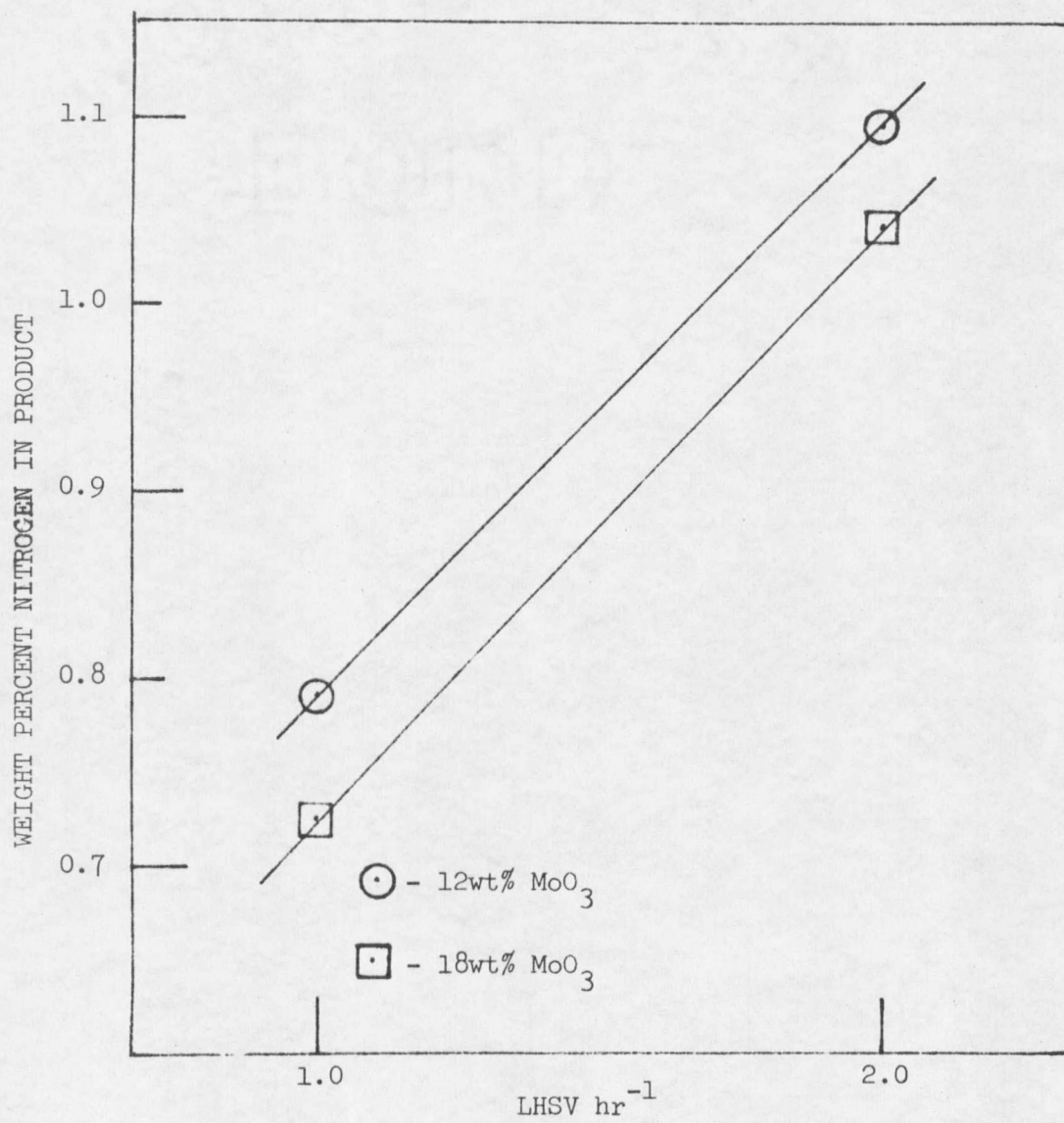


FIGURE 9. MoO_3 EFFECTS ON DENITROGENATION

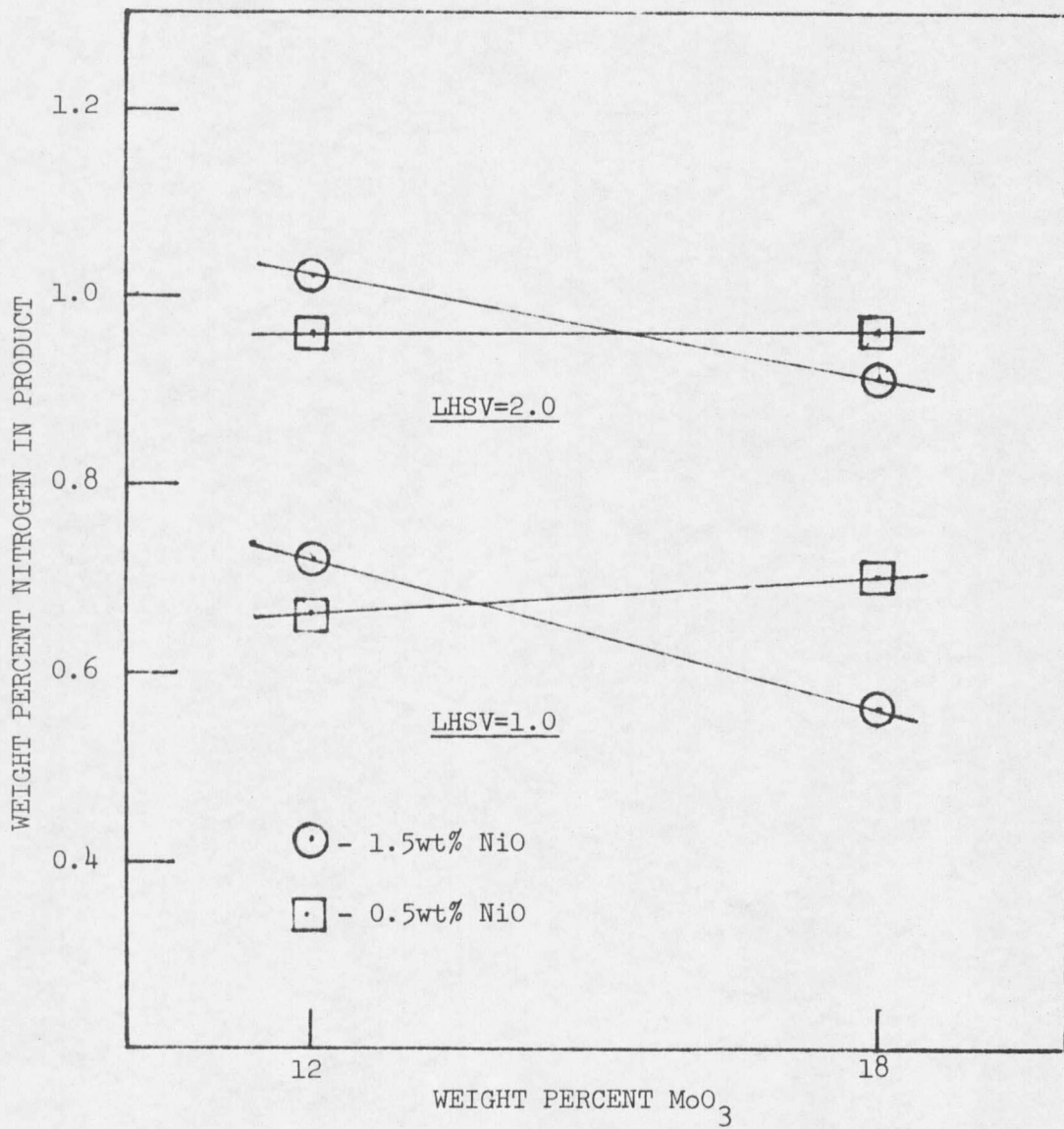


FIGURE 10. NICKEL MOLYBDATE INTERACTIONS AFFECTING DENITROGENATION

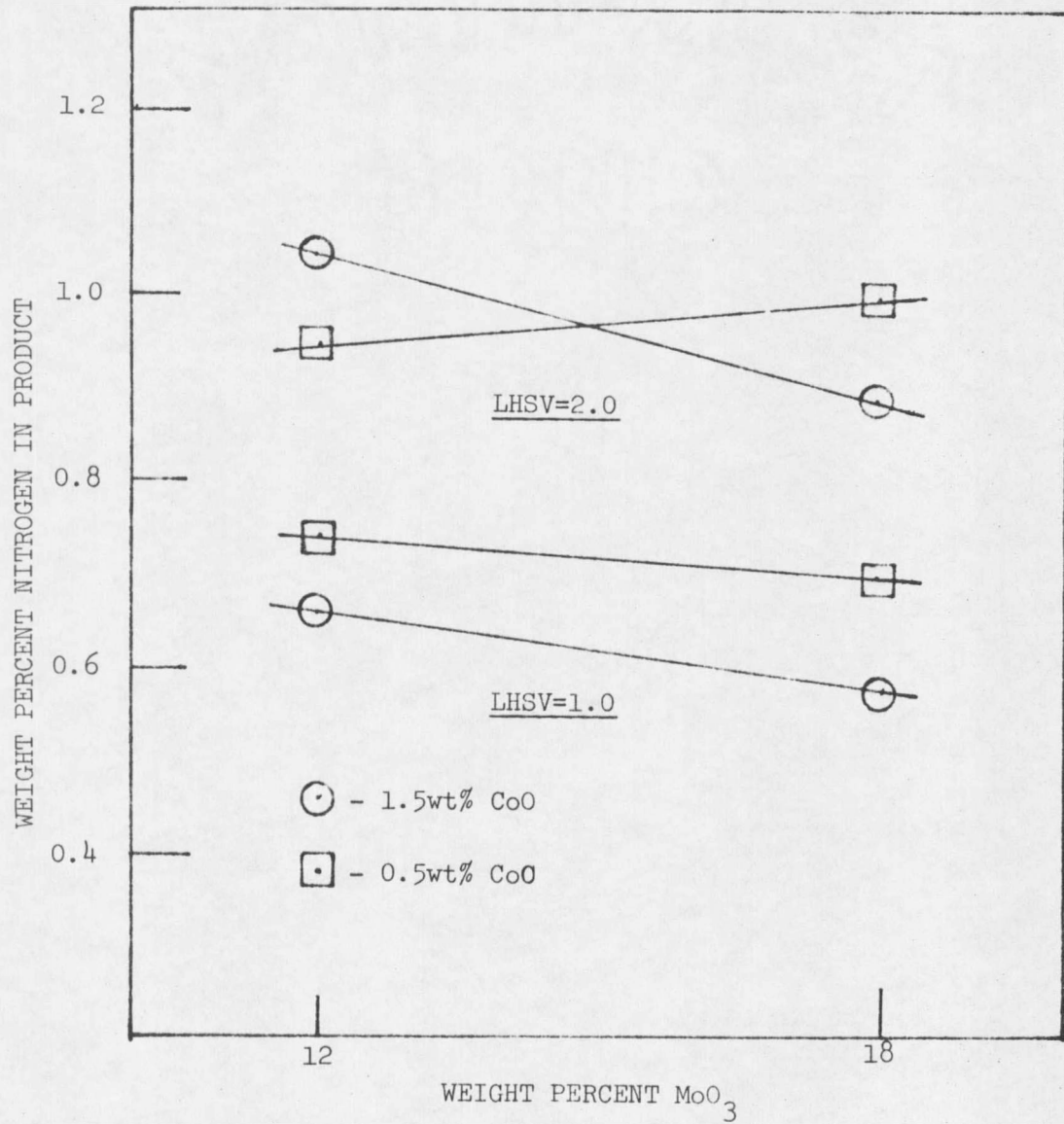


FIGURE 11. COBALT MOLYBDATE INTERACTIONS AFFECTING DENITROGENATION

Table XII

Ni-Co-W Optimization
Ketjen 003-E 1/16" Support Data

Al_2O_3	SiO_2	Na_2O	S A	P V	P.D. ¹
bal.	1.33%	.01%	240 m ² /g	.7 cc/g	117 Å

Catalyst Data

Catalyst	NiO	CoO	WO ₃
MSU-GRH-1	6.10%	2.85%	19.91%
MSU-GRH-2	2.91%	2.91%	18.84%
MSU-GRH-3	6.06%	6.12%	18.53%
MSU-GRH-4	3.13%	5.90%	19.02%
MSU-GRH-5	5.88%	0	18.00%

¹ Average Pore Diameter = $40,000 \times \text{P.V.}/\text{S.A.}$ in Å

results and sulfur removal, but proved not to be particularly good at removing nitrogen. An analysis of variance assuming a 2^3 factorial design was performed on the data but there were not sufficient data points to make any conclusions regarding metal loading effects.

Some of the most important data obtained was from the temperature study performed using Harshaw HT-400 E 1/16" (Co-Mo) catalyst. Data for these runs is listed in Table XIII, Runs C-14, C-38, and C-39. Complete data is listed in Appendix C. This catalyst was tested for 12 hours at the same space velocity (LHSV=2.0) and at three different temperatures (400°C, 425°C, and 450°C). Figure 12 shows denitrogenation vs. hours on stream for the three temperatures. As can be seen in the figure there was high deactivation during the first six hours and even moderate deactivation up to 12 hours. All runs in this thesis work were only 12-13 hours. Thus all data points were taken during a time when catalyst deactivation was a very critical factor. Figure 13 shows desulfurization vs. hours on stream for Harshaw HT-400-E 1/16" catalyst for the three temperatures. As can be seen from the figure desulfurization was affected less than denitrogenation. Figure 14 shows ASTM distillations for the three temperatures. Improvement in the distillate yield was obtained at successively higher temperatures, but higher temperatures increased gas make and also increased coke laydown on the catalyst. Increased temperature seemed to give better nitrogen removal, but a delicate balance must be made

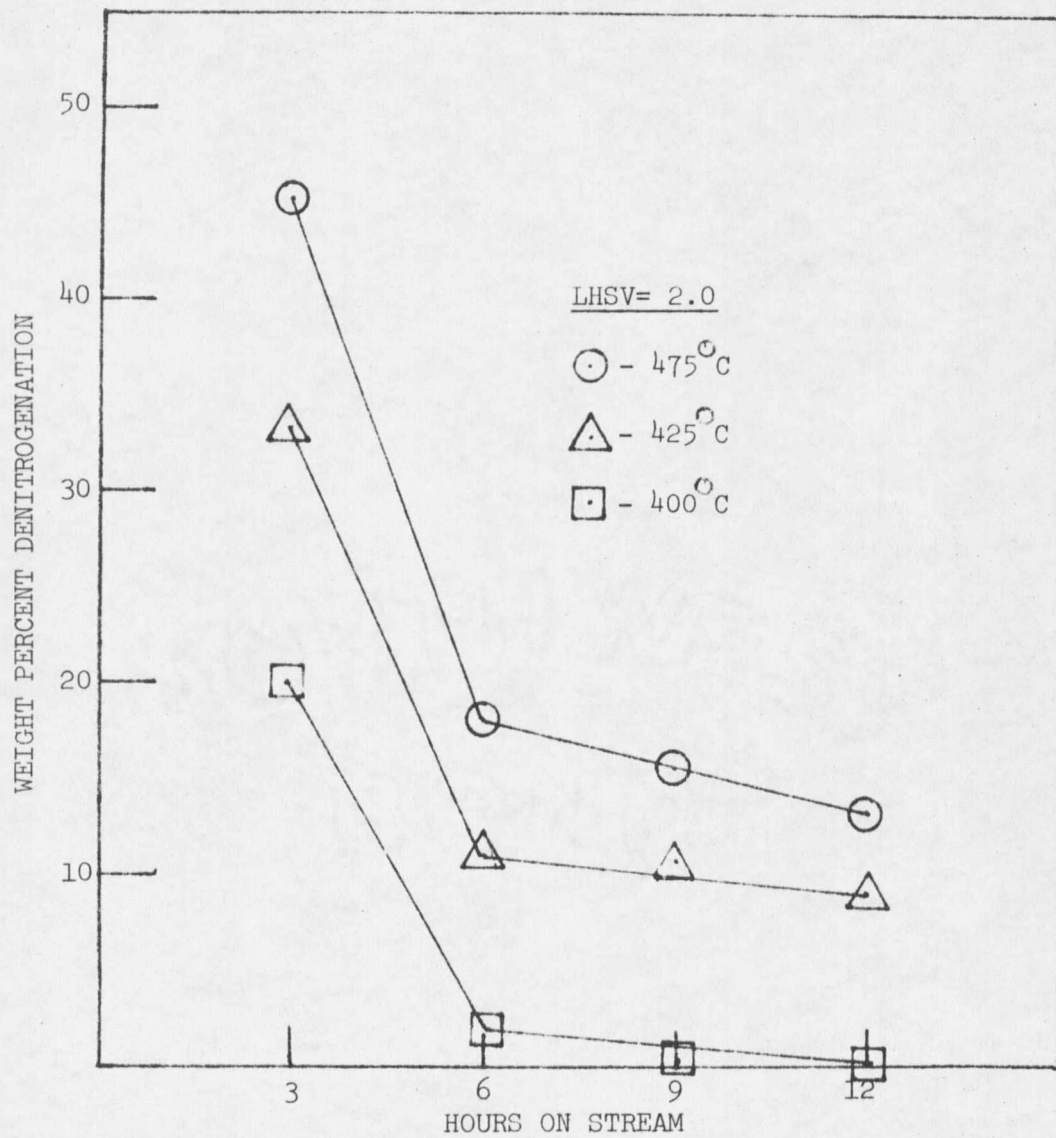


FIGURE 12. TEMPERATURE EFFECTS ON DENITROGENATION ACTIVITY OF HARSHAW HT-400 E1/16" CATALYST

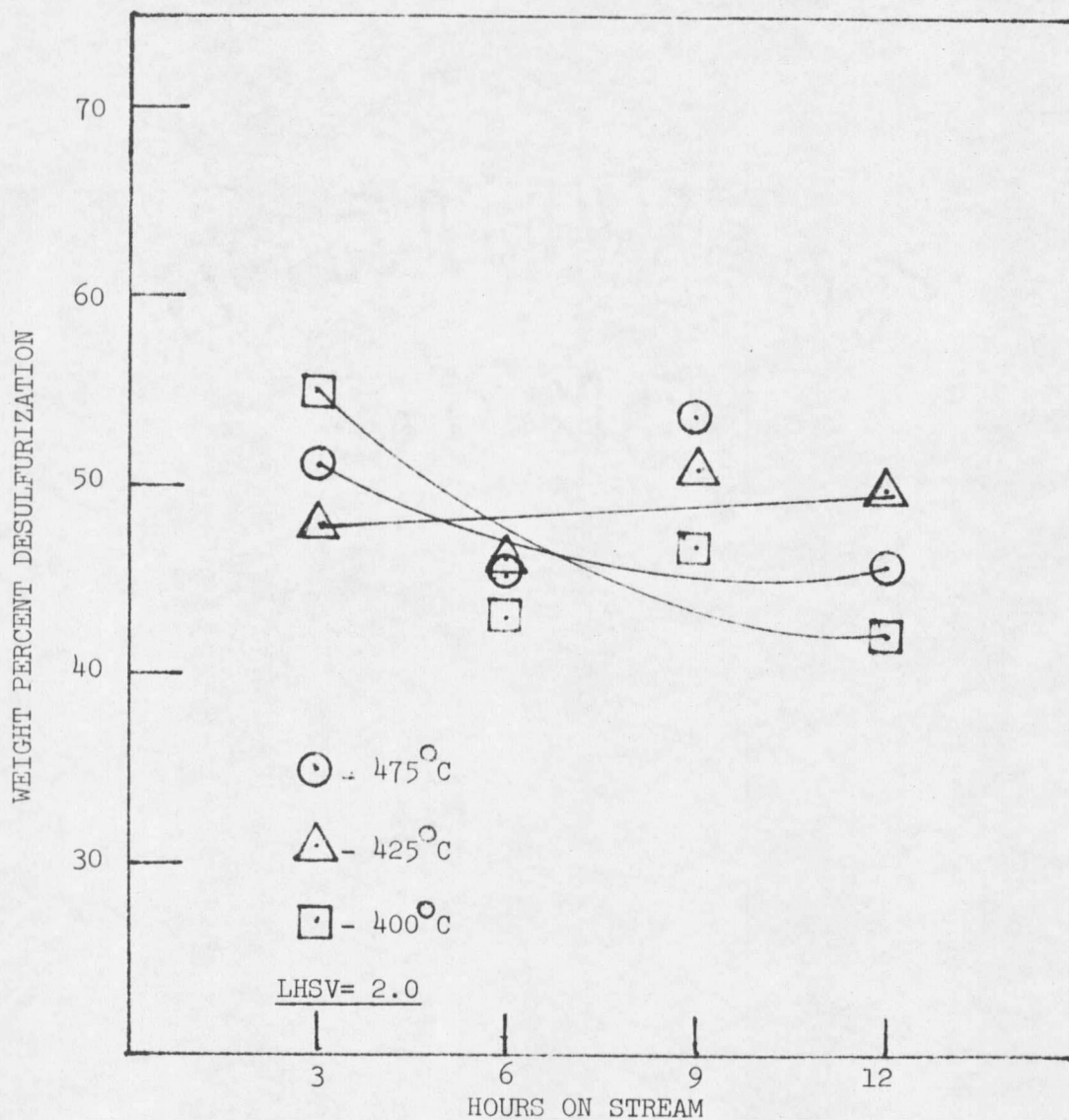


FIGURE 13. TEMPERATURE EFFECTS ON DESULFURIZATION ACTIVITY OF HARSHAW HT-400 E1/16" CATALYST

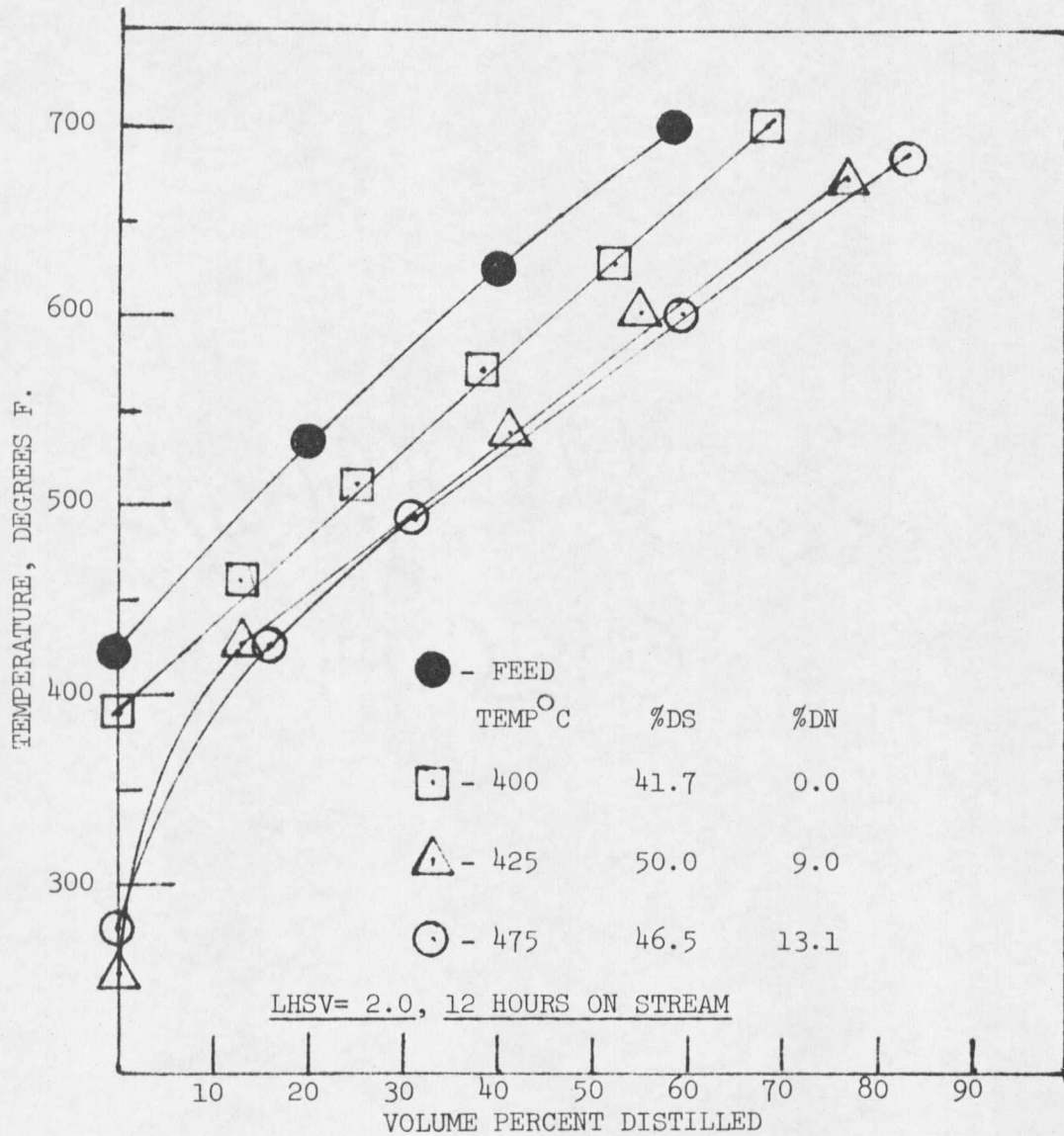


FIGURE 14. LIQUID YIELDS vs. TEMPERATURE FOR HARSHAW HT-400 E1/16" CATALYST

Table XIII

Data Summary of Continuous Runs on SRC Vacuum Flash Feed

Run	Catalyst	LHSV*	% DN**	% DS***	Yield
C-1	Shell 324-E 1/16"	1.0	38.8	70.5	76.9
		1.5	15.4	61.8	74.2
		2.0	8.5	49.5	68.9
C-3	Harshaw Co-Mo-0401-T 1/8"	1.0	19.2	54.2	76.4
		1.5	12.7	59.9	72.8
		2.0	3.8	38.8	74.5
C-4	Harshaw HT-400-E 1/16"	1.0	33.8	67.1	75.6
		1.5	32.3	53.9	78.1
		2.0	26.2	55.3	73.8
C-5	Harshaw HT-400-E 1/8"	1.0	18.8	62.3	77.2
		1.5	20.5	56.4	79.2
		2.0	10.1	34.3	67.6
C-6	Harshaw HT-500-E 1/8"	1.0	18.5	53.1	78.1
		1.5	20.0	58.8	71.7
		2.0	13.1	53.6	75.0
C-7	Shell 344-E 1/16"	1.0	31.1	73.9	74.6
		1.5	37.0	61.2	76.7
		2.0	17.7	65.2	75.2
C-8	Harshaw Ni-4401-T 1/8"	1.0	15.2	66.3	73.4
		1.5	17.8	38.2	74.2
		2.0	13.5	41.5	72.2
C-9	Cyanamid HDS-20A 1/16" Trilobe	1.0	18.4	62.5	83.9
		1.5	16.7	70.8	81.4
		2.0	11.0	69.4	77.3
C-10	Cyanamid HDS-9AE 1/16"	1.0	21.1	61.1	81.6
		1.5	26.3	62.5	81.2
		2.0	21.1	61.1	80.5
C-11	Harshaw Co-Mo-0603-T 1/8"	1.0	13.2	54.2	77.7
		1.5	15.4	45.8	80.9
		2.0	4.4	54.9	75.5
C-12	Harshaw Ni-4301-T 1/8"	1.0	9.6	61.1	74.6
		1.5	10.5	51.4	80.1
		2.0	2.2	48.6	72.5

Table XIII (continued)

Run	Catalyst	LHSV*	% DN**	% DS***	Yield
C-13	Harshaw Ni-4303-T 1/8"	1.0	11.4	53.5	81.8
		1.5	15.8	55.6	79.8
		2.0	11.4	48.6	76.6
C-14	Harshaw HT-400-E 1/16"				
	C-14-1 (Temp. 400°C)	2.0	20.2	54.9	69.7
	C-14-2 " "	2.0	1.8	43.1	71.7
	C-14-3 " "	2.0	-0-	47.2	72.8
	C-14-4 " "	2.0	-0-	41.7	68.4
C-15	Harshaw HT-100-E 1/12"	1.0	17.1	56.2	78.7
		1.5	21.5	51.4	78.6
		2.0	6.0	54.2	72.0
C-16	Harshaw Ni-3250-T 1/8"	1.0	18.0	21.5	73.5
		1.5	14.5	16.0	73.8
		2.0	4.8	18.1	68.6
C-17	Harshaw Ni-1601-T 1/8"	1.0	30.3	20.1	74.9
		1.5	32.9	27.8	80.7
		2.0	24.1	4.2	76.1
C-18	MSU STK-5-2-1-E 1/16"	1.0	32.9	47.9	77.2
		1.5	39.5	47.9	76.7
		2.0	29.8	39.6	75.6
C-19	MSU STK-5-2-2-E 1/16"	1.0	46.5	56.2	86.4
		1.5	54.8	65.3	88.6
		2.0	35.1	53.5	78.9
C-20	MSU STK-5-2-3-3E	1.0	32.0	58.3	79.9
		1.5	36.8	54.9	67.7
		2.0	30.7	52.1	77.1
C-21	MSU STK-5-2-5-2E	1.0	34.2	64.6	79.5
		1.5	37.7	61.1	82.2
		2.0	30.3	48.6	78.0
C-22	MSU STK-5-2-6-E 1/16"	1.0	36.0	72.9	85.4
		1.5	39.0	74.3	83.1
		2.0	31.1	70.1	81.4
C-23	MSU GRH-1-E 1/16"	1.0	18.2	72.2	87.0
		1.5	--	66.0	90.0
		2.0	5.7	47.9	76.4

Table XIII (continued)

Run	Catalyst	LHSV*	% DN**	% DS***	Yield
C-24	MSU GRH-2-E 1/16"	1.0	15.6	59.7	84.1
		1.5	--	63.9	84.4
		2.0	4.9	66.7	81.1
C-25	MSU GRH-3-E 1/16"	1.0	18.0	56.1	87.5
		1.5	24.2	61.1	86.0
		2.0	6.6	47.8	82.1
C-26	MSU GRH-4-E 1/16"	1.0	22.5	54.7	84.5
		1.5	23.8	56.0	87.0
		2.0	6.1	51.1	80.4
C-27	MSU GRH-5-E 1/16"	1.0	20.7	54.3	86.1
		1.5	29.3	61.1	86.1
		2.0	8.6	43.1	77.2
C-28	Ketjen 330-3-E 1/16"	1.0	15.1	55.8	84.1
		1.5	15.8	48.3	83.4
		2.0	5.2	45.8	81.8
C-29	Houdry HR-811-E 1/16"	1.0	19.3	52.2	84.6
		1.5	18.5	56.9	83.4
		2.0	4.4	39.6	81.7
C-30	MSU-4003-E 1/16"	1.0	22.6	72.2	82.4
		1.5	30.1	67.8	82.6
		2.0	13.6	58.1	80.1
C-31	MSU-7003-E 1/16"	1.0	21.9	55.4	81.5
		1.5	23.9	68.1	85.5
		2.0	14.3	62.5	79.6
C-32	MSU-3003-E 1/16"	1.0	21.5	67.4	86.9
		1.5	18.0	58.3	86.5
		2.0	9.4	59.0	78.2
C-33	MSU-8003-E 1/16"	1.0	25.0	71.4	87.2
		1.5	34.8	76.8	87.0
		2.0	8.2	45.3	84.6
C-34	MSU-1003-E 1/16"	1.0	23.6	61.8	84.7
		1.5	24.2	58.3	83.4
		2.0	11.1	46.5	82.0

Table XIII (continued)

Run	Catalyst	LHSV*	% DN**	% DS***	Yield
C-35	MSU-5003-E 1/16"	1.0	19.3	58.3	85.0
		1.5	18.3	53.5	83.0
		2.0	10.2	59.7	81.1
C-36	MSU-6003-E 1/16"	1.0	23.0	65.3	85.2
		1.5	19.9	66.0	84.6
		2.0	8.2	58.3	80.3
C-37	MSU-2003-E 1/16"	1.0	32.2	71.0	86.6
		1.5	31.6	66.7	86.8
		2.0	15.6	59.0	81.0
C-38	Harshaw HT-400-E 1/16"				
	C-38-1 (Temp. 425°C)	2.0	33.2	47.6	85.7
	C-38-2 " "	2.0	11.0	45.1	80.5
	C-38-3 " "	2.0	10.8	51.4	78.8
	C-38-4 " "	2.0	9.0	50.0	76.8
C-39	Harshaw HT-400-E 1/16"				
	C-39-1 (Temp. 475°C)	2.0	45.1	50.7	90.9
	C-39-2 " "	2.0	18.0	45.8	84.1
	C-39-3 " "	2.0	15.6	54.2	83.2
	C-39-4 " "	2.0	13.1	46.5	82.8

* LHSV - Liquid Hourly Space Velocity

** % DN - Weight Percent Denitrogenation

*** % DS - Weight Percent Desulfurization

Notes: Runs C-1 through C-8 Feedstock contained: .644% S and 1.30%
 Runs C-9 through C-22 Feedstock contained: .72% S and
 1.14% N
 Runs C-23 through C-39 Feedstock contained: .72% S and
 1.22% N

between heteroatom removal, gas make, and catalyst coking to hydro-treat a syncrude.

Best Catalyst Performance in Trickle Bed Reactor

The best nitrogen removal using a commercial catalyst was with Harshaw HT-400 E 1/16" (Co-Mo) at 450°C. Figure 15 shows ASTM distillations and heteroatom removal data for this catalyst at two space velocities. The best sulfur removal using a commercial catalyst was with Cyanamid HDS-20A 1/16-inch Trilobe (Co-Mo) at 450°C. Figure 16 shows the ASTM distillations and heteroatom removal for this catalyst at two space velocities.

The best nitrogen removal obtained by any catalyst, commercial or fabricated, was with MSU STK-5-2-2-1.5E (Ni-Co-Mo) catalyst. Figures 17, 18, and 19 compare this catalyst to three classes of commercial catalysts. Figure 17 compares commercial Ni-W catalysts, Figure 18 compares commercial Co-Mo catalysts and Figure 19 compares commercial Ni-Mo catalysts. In each case the MSU fabricated catalyst outperformed the best commercial catalysts that were tested.

The best sulfur removal obtained by any catalyst, commercial or fabricated was with MSU STK-5-2-6-1.5E (Ni-Co-Mo) catalyst. Figures 20, 21, and 22 show this catalyst compared to the three classes of commercial catalysts. Figure 20 compares MSU STK-5-2-6 with commercial Ni-W catalysts, Figure 21 with commercial Co-Mo catalysts, and Figure 22 with commercial Ni-Mo catalysts.

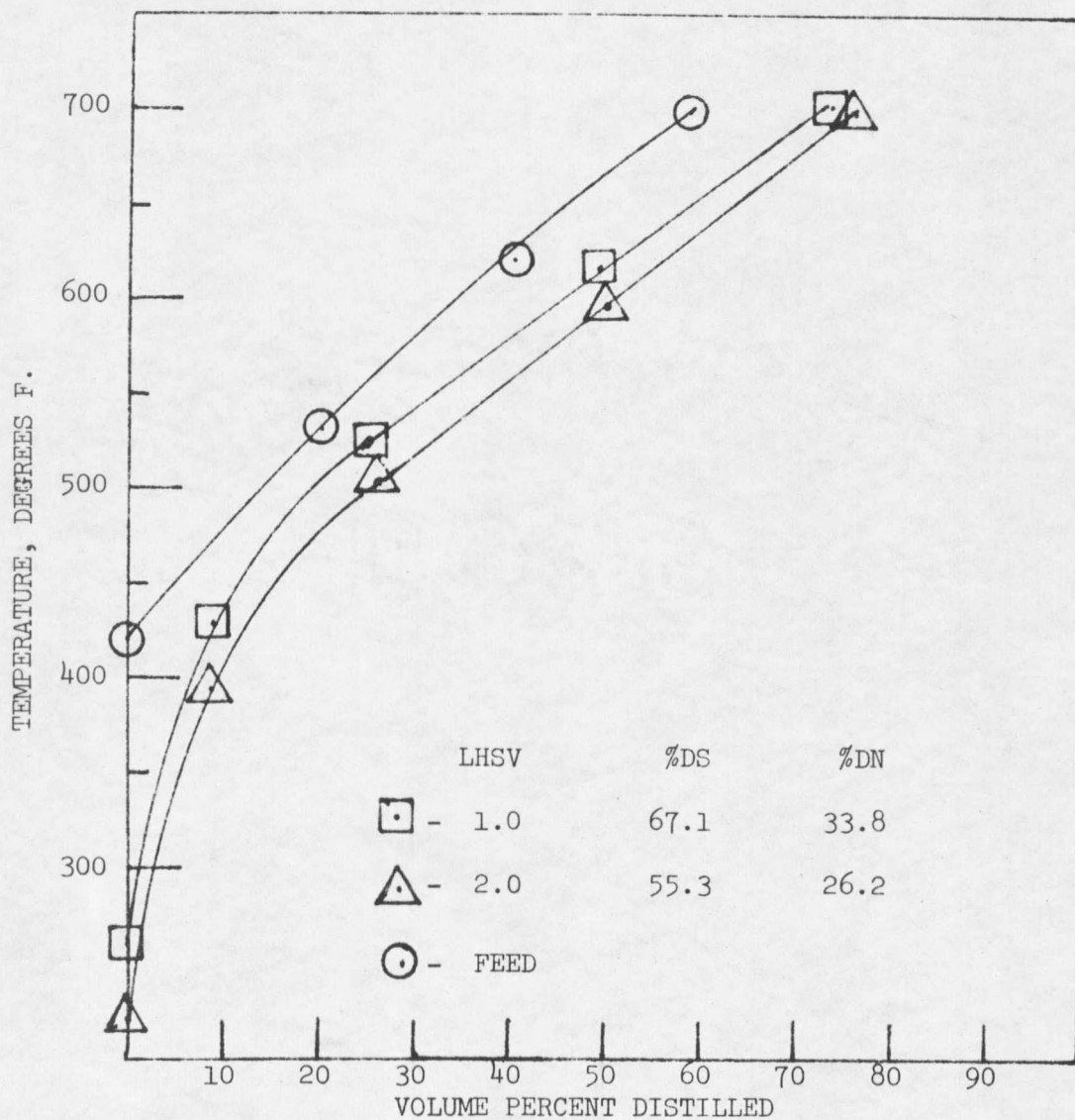


FIGURE 15. HARSHAW HT-400 E1/16" CATALYST PERFORMANCE AT 450 C--BEST COMMERCIAL DENITROGENATION

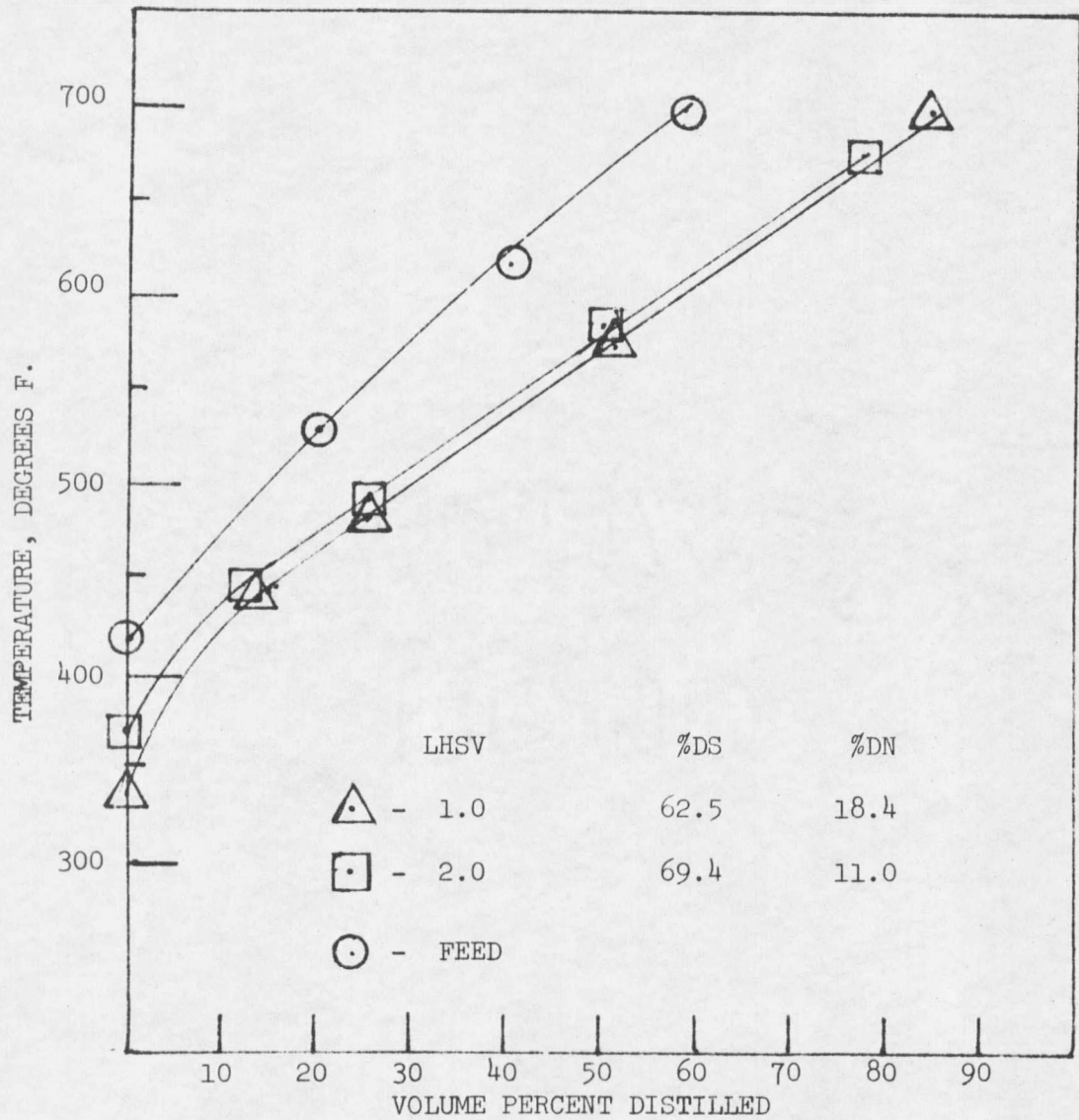


FIGURE 16. CYANAMID HDS-20A 1/16" TRILOBE PERFORMANCE AT 450 C--BEST COMMERCIAL DESULFURIZATION

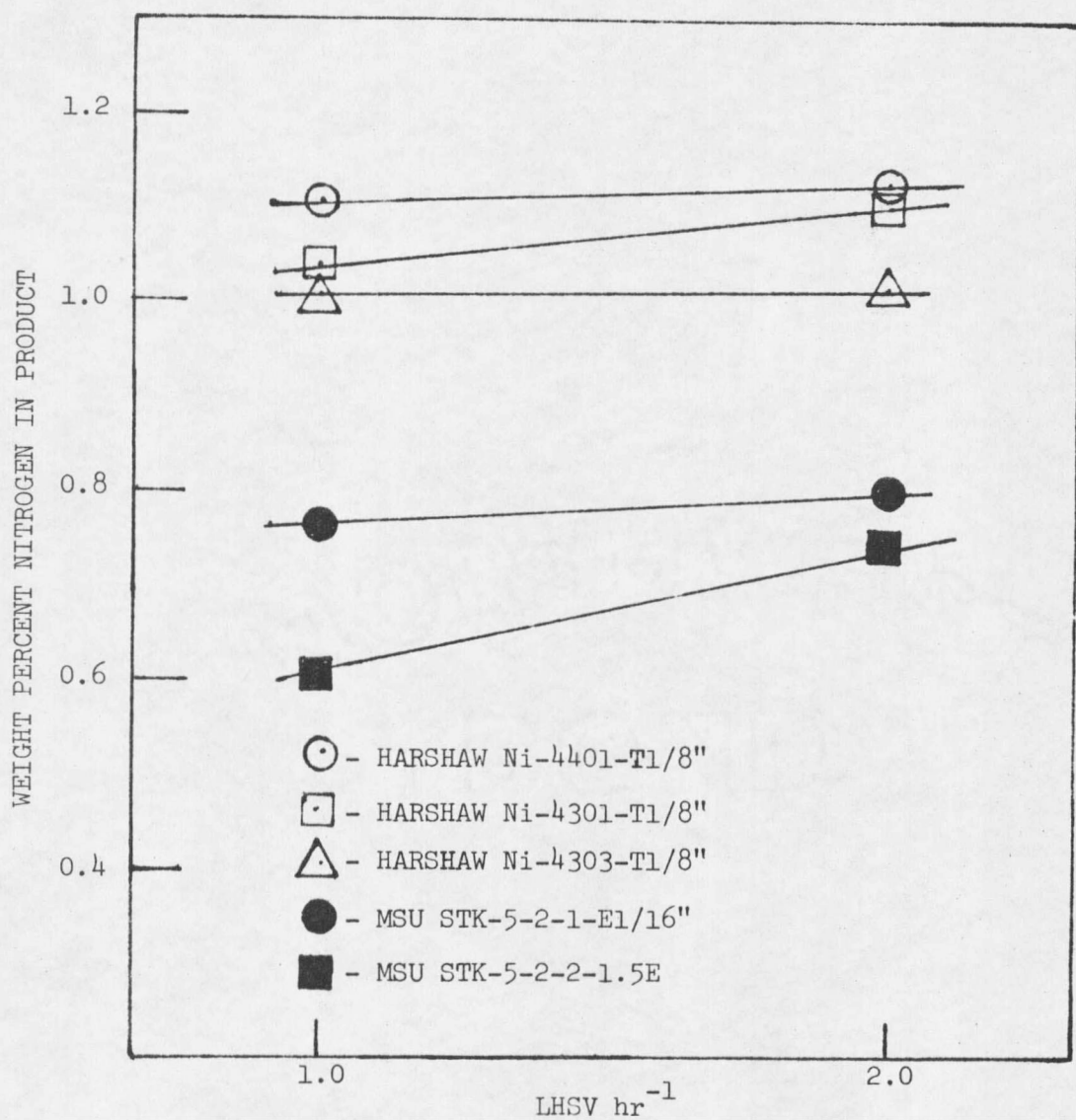


FIGURE 17. DENITROGENATION ACTIVITY OF MSU CATALYSTS vs. COMMERCIAL NICKEL TUNGSTEN CATALYSTS

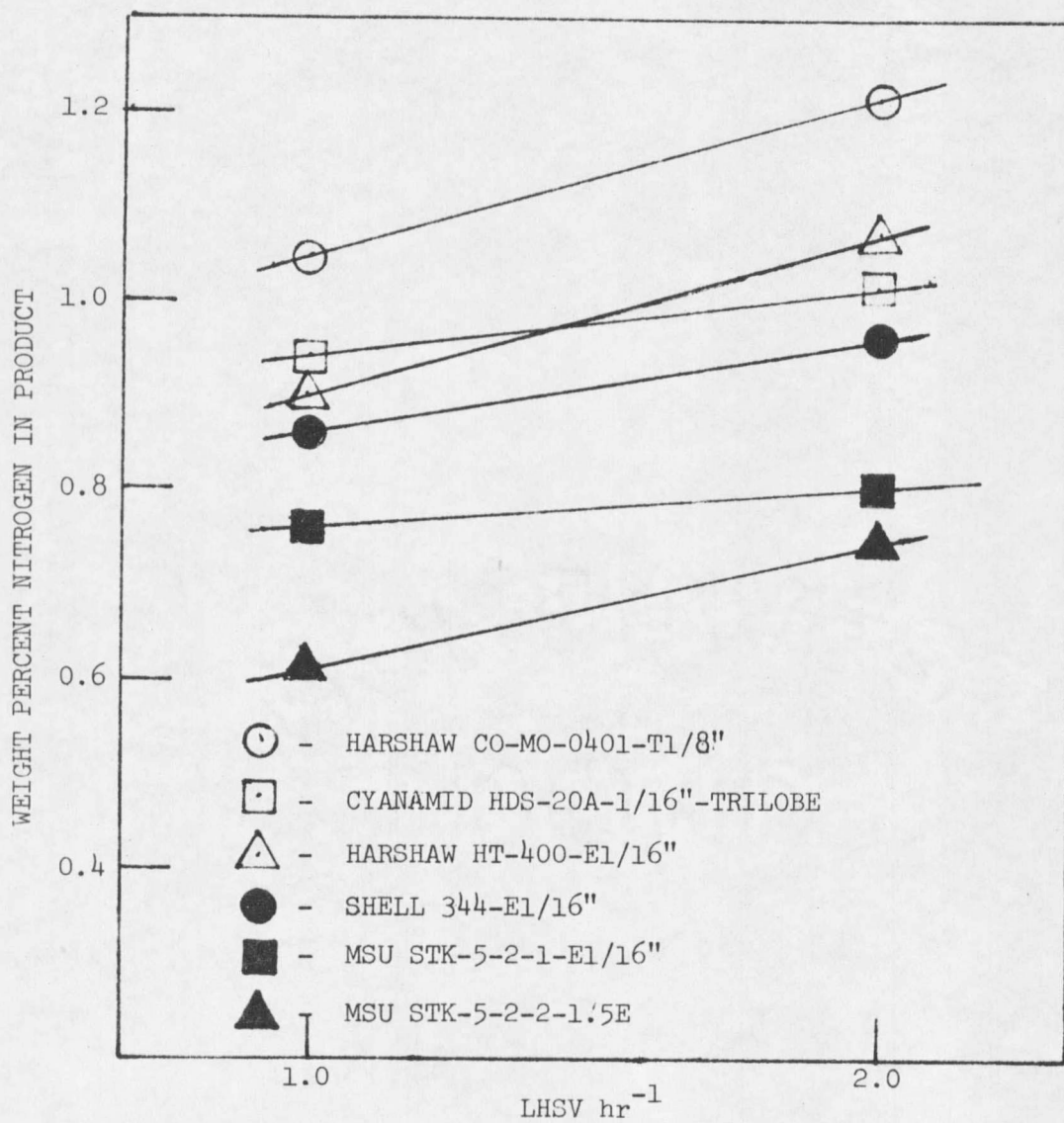


FIGURE 18. DENITROGENATION ACTIVITY OF MSU CATALYSTS vs. COMMERCIAL COBALT MOLYBDATE CATALYSTS

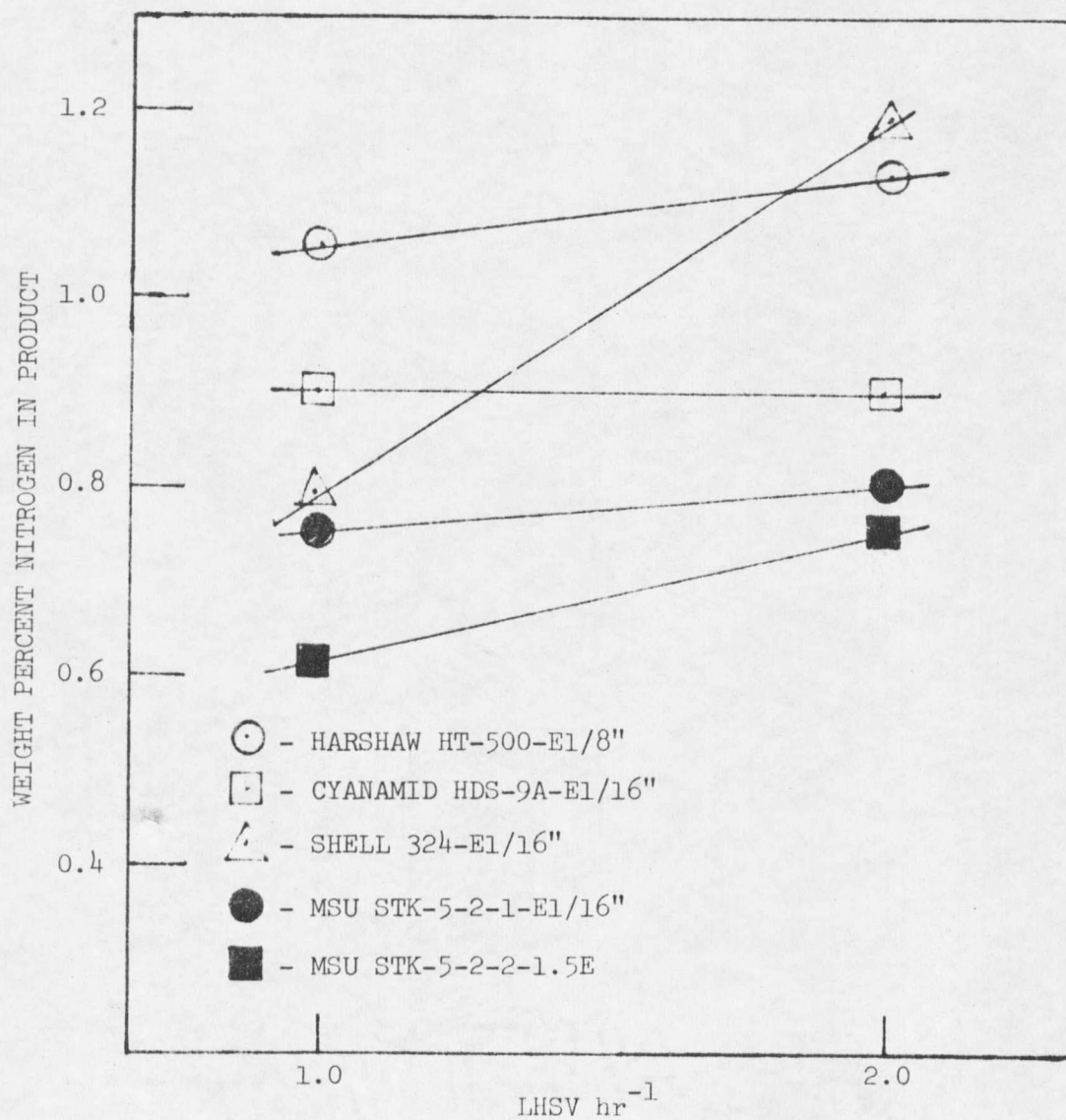


FIGURE 19. DENITROGENATION ACTIVITY OF MSU CATALYSTS vs. COMMERCIAL NICKEL MOLYBDATE CATALYSTS

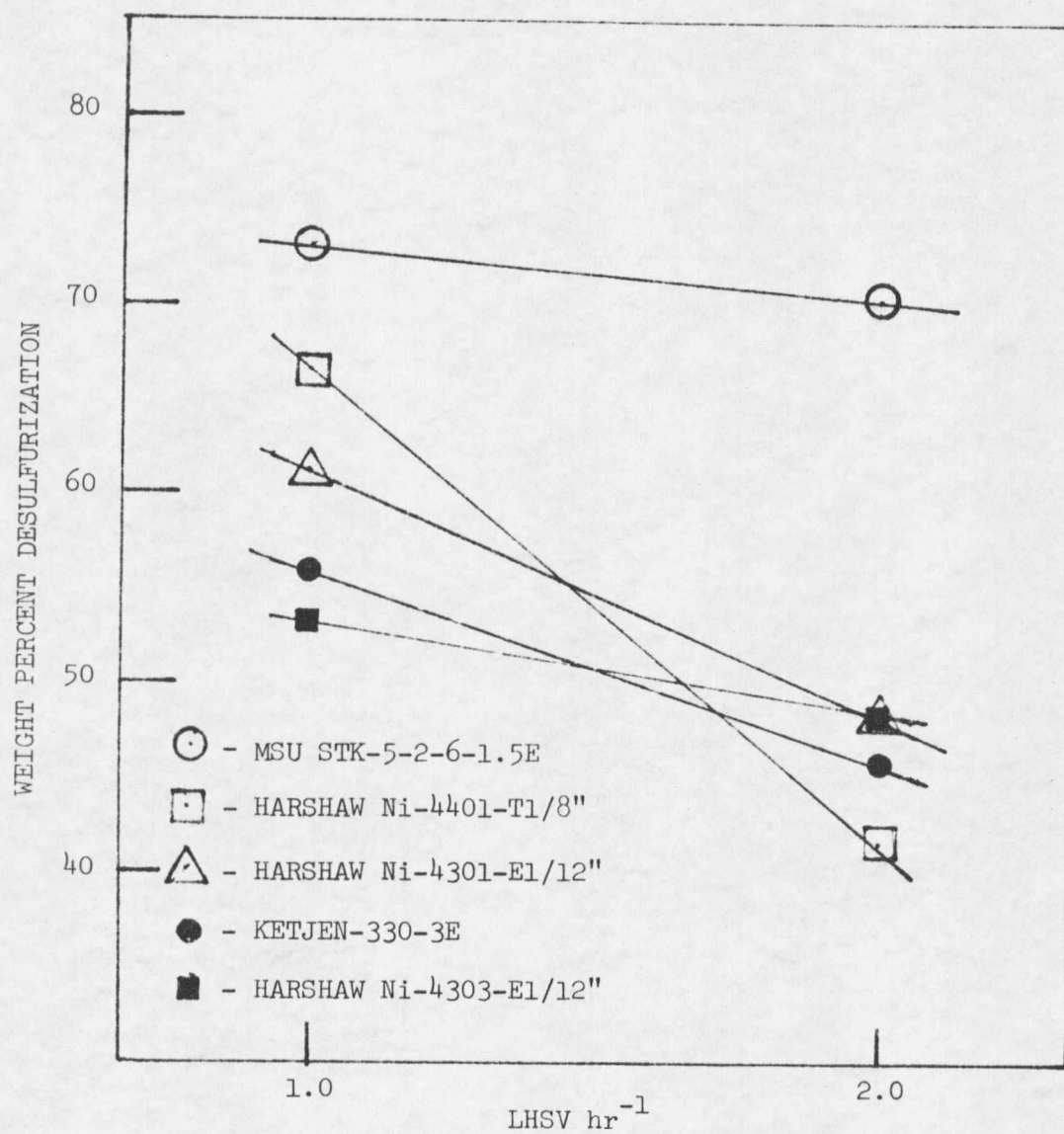


FIGURE 20. DESULFURIZATION ACTIVITY OF MSU STK-5-2-6-1.5E vs. COMMERCIAL NICKEL TUNGSTEN CATALYSTS

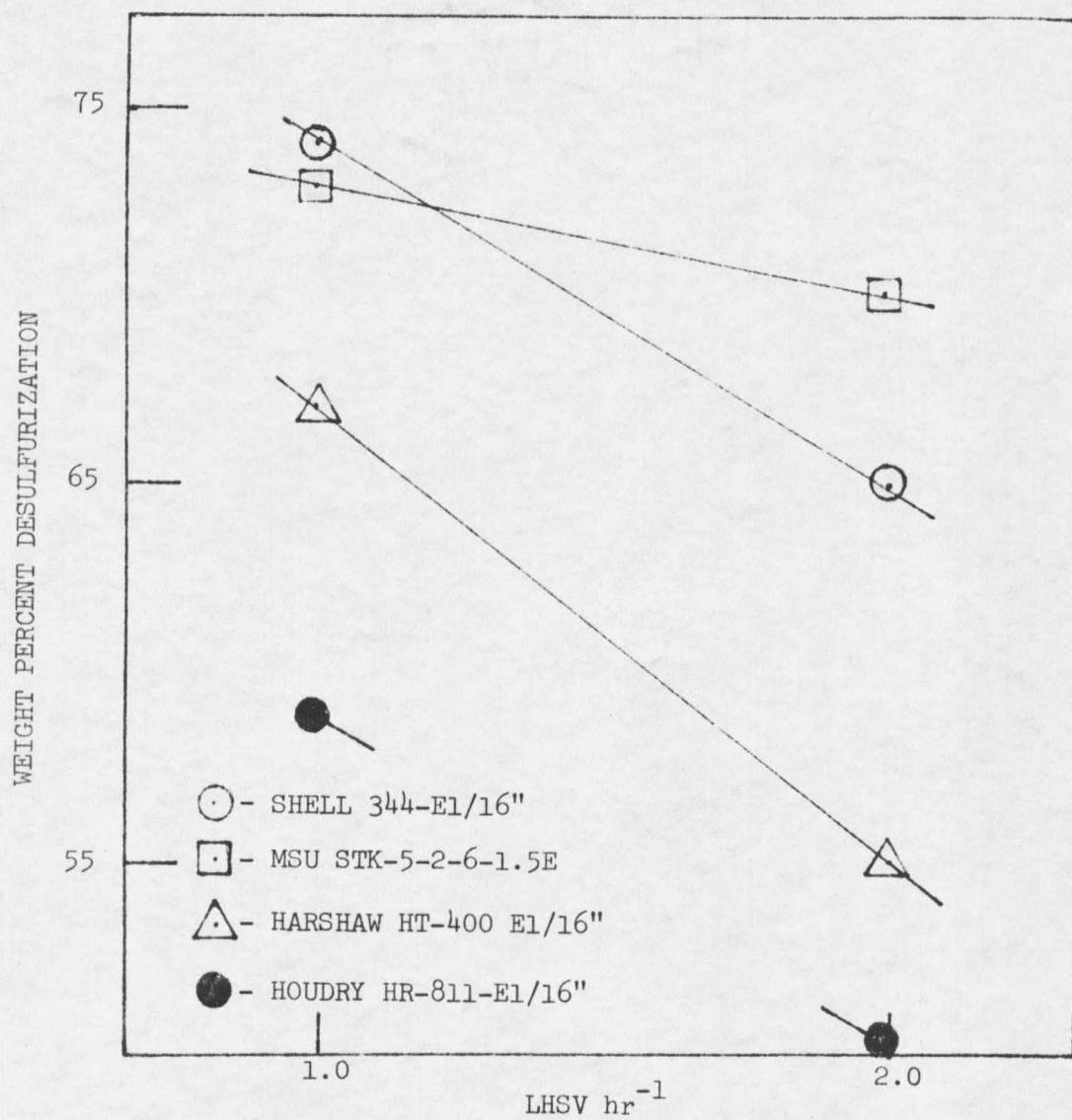


FIGURE 21. DESULFURIZATION ACTIVITY OF MSU STK-5-2-6-1.5E vs. COMMERCIAL COBALT MOLYBDATE CATALYSTS

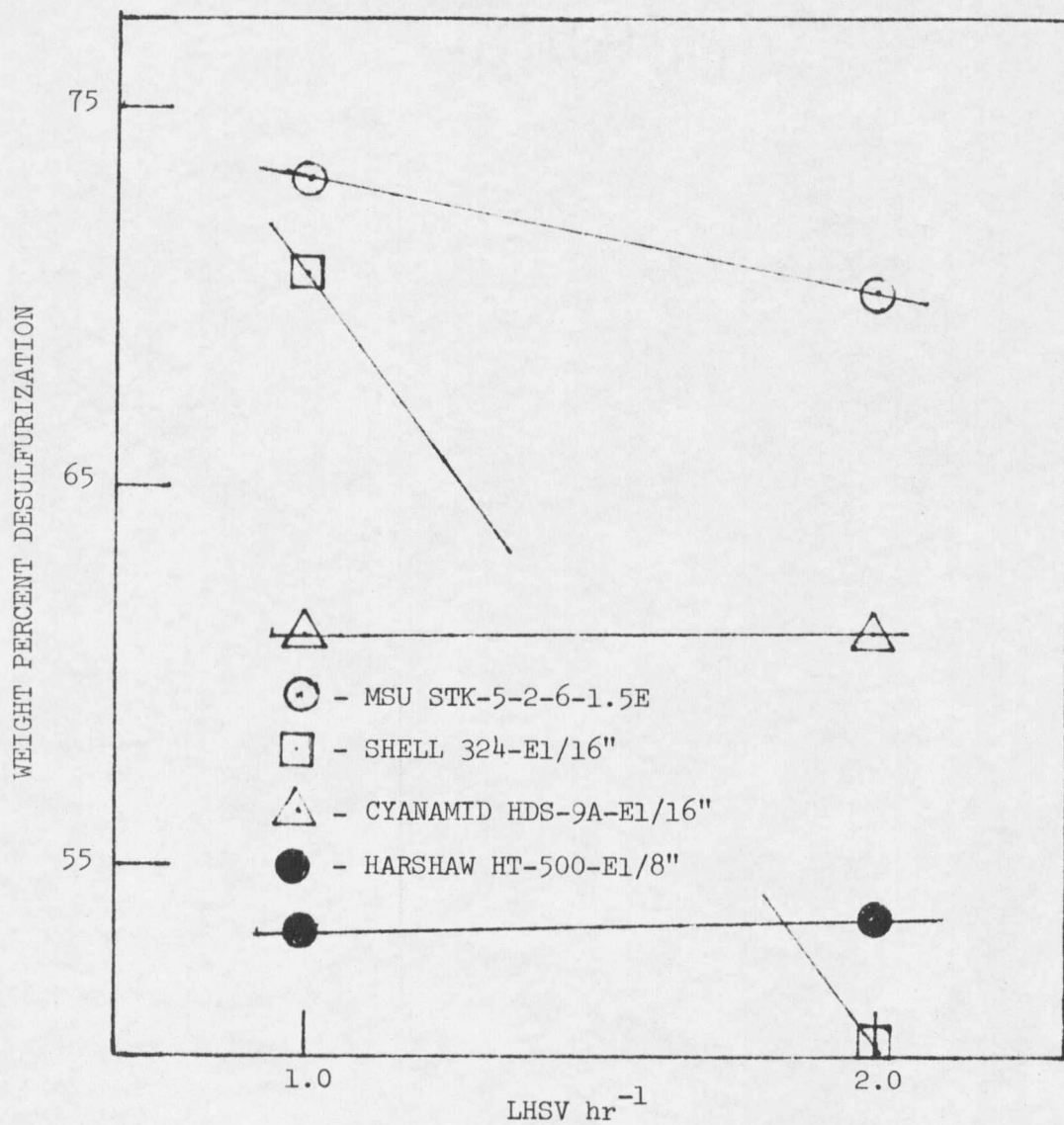


FIGURE 22. DESULFURIZATION ACTIVITY OF MSU STK-5-2-6-1.5E vs. COMMERCIAL NICKEL MOLYBDATE CATALYSTS

CONCLUSIONS

1. SRC Vacuum Flash Feed was a more suitable feedstock for trickle bed operations than trying to remix solid SRC with a solvent.
2. Pore diffusion greatly affected catalyst performance in the trickle bed reactor.
3. Film diffusion was also very important in the trickle bed reactor.
4. Increased MoO_3 concentrations favored better denitrogenation.
5. Higher concentrations of Ni-Mo improved denitrogenation.
6. Higher concentrations of Co-Mo improved denitrogenation.
7. Higher temperatures improved denitrogenation.
8. Catalyst deactivation was very marked during the first 12 hours of testing in a trickle bed reactor.
9. Higher distillate yields were obtained with higher temperatures at the expense of increased gas make and catalyst coking.
10. Harshaw HT-400 E 1/16" catalyst gave the best nitrogen removal at 450°C of all commercial catalysts tested in the trickle bed reactor.
11. Cyanamid HDS-20A 1/16" Trilobe gave the best sulfur removal at 450°C of all commercial catalysts tested in the trickle bed reactor.
12. MSU STK-5-2-2-1.5E catalyst gave the best nitrogen removal at 450°C of all catalysts tested in the trickle bed reactor.
13. MSU STK-5-2-6-1.5E catalyst gave the best sulfur removal at 450°C of all catalysts tested in the trickle bed reactor.

Recommendations for Future Work

1. Use of a longer reactor so two catalyst zones could be used. The first zone using an inexpensive cracking catalyst such as a chromium alumina to knock down metals concentrations in feedstock before they can deposit in the second hydrotreating zone.
2. Use of a 1-1/2 inch I.D. diameter reactor and a catalyst bed that is longer to improve diffusion characteristics of the reactor.
3. Start up the trickle bed reactors at lower temperatures and gradually increase to run temperature. Introduction of oil on catalyst at lower temperatures should prevent much carbon laydown.
4. Longer trickle bed reactor runs. The data from the first 12 hours of operation is affected too much by initial catalyst deactivation.
5. More metal loading studies to get better data for optimization.
6. Pore volume distribution study to determine distribution of pore sizes needed to hydrotreat syncrudes.
7. Acquisition of linear elution adsorption chromatography capabilities to better characterize products.
8. Mass balance capabilities to use in the study of process conditions.
9. Fabrication of a small microreactor or acquisition of a Berty reactor to do kinetic and mechanistic studies.

APPENDIX A

CATALYST DATA

CATALYST DATA

Catalyst	Description
Girdler T-368C-T 1/8	3% Pd on alumina
Harshaw Co-Mo-0401-T 1/8	3% CoO, 9% MoO ₃ on alumina SA = 160 m ² /gr PV = .40 cc/gr
Harshaw Ni-4303 E 1/12	6% Ni, 19% W on silica alumina SA = 228 m ² /g PV = .37 cc/g
Harshaw Ni-4301 E 1/12	6% Ni, 19% W on alumina SA = 152 m ² /g PV = .54 cc/g
Harshaw HT-100 E 1/12	3.8% NiO, 16.8% MoO ₃ on alumina SA = 190 m ² /g PV = .54cc/g
Harshaw Ni-3250 T 1/8	50% Nickel on proprietary support SA = 150 m ² /g PV = .34 cc/g
Harshaw Ni-4401 T 1/8	6% Ni, 19% W on alumina SA ~ 150 m ² /g PV ~ .5 cc/g
Harshaw Cr-0304 T 1/8	33% Cr ₂ O ₃ on silica alumina SA - 120 m ² /g PV - .26 cc/g
Harshaw Mo-1201 T 1/8	10% MoO ₃ on alumina SA - 160 m ² /g PV - .36 cc/g
Harshaw Cr-0103 T 1/8	12% Cr ₂ O ₃ on alumina SA - 63 m ² /g PV - .35 cc/g

Catalyst	Description
Harshaw Co-Mo-0603 T 1/8	3% CoO, 12% MoO ₃ on alumina SA - 166 m ² /g PV - .40 cc/g
Harshaw Ni-3210 T 3/16	35% nickel on proprietary support SA - 175 m ² /g PV - .45 cc/g
Harshaw W-0801 T 1/8	10% WO ₃ on alumina SA - 145 m ² /g PV - .36 cc/g
Harshaw Cr-0105 T 1/8	9% CR ₂ O ₃ , 1.5% K ₂ O on alumina SA - 67 m ² /g PV - .34 cc/g
Harshaw W-0101 T 1/8	10% WO ₃ on alumina SA - 75 m ² /g PV - .37 cc/g
Harshaw HT-400 E 1/16, E 1/8	3% CoO, 15% MoO ₃ on alumina SA - 220 m ² /g PV - .5 cc/g
Harshaw V-0601 T 1/8	10% V ₂ O ₅ on alumina SA - 115 m ² /g PV - .28 cc/g
Harshaw HT-500 E 1/8	3.17% NiO, 15.5 MoO ₃ on alumina SA - 210 m ² /g PV - .49 cc/g
Ketjen HC-5-1.5 E	6.5% NiO, 21% WO ₃ on alumina SA - 200 m ² /g PV - .62 cc/g
Ketjen 330-3 E	6.62% NiO, 19.8% WO ₃ , 1.2% SiO ₂ , bal. alumina SA - 193 m ² /g PV .43 cc/g

Catalyst	Description
MSU STK-6	1.5% CoO, 1.2% NiO 18.0% MoO ₃ on Norton 6176 alumina
Shell 324 E 1/16	3% NiO, 13% MoO ₃ on alumina
Shell 344-E 1/16	2.4% CoO, 9.9% MoO ₃ on alumina
MSU STK e-5-E 1/16	1.2% CoO, 0.4% NiO 18.2% MoO ₃ on Norton 6176 alumina
MSU STK-8-2 E 1/16	1.4% NiO, 9.5% MoO ₃ 11.2% N on Norton 6176
MSU STK-10-E 1/16	2.6% NiO, 18.9% MoO ₃ 0.9% Fe, 1.7% CoO on Norton 6176
MSU STK-11-E 1/16	1.2% NiO, 11% MoO ₃ 3.7% Cr on Norton 6176
MSU STK-14-E 1/16	2.3% NiO, 17.4% MoO ₃ , 1.8% Cu on Norton 6176
MSU STK-9-E 1/16	2% ZnO, 21% MoO ₃ on Norton 6176
MSU STK-12-E 1/16	2% NiO, 17.8% MoO ₃ 1.7% ZnO on Norton 6176
MSU STK-13-E 1/16	3% NiO, 11% MoO ₃ , 0.5% Fe on Norton 6176
MSU STK-8-1-E 1/16	1.4% NiO, 8.6% MoO ₃ , 11% WO ₃ on Norton 6176
Cyanamid HDS-20A Trilobe 1/16	5% CoO, 16.2% MoO ₃ , on alumina SA - 230 m ² /g PV - .52 cc/g
Cyanamid HDS-9A 1/16	3-4 NiO, 17.5-18.5% MoO ₃ on alumina

Catalyst	Description
Harshaw Ni-1601-T 1/8	3-4% each NiO, CoO, Fe ₂ O ₃ on alumina SA - 78 m ² /g PV - .28 cc/g
MSU STK-5-2-1 E 1/16	.48% NiO, .75% CoO, 23.9% MoO ₃ on Norton 6176 support
MSU STK-5-2-2-1.5 E	.26% NiO, 1.15% CoO 13.1% MoO ₃ on Ketjen- 003-1.5E support
MSU STK-5-2-3-3E	.5% NiO, 1.1% CoO, 16.4% MoO ₃ on Ketjen- 000-3E
MSU STK-5-2-5-2E	.5% NiO, .8% CoO, 14.0% MoO ₃ on Ketjen- 005-2E
MSU STK-5-2-6-1.5E	.2% NiO, 1.1% CoO, 15.5% MoO ₃ on Ketjen- 006-1.5E
MSU GRH-1-1.5E	6.1% NiO, 2.85% CoO, 19.9% WO ₃ on Ketjen- 003-1.5E
MSU GRH-2-1.5E	2.91% NiO, 2.91% CoO, 18.84% WO ₃ on Ketjen- 003-1.5E
MSU GRH-3-1.5E	6.06% NiO, 6.12% CoO 18.53% WO ₃ on Ketjen- 003-1.5E
MSU GRH-4-1.5E	3.13% NiO, 5.90% CoO, 19.02% WO ₃ on Ketjen- 003-1.5E
MSU GRH-5-1.5E	5.88% NiO, 18.00% WO ₃ on Ketjen-003-1.5E
Houdry HR-811-E 1/16	3% CoO, 15.0% MoO ₃ on alumina SA - > 300 m ² /g

Catalyst	Description
MSU 1003	1.4% NiO, 3.0% CoO, 18.0% MoO ₃ on Ketjen- 003-1.5E
MSU 2003	1.4% NiO, 1.4% CoO, 19.1% MoO ₃ on Ketjen- 003-1.5E
MSU 3003	.5% NiO, 3.6% CoO, 17.7% MoO ₃ on Ketjen-003-1.5E
MSU 4003	.5% NiO, 1.6% CoO, 17.4% MoO ₃ on Ketjen - 003-1.5E
MSU 5003	1.8% NiO, 3.1% CoO, 10.3% MoO ₃ on Ketjen-003-1.5E
MSU 6003	1.7% NiO, 1.4% CoO, 13.2% MoO ₃ on Ketjen-003-1.5E
MSU 7003	.5% NiO, 3% CoO, 11.6% MoO ₃ on Ketjen-003-1.5E
MSU 8003	.5% NiO, 1.8% CoO, 11.7% MoO ₃ on Ketjen-003-1.5E

Support Data

Support	% Al ₂ O ₃	% SiO ₂	% Na ₂ O	S ₂ A m ² /g	P V cc/g	P.D.* Å
Norton 6176	99.85	.12	.014	250	.9	152
Ketjen-003-1.5E	bal.	1.33	.01	240	.7	117
Ketjen-006-1.5E	bal.	.37	.10	200	.73	146
Ketjen-005-2E	bal.	.55	.06	150	.64	171
Ketjen-000-3E	bal.	1.5	.13	230	.64	111

*Average Pore Diameter = $40,000 \times \text{P.V.} / \text{SA}$ in Å

APPENDIX B

BATCH RUN DATA

BATCH RUN DATA

Bomb Run #1B

No catalyst
 50 gr solid 1/4-inch SRC
 150 gr Pyridine
 Initial H₂ Pressure - 1000 psig
 Temperature - 405°C
 Residence Time - 30 min.

Bomb Run #2B

No catalyst
 50 gr solid 1/4-inch SRC
 150 gr Pyridine
 Initial H₂ Pressure - 540 psig
 Temperature 400°C
 Residence Time - 30 min.

Bomb Run #3B

No catalyst
 50 gr solid 1/4-inch SRC
 100 gr SRC Light Oil
 Initial H₂ Pressure - 200 psig
 Temperature - 405°C
 Residence Time - 30 min.

Bomb Run #4B

Catalyst	H ₂ Take-Up psig	Dist Vol%	Yield Wt%	% Des	% Den
Girdler T-368C	375	74.0	67.3	2.0	13.0

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
11.8	322	42.0	344
20.2	330	50.4	349
33.6	339	62.2	367
		70.6	389
		74.0	700

Bomb Run #5 - 75 gr SRC/150 gr SRC Light Oil

Catalyst	H ₂ Take-Up psig	Dist Vol%	Yield Wt%	% Des	% Den
Harshaw Co-Mo-0401T 1/8	1700	73.2	NA	42.2	35.8

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
13.1	326	70.5	422
26.1	342	71.9	470
52.3	350	73.2	678
66.7	382		

Bomb Run #6B - 75 gr SRC/75 gr SRC Light Oil

Catalyst - Co-Mo-0401 T 1/8" Harshaw

H₂ Consumption - 700 psig

Not Analyzed - Representative sample not obtainable

Bomb Run #7B - 112 gr SRC/112 gr SRC Light Oil

Catalyst - Harshaw Co-Mo-0401 T 1/8"

H₂ Consumption - 1050 psig

Not Analyzed - Representative Sample not obtainable

Bomb Run #8B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Co-Mo-0401 T 1/8"

Temp - 415°C

Residence Time - 30 min.

H ₂ Uptake	Dist.	Yield	% Des	% Den
1560	74.1	NA	44	45.4

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.3	260	51.4	348
21.6	318	61.7	363
30.8	328	71.0	464
41.2	341	74.1	650

Bomb Run #9B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-4303 E 1/12

Temp. - 413°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield	% Des Wt%	% Den Wt%
1740	76.3	NA	46.0	0

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)
10.2	240	51.9	349
20.3	318	61.0	359
30.5	333	70.2	381
40.6	341	76.3	700

Bomb Run #10B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-4301

Temp. - 410°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1580	75.8	70.1	54.0	23.6

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)
9.3	304	51.1	349
24.7	332	61.9	365
30.9	337	71.2	450
43.3	344	75.8	680

Bomb Run #11B - 75 gr/150 gr SRC Light Oil

Catalyst - Harshaw HT-100 E 1/12

Temp. - 415°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1975	74.4	69.6	53.0	31.1

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.3	240	50.6	348
23.7	322	63.3	365
31.6	332	69.6	388
42.7	342	74.4	680

Bomb Run #12B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-3250 T 1/8

Temp. - 415°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1910	NA	NA	NA	NA

Sample bottle broke

Rerun Bomb #19

Bomb Run #13B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-4401 E 1/10

Temp. - 420°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1230	75.3	69.0	44.0	29.7

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
9.4	285	56.5	352
20.7	325	64.0	364
37.6	340	69.7	384
47.1	345	75.3	640

Bomb Run #14B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw CR-0304 T 1/8

Temp. - 415°C

Residence Time - 30 min

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
350	75.6	44.7	0	19.0

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
7.9	317	47.3	347	74.1	568
23.6	333	66.2	371	75.6	610
34.7	339	70.9	389		

Bomb Run #15B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Mo-1201 T 1/8

Temp. - 420°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1225	74.9	69.6	10	1

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)
11.7	280	53.3	351
25.0	329	61.6	360
33.3	337	69.9	389
45.0	345	74.9	700

Bomb Run #16B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw CR-0103 T 1/8

Temp. - 420°C

Residence Time - 30 min.

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H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
350	73.1	67.9	0	2

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
8.4	349	53.8	356
20.2	332	62.2	367
33.6	341	70.6	408
42.0	347	73.1	700

Bomb Run #17B - 75 gr SRC/150 gr SRC Light Oil

No catalyst

Temp. - 420°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
310	71.2	66.8	NA	9.9

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.8	323	51.1	354
25.6	335	60.3	367
36.5	341	65.7	400
42.0	345	71.2	700

Bomb Run #18B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Co-Mo-0603 T 1/8

Temp. - 415°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1760	78.0	69.9	0	36.0

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.0	221	54.2	349
20.3	319	62.7	358
33.9	332	71.2	377
45.8	342	78.0	700

Bomb Run #19B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-3250 T 1/8

Temp. - 418°C

Residence Time - 30 min.

<u>H₂ Uptake</u>	<u>Dist.</u>	<u>Yield</u>	<u>% Des</u>	<u>% Den</u>
<u>psig</u>	<u>Vol%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
1700	76.6	69.6	0	12.0

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.8	310	63.8	363
25.5	330	75.3	420
38.3	343	76.6	700
51.1	351		

Bomb Run #20B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw Ni-3210 T 3/16

Temp. - 410°C

Residence Time - 1 hour

<u>H₂ Uptake</u>	<u>Dist.</u>	<u>Yield</u>	<u>% Des</u>	<u>% Den</u>
<u>psig</u>	<u>Vol%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
525	73.8	NA	0	8

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
9.0	325	54.0	351
21.6	333	63.0	365
30.6	338	69.3	400
45.0	347	73.8	700

Bomb Run #21B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw W-0801 T 1/8

Temp. - 413°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
580	74.6	67.8	0	5

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
11.2	320	56.0	354
22.4	334	67.2	378
33.6	340	71.8	470
46.6	347	74.6	700

Bomb Run #22B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw CR-0105 T 1/8

Temp. - 410°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
450	76.7	70.5	0	0

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.9	328	59.7	357
24.2	334	69.4	372
35.5	341	72.6	395
48.4	349	76.7	700

Bomb Run #23B - 75 gr SRC/150 gr SRC Light Oil

Catalyst Harshaw W-0101 T 1/8

Temp. - 413°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
350	73.4	68.7	0	21

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.5	325	59.1	362
21.5	335	66.2	379
35.8	342	71.6	525
50.1	352	73.4	700

Bomb Run #24B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw HT-400 E 1/16

Temp. - 415°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1900	79.5	72.1	57	16

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.7	210	54.1	349
23.7	324	64.3	360
33.8	331	76.1	440
42.3	338	79.5	700

Bomb Run #25B - 75 gr SRC/150 gr SRC Light Oil

Catalyst - Harshaw V-0601 T 1/8

Temp. - 410°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
500	74.5	69.2	0	15.1

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
9.6	326	53.5	354
22.9	334	63.0	365
32.5	340	71.6	520
40.1	346	74.5	700

Bomb Run #26B - 200 gr SRC Vacuum Flash Feed

Catalyst - Harshaw HT-400 E 1/16

Temp. - 420°C

Residence Time - 1 hour

<u>H₂ Uptake</u>	<u>Dist.</u>	<u>Yield</u>	<u>% Des</u>	<u>% Den</u>
<u>psig</u>	<u>Vol%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
1500	68.4	65.6	34.8	25.4

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.0	425	50.3	624
24.1	512	56.3	653
34.2	558	58.4	667
40.2	578	68.4	700

Bomb Run #27B - 200 gr SRC Vacuum Flash Feed

Catalyst - Harshaw HT-500 E 1/8

Temp. - 420°C

Residence Time - 1 hour

<u>H₂ Uptake</u>	<u>Dist.</u>	<u>Yield</u>	<u>% Des</u>	<u>% Den</u>
<u>psig</u>	<u>Vol%</u>	<u>Wt%</u>	<u>Wt%</u>	<u>Wt%</u>
1675	64.5	61.6	33.2	16.9

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
7.8	426	50.8	627
19.6	492	56.7	660
29.3	533	58.7	670
39.1	573	64.5	700

Bomb Run #28B - 200 gr SRC Vacuum Flash Feed

Catalyst - Ketjen HC-5-1.5E

Temp. - 415°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1070	61.9	57.7	5.8	27.0

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)
10.3	453	49.6	651
20.6	510	53.7	674
31.0	558	55.8	692
41.3	605	61.9	700

Bomb Run #29B - 200 gr SRC Vacuum Flash Feed

Catalyst - Ketjen-300-3E

Temp. - 420°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1390	66.2	61.2	37.3	12.3

ASTM Distillation

Vol %	Temp. (°F)	Vol %	Temp. (°F)
12.5	451	52.4	631
20.0	490	54.9	641
30.0	537	57.4	672
40.0	581	66.2	700

Bomb Run #30B - 200 gr SRC Vacuum Flash Feed

Catalyst - Harshaw Co-Mo-0401 T 1/8

Temp. - 420°C

Residence Time - 30 min.

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1520	67.9	61.4	36.0	29.5

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
13.6	466	48.9	624
21.7	495	54.3	651
29.9	530	57.0	665
43.5	600	67.9	700

Bomb Run #31B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-6 E 1/16

Temp. - 415°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1850	65.1	64.4	17.7	1.5

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
12.5	441	47.6	604
20.0	494	55.1	638
27.5	517	60.1	670
40.1	573	65.1	700

Bomb Run #32B - 200 gr SRC Vacuum Flash Feed

Catalyst - Shell 324 E 1/16

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1840	75.7	72.4	75.3	27.5

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.5	444	52.6	617
21.0	497	63.1	677
31.5	537	75.7	700
42.0	575		

Bomb Run #33B - 200 gr SRC Vacuum Flash Feed

Catalyst - Shell 344 E 1/16

Temp. - 420°C

Residence Time - 1 hour

<u>H₂ Uptake</u> <u>psig</u>	<u>Dist.</u> <u>Vol%</u>	<u>Yield</u> <u>Wt%</u>	<u>% Des</u> <u>Wt%</u>	<u>% Den</u> <u>Wt%</u>
1600	76.0	75.2	52.5	18.8

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
8.6	430	46.7	610
17.2	481	51.8	632
25.9	524	60.5	664
34.6	567	76.0	700

Bomb Run #34B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-5 E 1/16

Temp. - 415°C

Residence Time - 1 hour

<u>H₂ Uptake</u> <u>psig</u>	<u>Dist.</u> <u>Vol%</u>	<u>Yield</u> <u>Wt%</u>	<u>% Des</u> <u>Wt%</u>	<u>% Den</u> <u>Wt%</u>
1440	73.7	75.0	44.1	20.2

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.2	446	51.2	622
20.5	508	61.4	680
32.8	557	67.5	686
40.9	588	73.7	700

Bomb Run #35B - 200 gr SRC Vacuum Flash Feed

Catalyst - Harshaw Ni-4401 T 1/8

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1340	65.9	66.2	35.7	20.4

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
16.5	486	43.2	610
20.6	510	51.4	652
30.9	558	65.9	700

Bomb Run #36B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-8-2 E 1/16

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1630	77.1	77.4	47.7	21.5

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
8.6	427	42.8	587
17.1	468	51.4	632
25.7	518	59.9	658
34.2	562	77.1	694

Bomb Run #37B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-10 E 1/16

Temp. - 417°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	97 Yield Wt%	% Des Wt%	% Den Wt%
1280	69.1	68.4	28.3	12.0

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.3	440	53.6	654
22.7	512	69.1	700
31.0	555		
41.3	595		

Bomb Run #38B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-11 E 1/16

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1475	69.5	72.1	38.9	12.0

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.2	459	47.0	628
22.5	518	57.1	644
30.6	554	69.5	700

Bomb Run #39B - 200 gr SRC Vacuum Flash Feed

Catalyst - Harshaw 4303 E 1/12

Temp. - 425°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1415	66.1	67.0	42.1	19.4

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.0	448	40.0	598
20.0	520	50.0	638
34.0	574	66.1	700

Bomb Run #40B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-14-E 1/16

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1470	76.2	73.8	50.8	10.2

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.7	460	53.6	649
21.4	570	64.4	675
32.2	568	76.2	700
42.9	603		

Bomb Run #41B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-9-E 1/16

Temp. - 425°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1475	64.6	65.6	8.7	14.9

ASTM Distillation

<u>Vol %</u>	<u>Temp(°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.4	462	52.1	652
20.8	518	64.6	700
31.3	560		
41.7	606		

Bomb Run #42B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-12-E 1/16

Temp. - 430°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1400	61.7	68.5	46.7	16.1

ASTM Distillation

<u>Vol %</u>	<u>Temp. (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
9.9	447		
19.9	498	49.8	630
33.9	558	59.8	684
39.8	586	61.7	700

Bomb Run #43B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-13-E 1/16

Temp. - 420°C

Residence Time - 1 hour

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1500	66.2	66.0	21.0	21.7

ASTM Distillation

<u>Vol %</u>	<u>Temp (°F)</u>	<u>Vol %</u>	<u>Temp. (°F)</u>
10.2	442	40.8	596
20.4	517	57.0	641
34.6	561	66.2	700

Bomb Run #44B - 200 gr SRC Vacuum Flash Feed

Catalyst - MSU STK-8-1-E 1/16

Temp. - 425°C

Residence Time - 1 hour

100

H ₂ Uptake psig	Dist. Vol%	Yield Wt%	% Des Wt%	% Den Wt%
1560	70.5	65.7	15.7	29.4

ASTM Distillation

<u>Vol %</u>	<u>Temp.(°F)</u>	<u>Vol %</u>	<u>Temp.(°F)</u>
10.8	456	43.4	594
21.7	508	55.4	652
32.6	552	76.5	700

Notes: Batch runs 4B - 25B

Feedstock % S = .50 wt%
Feedstock % N = 1.06 wt%

Feed ASTM Distillation for Runs 4B - 25B
corresponds to Blank Run #17

Batch Runs 26B - 44B

Feedstock % S = .644 wt%
Feedstock % N = 1.20 wt%

Feed ASTM Distillation for Runs 26B-44B

<u>Vol %</u>	<u>Temp.(°F)</u>	<u>Vol %</u>	<u>Temp.(°F)</u>
IBP	410	44.9	641
9.0	480	50.3	684
21.5	536	52.1	694
30.5	578		
39.5	615		

wt% recovered = 58.6%

- All Batch runs contained 25 ml of presulfided catalyst
- Initial Hydrogen Pressure = 2500 ± 100 psig
- % DeS - wt% desulfurization
- % DeN - wt% denitrogenation

APPENDIX C

CONTINUOUS TRICKLE BED CATALYST TESTS

CONTINUOUS TRICKLE BED CATALYST TESTS

Run C-1

Catalyst - Shell 324 E 1/16.

Temp - 420°C

Pressure - 1000 psig

Sample #	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt %	% DeS	% DeN
C-1-1	1.0	10,000	76.9	75.7	70.5	38.8
C-1-2	1.5	10,000	74.2	74.2	61.8	15.4
C-1-3	2.0	10,000	68.9	65.6	49.5	8.5

ASTM Distillations

C-1-1		C-1-2		C-1-3	
Vol %	Temp. (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	255	IBP	245	IBP	320
10.4	407	8.3	450	10.4	460
20.8	468	16.7	492	20.9	510
31.2	514	33.3	568	31.3	561
41.6	555	41.7	595	39.7	589
52.0	588	50.0	632	48.0	627
60.2	628	58.3	660	60.6	680
68.6	673	66.7	692	68.9	700
76.9	700	71.7	694		

Run C-2

Catalyst - Shell 324 E 1/16

Sample #	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt %	% DeS	% DeN
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Catalyst Test - reactor failure - involuntary shut down

Run C-3

Catalyst - Harshaw Co-Mo-0401 T 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-3-1	1.0	10,000	76.4	76.4	54.2	19.2
C-3-2	1.5	10,000	72.8	59.6	50.9	12.7
C-3-3	2.0	10,000	74.5	NA	38.8	3.8

ASTM Distillations

C-3-1		C-3-2		C-3-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	223	IBP	270	IBP	180
8.3	426	8.5	435	8.7	449
16.6	463	16.9	478	17.3	496
29.1	540	25.4	531	27.7	545
34.1	557	35.6	568	34.7	567
42.4	579	42.4	592	43.3	600
49.8	603	50.8	623	52.0	633
58.2	642	59.3	664	60.6	667
66.5	680	67.8	698	67.6	688
76.4	700	72.8	700	74.5	700

Run C-4

Catalyst - Harshaw HT-400 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-4-1	1.0	10,000	75.6	76.6	67.1	33.8
C-4-2	1.5	10,000	78.1	75.0	53.9	32.3
C-4-3	2.0	10,000	73.8	74.0	55.3	26.2

ASTM Distillations

C-4-1		C-4-2		C-4-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	221	IBP	220	IBP	260
8.4	394	8.5	426	8.2	423
16.8	468	17.0	481	16.4	484
26.0	507	25.5	519	25.4	524
33.6	541	34.0	548	32.8	543
42.0	567	42.5	575	41.0	577
50.4	597	51.0	603	49.2	616
58.8	623	59.4	622	57.4	654
67.2	674	68.0	661	68.8	685
75.6	700	781	700	73.8	700

Run C-5

Catalyst - Harshaw HT-400 E 1/8

Temp - 450°C

Pressure - 100 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield		% DeS	% DeN
			Vol %	Wt%		
C-5-1	1.0	10,000	77.2	76.8	62.3	18.8
C-5-2	1.5	10,000	79.2	78.2	56.4	20.5
C-5-3	2.0	10,000	67.6	66.6	34.3	10.1

ASTM Distillations

C-5-1		C-5-2		C-5-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	246	IBP	328	IBP	343
8.6	431	8.5	429	8.2	463
17.2	453	16.9	486	16.5	506
25.8	503	25.4	524	24.7	544
34.3	554	33.8	55.9	32.9	578
42.9	586	52.4	628	42.8	616
60.1	649	59.2	649	49.4	641
68.7	680	72.8	690	57.7	679
77.2	700	79.2	700	67.6	700

Run C-6

Catalyst - Harshaw HT-500-E 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-6-1	1.0	10,000	78.1	79.3	53.1	18.5
C-6-2	1.5	10,000	71.7	71.1	58.8	20.0
C-6-3	2.0	10.00	75.0	72.9	53.6	53.6

ASTM Distillations

C-6-1		C-6-2		C-6-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	242	IBP	252	IBP	367
8.3	434	8.3	434	8.7	456
16.6	479	16.7	485	18.3	504
24.9	524	25.0	525	26.2	541
34.0	552	33.3	560	34.9	572
41.5	583	41.7	587	43.6	608
49.8	610	50.0	616	52.4	641
58.1	638	58.4	642	61.1	670
66.4	680	71.7	700	75.0	694
78.1	700				

Run C-7

Catalyst - Shell 344 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-7-1	1.0	10,000	74.6	75.2	73.9	31.1
C-7-2	1.5	10,000	76.7	79.5	61.2	37.0
C-7-3	2.0	10,000	75.2	75.9	65.2	17.7

ASTM Distillations

C-7-1		C-7-2		C-7-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	227	IBP	222	IBP	184
8.3	390	8.4	379	8.2	430
16.6	461	16.8	453	16.4	483
24.9	498	25.2	486	24.5	515
33.2	536	33.6	526	32.7	548
41.4	565	41.9	560	45.8	598
49.7	594	50.3	592	49.0	612
58.0	626	58.7	619	57.2	641
66.3	665	67.1	654	65.4	673
74.6	700	76.7	700	75.9	692

Run C-8

Catalyst - Harshaw Ni-4401 T 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-8-1	1.0	10,000	73.4	75.8	66.3	15.2
C-8-2	1.5	10,000	74.2	73.5	38.2	17.8
C-8-3	2.0	10,000	72.2	67.9	41.5	13.5

ASTM Distillations

C-8-1		C-8-2		C-8-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	225	IBP	204	IBP	418
8.3	441	8.8	430	13.9	493
16.7	488	17.5	484	29.1	555
25.0	524	26.3	520	41.6	609
33.4	563	35.1	555	55.5	654
41.7	594	43.8	596	66.6	670
50.0	626	52.6	630	72.2	700
58.4	655	61.4	660		
66.7	684	74.2	700		
73.4	700				

Run C-9

Catalyst - Cyanamid HDS-20A Trilobe 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-9-1	1.0	10,000	83.9	80.2	62.5	18.4
C-9-2	1.5	10,000	81.4	80.5	70.8	16.7
C-9-3	2.0	10,000	77.3	76.0	69.4	11.0

ASTM Distillations

C-9-1		C-9-2		C-9-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	336	IBP	370	IBP	368
12.7	447	12.3	440	12.5	447
25.4	488	24.7	487	24.9	492
38.1	524	37.0	539	47.4	577
50.8	576	50.6	585	49.8	585
63.6	623	61.7	630	62.3	636
76.3	674	74.0	690	77.3	674
83.9	700	81.4	696		

Run C-10

Catalyst - Cyanamid HDS-9A 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-10-1	1.0	10,000	81.6	77.0	61.1	21.1
C-10-2	1.5	10,000	81.2	82.1	62.5	26.3
C-10-3	2.0	10,000	80.5	77.8	61.1	21.1

ASTM Distillations

C-10-1		C-10-2		C-10-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	392	IBP	360	IBP	372
12.8	447	15.2	439	12.6	445
25.5	489	25.4	479	28.9	500
38.3	535	38.1	518	37.7	525
51.0	579	50.8	560	50.3	578
63.8	623	63.5	610	62.9	631
81.6	700	81.2	666	80.5	700

Run C-11

Catalyst - Harshaw Co-Mo-0603 T 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-11-1	1.0	10,000	77.7	79.0	54.2	13.2
C-11-2	1.5	10,000	80.9	79.1	45.8	15.4
C-11-3	2.0	10,000	75.5	70.7	54.9	4.4

ASTM Distillations

C-11-1		C-11-2		C-11-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	280	IBP	268	IBP	294
13.0	422	12.4	424	13.0	430
25.9	472	24.9	467	26.0	482
46.6	558	37.4	517	39.0	533
59.6	616	49.8	564	52.0	589
64.8	638	62.2	612	65.0	643
77.7	700	74.7	678	75.5	700
		80.9	700		

Run C-12

Catalyst - Harshaw 4301-E 1/12

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield		% DeS	% DeN
			Vol %	Wt%		
C-12-1	1.0	10,000	74.6	76.5	61.1	9.6
C-12-2	1.5	10,000	80.1	76.2	51.4	10.5
C-12-3	2.0	10,000	72.5	71.3	48.6	2.2

ASTM Distillations

C-12-1		C-12-2		C-12-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	217	IBP	328	IBP	368
12.0	430	12.9	446	13.2	444
26.5	491	25.8	493	26.4	497
36.1	530	38.8	546	39.6	556
48.2	584	51.7	595	52.7	610
60.2	640	64.6	648	65.9	680
74.6	700	80.1	686	72.5	700

Run C-13

Catalyst - Harshaw Ni-4303 E 1/12

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield		% DeS	% DeN
			Vol %	Wt%		
C-13-1	1.0	10,000	81.8	79.3	53.5	11.4
C-13-2	1.5	10,000	79.8	78.0	55.6	15.8
C-13-3	2.0	10,000	76.6	70.8	48.6	11.4

ASTM Distillations

C-13-1		C-13-2		C-13-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	281	IBP	300	IBP	360
10.2	424	10.2	423	10.5	439
20.4	458	20.5	458	21.0	473
30.7	498	30.7	495	31.5	516
40.9	537	40.9	538	42.0	556
51.1	580	51.2	587	52.5	602
61.3	619	61.4	623	63.0	646
71.6	670	71.7	680	76.6	700
81.8	700	79.8	700		

Run C-14

Catalyst - Harshaw HT-400 E 1/16

Temp - 400°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-14-1*	2.0	10,000	69.7	66.4	54.9	20.2
C-14-2*	2.0	10,000	71.7	73.0	43.1	1.8
C-14-3*	2.0	10,000	72.8	73.1	47.2	-0-
C-14-4*	2.0	10,000	68.4	68.9	41.7	-0-

* - Samples at 3 hour intervals

ASTM Distillations

C-14-1		C-14-2		C-14-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	400	IBP	385	IBP	391
10.7	457	10.2	450	12.6	436
21.4	490	20.5	497	27.6	516
34.3	548	31.8	542	37.6	560
42.9	582	41.0	586	50.2	610
53.6	625	51.2	627	62.8	662
64.3	688	61.4	676	72.8	684
69.7	700	71.7	696		

C-14-4

Vol %	Temp. (°F)
IBP	389
12.7	460
25.3	508
38.0	570
52.0	625
68.4	700

Run C-15

Catalyst - Harshaw HT-100 E 1/12

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-15-1	1.0	10,000	78.7	78.1	56.2	17.1
C-15-2	1.5	10,000	78.6	77.7	51.4	21.5
C-15-3	2.0	10,000	72.0	71.1	54.2	6.0

ASTM Distillations

C-15-1		C-15-2		C-15-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	330	IBP	321	IBP	383
10.1	427	10.2	421	10.2	440
20.2	466	20.4	462	20.3	479
32.3	510	31.6	504	30.4	519
40.4	541	59.2	613	40.6	562
50.4	581	71.4	678	50.7	605
60.5	619	78.6	700	60.9	658
70.6	665			72.0	700
78.7	700				

Run C-16

Catalyst - Harshaw Ni-3250 T 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-16-1	1.0	10,000	73.5	74.4	21.5	18.0
C-16-2	1.5	10,000	73.8	72.6	16.0	14.5
C-16-3	2.0	10,000	68.6	66.7	18.1	4.8

ASTM Distillations

C-16-1		C-16-2		C-16-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	390	IBP	--	IBP	414
10.2	438	5	422	10.2	455
20.4	472	10.1	444	20.5	488
30.6	513	20.2	478	35.8	568
40.8	552	30.3	518	43.0	590
51.0	599	41.4	563	51.2	626
64.3	661	52.6	606	61.4	690
73.5	700	60.6	641	68.6	700
		73.8	700		

Run C-17

Catalyst - Harshaw Ni-1601 T 1/8

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-17-1	1.0	10,000	74.9	77.3	20.1	30.3
C-17-2	1.5	10,000	80.7	78.0	27.8	32.9
C-17-3	2.0	10,000	76.1	74.6	4.2	24.1

ASTM Distillations

C-17-1		C-17-2		C-17-3	
Vol %	Temp. (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	--	IBP	403	IBP	378
4	453	10.3	440	10.3	446
12.4	453	20.7	470	20.6	487
20.2	482	31.0	514	30.9	527
30.4	528	41.4	540	41.2	572
40.5	564	51.7	580	53.5	626
50.6	608	62.0	620	61.7	659
60.7	652	72.4	679	76.1	676
74.9	697	80.7	700		

Run C-18

Catalyst - MSU STK-2-1 E1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-18-1	1.0	10,000	77.2	77.3	47.9	32.9
C-18-2	1.5	10,000	76.7	77.7	47.9	39.5
C-18-3	2.0	10,000	75.6	77.0	39.6	29.8

ASTM Distillations

C-18-1		C-18-2		C-18-3	
Vol %	Temp. (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	350	IBP	287	IBP	306
10.0	418	10.2	418	9.9	422
20.1	457	20.4	459	19.9	467
30.1	498	30.7	500	31.8	522
40.1	541	40.9	545	39.8	554
50.2	583	51.1	581	50.7	602
60.2	621	61.4	626	59.7	643
70.2	676	71.6	686	69.6	692
77.2	700	76.7	700	75.6	700

Run C-19

Catalyst - MSU STK-5-2-2 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-19-1	1.0	10,000	86.4	85.4	56.2	46.5
C-19-2	1.5	10,000	88.6	89.6	65.3	54.8
C-19-3	2.0	10,000	78.9	79.2	53.5	35.1

ASTM Distillations

C-19-1		C-19-2		C-19-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	262	IBP	218	IBP	329
10.3	394	10.1	398	8.1	425
15.4	425	20.1	454	20.2	462
20.6	450	30.2	487	30.3	509
41.1	523	44.3	541	42.5	562
51.4	566	50.4	564	50.6	597
60.7	600	61.4	600	60.7	638
61.7	607	70.5	638	78.9	700
72.0	649	88.6	700		
86.4	685				

Run C-20

Catalyst - MSU STK-2-3-E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-20-1	1.0	10,000	79.9	77.8	58.3	32.0
C-20-2	1.5	10,000	67.7	65.7	54.9	36.8
C-20-3	2.0	10,000	77.1	76.9	52.1	30.7

ASTM Distillations

C-20-1		C-20-2		C-20-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	300	IBP	308	IBP	268
10.2	425	10.1	425	9.1	425
20.5	465	22.2	469	22.3	478
36.9	526	30.3	500	30.4	511
41.0	544	42.4	557	40.6	555
51.2	580	50.5	590	51.7	600
61.4	623	53.6	600	60.9	639
71.7	666	60.6	634	77.1	686
79.9	670	67.7	700		

Run C-21

Catalyst - MSU STK-5-2-5

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-21-1	1.0	10,000	79.5	76.1	64.6	34.2
C-21-2	1.5	10,000	82.2	81.6	61.1	37.7
C-21-3	2.0	10,000	78.0	77.2	48.6	30.3

ASTM Distillations

C-21-1		C-21-2		C-21-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	308	IBP	234	IBP	340
10.2	423	10.2	425	8.2	425
20.4	463	20.4	468	20.4	476
30.6	500	30.6	505	30.6	513
40.8	541	40.8	548	40.8	549
51.0	584	51.0	588	54.9	600
61.2	620	61.2	626	61.2	612
71.4	674	71.4	671	78.0	700
79.5	700	81.6	700		

Run C-22

Catalyst - MSU STK-5-2-6 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-22-1	1.0	10,000	85.4	83.3	72.9	36.0
C-22-2	1.5	10,000	83.1	82.6	74.3	39.0
C-22-3	2.0	10,000	81.4	79.1	70.1	31.1

ASTM Distillations

C-22-1		C-22-2		C-22-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	246	IBP	262	IBP	294
10.1	397	10.2	423	10.1	425
16.0	425	20.4	469	20.6	459
20.3	449	30.7	506	30.9	501
30.4	483	40.9	541	41.2	540
40.6	522	51.2	577	51.5	581
50.7	562	58.3	600	57.3	600
60.9	602	61.4	615	61.8	619
71.0	629	71.6	661	72.1	648
85.4	700	83.1	700	76.5	658
				81.4	700

Run C-23

Catalyst - MSU GRH-1-E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-23-1	1.0	10,000	87.0	84.8	72.2	18.2
C-23-2	1.5	10,000	90.0	NA	66.0	NA
C-23-3	2.0	10,000	76.4	76.0	47.9	5.7

ASTM Distillations

C-23-1		C-34-2		C-23-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	201	IBP	208	IBP	229
10.1	406	10.1	375	8.6	425
13.8	425	19.8	425	10.6	438
20.3	453	20.2	428	21.1	470
30.4	482	30.4	485	31.6	517
40.6	524	40.5	513	42.2	551
50.7	561	50.6	548	52.7	594
60.8	596	60.7	584	63.3	640
62.1	600	64.9	600	73.8	681
71.0	638	70.8	621	76.4	694
81.1	661	80.9	670		
87.0	700	90.0	700		

Run C-24

Catalyst - MSU GRH-2-E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-24-1	1.0	10,000	84.1	82.5	59.7	15.6
C-24-2	1.5	10,000	84.4	80.4	63.9	NA
C-24-3	2.0	10,000	81.1	78.5	66.7	4.9

ASTM Distillations

C-24-1		C-24-2		C-24-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	210	IBP	219	IBP	241
14.2	425	12.0	425	8.5	425
20.5	465	20.0	460	20.3	458
30.8	494	30.0	497	30.4	486
41.0	524	40.0	536	40.6	535
51.3	571	50.0	578	50.7	583
59.3	600	55.0	600	60.8	616
61.6	618	70.0	668	71.0	637
71.8	653	84.4	69.2	76.9	651
84.1	700			78.5	700

Run C-25

Catalyst - MSU GRH-3-E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-25-1	1.0	10,000	87.5	82.2	56.1	18.0
C-25-2	1.5	10,000	86.0	85.8	61.1	24.2
C-25-3	2.0	10,000	82.1	76.8	47.8	6.6

ASTM Distillations

C-25-1		C-25-2		C-25-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	236	IBP	231	IBP	232
12.8	425	10.2	398	8.8	425
20.4	443	15.9	425	10.5	431
30.6	480	20.4	446	21.0	475
40.8	519	30.6	494	31.5	507
51.0	558	40.9	529	42.0	559
61.2	599	51.1	563	52.5	600
71.4	623	60.9	600	63.0	640
87.5	691	71.5	639	82.1	698
		86.0	700		

Run C-26

Catalyst - MSU GRH-4 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-26-1	1.0	10,000	84.5	82.2	54.7	22.5
C-26-2	1.5	10,000	87.0	85.4	56.0	23.8
C-26-3	2.0	10,000	80.4	76.5	51.1	6.1

ASTM Distillations

C-26-1		C-26-2		C-26-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	224	IBP	210	IBP	232
10.2	401	10.1	381	8.1	425
14.6	425	16.2	425	10.4	442
20.5	448	20.3	452	20.8	471
30.8	491	30.4	479	31.2	508
41.0	520	40.6	514	41.6	547
51.3	567	50.7	554	52.0	592
60.3	600	60.9	591	55.3	600
71.8	657	71.0	626	62.4	631
84.5	700	81.2	662	77.1	655
		87..0	700	80.4	700

Run C-27

Catalyst - MSU GRH-5 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-27-1	1.0	10,000	86.1	82.7	54.3	20.7
C-27-2	1.5	10,000	86.1	83.9	61.1	29.3
C-27-3	2.0	10,000	77.2	75.6	43.1	8.6

ASTM Distillations

C-27-1		C-27-2		C-27-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	221	IBP	219	IBP	271
10.2	399	10.1	402	10.0	425
14.1	425	14.6	425	20.8	468
20.4	451	20.3	439	31.1	491
40.8	519	30.4	482	41.5	543
51.0	555	40.5	521	57.9	582
61.2	589	50.7	561	58.8	600
67.1	600	60.8	597	62.3	620
71.4	624	70.9	639	72.7	649
84.6	641	81.1	681	77.2	700
86.1	700	86.1	689		

Run C-28

Catalyst - Ketjen-330-3E

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-28-1	1.0	10,000	84.1	80.6	55.8	15.1
C-28-2	1.5	10,000	83.4	80.7	48.3	15.8
C-28-3	2.0	10,000	81.8	74.3	45.8	5.2

ASTM Distillations

C-28-1		C-28-2		C-28-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol. %	Temp. (°F)
IBP	209	IBP	221	IBP	230
10.5	425	10.2	424	13.0	425
20.6	459	20.4	474	31.4	504
30.8	492	30.6	503	41.8	544
41.1	531	40.8	536	52.3	587
51.4	574	57.0	577	52.3	600
59.2	600	61.2	611	62.7	614
72.0	662	71.4	651	73.2	650
84.1	689	83.4	700	81.8	700

Run C-29

Catalyst - Houdry HR-811 E 1/16.

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield		% DeS	% DeN
			Vol %	Wt%		
C-29-1	1.0	10,000	84.6	80.4	52.2	19.3
C-29-2	1.5	10,000	83.4		56.9	18.5
C-29-3	2.0	10,000	81.7		39.6	4.4

ASTM Distillations

C-29-1		C-29-2		C-29-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	219	IBP	184	IBP	256
10.2	398	10.2	391	8.0	425
14.0	425	16.7	425	10.3	440
20.3	447	20.3	460	20.6	481
30.5	489	30.5	497	31.0	519
40.6	527	40.6	530	41.3	560
40.8	568	50.8	562	58.6	600
59.2	600	61.0	600	61.9	630
71.1	649	71.1	639	72.2	672
84.6	691	79.2	664	81.7	688
		83.4	700		

Run C-30

Catalyst - MSU 4003-E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-30-1	1.0	10,000	82.4	79.2	72.2	22.6
C-30-2	1.5	10,000	82.6	83.4	67.8	30.1
C-30-3	2.0	10,000	80.1	77.5	58.1	13.6

ASTM Distillations

C-30-1		C-30-2		C-30-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	221	IBP	260	IBP	259
10.2	384	10.1	391	10.0	425
16.4	425	16.0	425	20	470
20.3	456	20.2	458	30	506
30.4	492	30.3	487	40	541
40.6	529	40.4	523	50.1	583
50.8	568	50.5	559	55.1	600
61.1	600	62.0	600	60.1	617
71.0	646	70.7	635	70.1	648
82.4	681	82.6	700	80.1	700

Run C-31

Catalyst - MSU 7003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-31-1	1.0	10,000	81.5	79.9	55.4	21.9
C-31-2	1.5	10,000	85.5	81.8	68.1	23.0
C-31-3	2.0	10,000	79.6	79.7	62.5	14.3

ASTM Distillations

C-31-1		C-31-2		C-31-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	229	IBP	299	IBP	269
10.1	418	10.2	405	12.3	425
20.3	460	12.8	425	20.5	451
30.4	508	20.3	468	30.7	496
40.6	541	30.5	503	40.9	534
50.7	582	40.6	539	51.2	583
60.9	615	50.8	572	61.4	620
71.0	667	59.1	600	71.6	652
81.5	700	85.5	700	79.6	682

Run C-32

Catalyst - MSU 3003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-32-1	1.0	10,000	86.9	83.1	67.4	21.5
C-32-2	1.5	10,000	86.5	83.0	58.3	18.0
C-32-3	2.0	10,000	78.2	74.2	59.0	9.4

ASTM Distillations

C-32-1		C-32-2		C-32-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	244	IBP	236	IBP	287
10.1	388	16.2	425	10.0	425
13.9	425	20.2	453	20.5	468
20.2	452	30.4	491	30.7	506
30.2	493	40.5	525	40.9	548
40.3	529	50.6	560	54.9	600
50.4	557	58.9	600	61.4	630
60.5	602	70.9	646	71.6	666
70.6	642	86.5	686	78.2	684
80.6	691				
86.9	698				

Run C-33

Catalyst - MSU 8003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-33-1	1.0	10,000	87.2	84.7	71.4	25.0
C-33-2	1.5	10,000	87.0	85.3	76.8	34.8
C-33-3	2.0	10,000	84.6	81.6	45.3	8.2

ASTM Distillations

C-33-1		C-33-2		C-33-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	218	IBP	243	IBP	329
10.5	425	13.6	425	7.4	425
20.2	456	20.3	461	20.4	485
30.4	487	30.4	492	30.6	520
40.4	522	40.6	521	40.8	559
50.6	557	50.7	554	51.0	600
62.6	600	60.9	588	61.1	635
70.8	632	66.7	600	71.3	670
87.2	683	71.0	623	84.6	681
		81.2	654		
		87.0	700		

Run C-34

Catalyst - MSU 1003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-34-1	1.0	10,000	84.7	81.6	61.8	23.6
C-34-2	1.5	10,000	83.4	80.2	58.3	24.2
C-34-3	2.0	10,000	82.0	76.8	46.5	11.1

ASTM Distillations

C-34-1		C-34-2		C-34-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	--	IBP	262	IBP	231
10.0	425	13.8	425	10.0	425
20.3	460	20.3	457	20.1	460
30.5	503	30.4	493	30.1	502
40.6	538	40.6	406	40.2	539
50.8	571	50.8	508	50.2	579
58.9	600	59.3	600	54.4	600
71.1	651	71.0	648	60.3	621
84.7	700	83.4	680	70.3	665
				82.0	691

Run C-35

Catalyst - MSU 5003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-35-1	1.0	10,000	85.0	81.3	58.3	19.3
C-35-2	1.5	10,000	83.0	78.5	53.5	18.3
C-35-3	2.0	10,000	81.1	77.8	59.7	10.2

ASTM Distillations

C-35-1		C-35-2		C-35-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	219	IBP	201	IBP	291
9.7	425	10.3	386	10.3	425
20.3	445	20.5	425	20.6	469
30.4	482	30.8	470	30.8	509
40.6	526	41.0	517	41.1	550
50.7	571	51.3	551	51.4	596
71.0	600	61.6	585	53.5	600
81.1	637	64.4	600	61.7	629
85.0	673	71.8	621	72.0	666
		84.1	700	80.6	685

Run C-36

Catalyst - MSU 6003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-36-1	1.0	10,000	85.2	81.4	65.3	23.0
C-36-2	1.5	10,000	84.6	81.1	66.0	19.9
C-36-3	2.0	10,000	80.3	75.3	58.3	8.2

ASTM Distillations

C-36-1		C-36-2		C-36-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	231	IBP	269	IBP	389
14.8	425	13.2	425	10.3	425
20.3	460	20.4	462	20.6	477
30.4	494	30.6	496	31.0	512
40.6	532	40.8	539	41.3	551
50.7	569	51.0	575	51.6	592
59.6	600	57.5	600	53.4	600
71.0	652	71.4	656	61.9	632
85.2	700	84.6	681	72.2	671
				80.3	681

Run C-37

Catalyst - MSU 2003 E 1/16

Temp - 450°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Vol %	Yield Wt%	% DeS	% DeN
C-37-1	1.0	10,000	86.6	83.3	71.0	32.2
C-37-2	1.5	10,000	86.8	82.9	66.7	31.6
C-37-3	2.0	10,000	81.0	77.8	59.0	15.6

ASTM Distillations

C-37-1		C-37-2		C-37-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	238	IBP	268	IBP	302
13.9	425	10.1	396	9.1	425
20.2	459	14.4	425	20.7	474
30.3	459	20.2	459	31.1	509
40.4	531	30.4	488	41.4	541
50.5	560	40.5	521	51.8	588
60.6	598	50.6	557	54.1	600
70.7	634	62.8	600	62.2	631
80.8	684	70.9	641	72.5	678
86.6	691	81.0	689	81.0	684
		86.8	700		

Run C-38

Catalyst - Harshaw HT-400 E 1/16

Temp - 425°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-38-1*	2.0	10,000	85.7	82.2	47.6	33.2
C-38-2*	2.0	10,000	80.5	74.8	45.1	11.0
C-38-3*	2.0	10,000	78.8	74.1	51.4	10.8
C-38-4*	2.0	10,000	76.8	71.4	50.5	9.0

ASTM Distillations

C-38-1		C-38-2		C-38-3	
Vol %	Temp(°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	233	IBP	257	IBP	--
10.2	379	10.3	406	11.6	425
17.1	425	20.6	461	20.7	471
30.6	476	31.0	495	31.0	502
40.8	513	41.3	536	41.4	537
51.0	552	51.6	581	51.7	586
61.2	588	58.2	600	55.7	600
65.1	600	72.2	649	62.1	630
71.4	633	80.5	670	72.4	656
85.7	660			78.8	671

C-38-4

Vol %	Temp (°F)
IBP	250
13.0	425
20.7	452
31.1	489
41.4	536
54.7	600
62.1	631
76.8	669

Run C-39

Catalyst - Harshaw HT-400 E 1/16

Temp - 475°C

Pressure - 1000 psig

Sample	LHSV	H ₂ flow SCF/BBL	Distillate Yield Vol %	Yield Wt%	% DeS	% DeN
C-39-1*	2.0	10,000	90.9	88.0	50.7	45.1
C-39-2*	2.0	10,000	84.1	79.6	45.8	18.0
C-39-3*	2.0	10,000	83.2	80.7	54.2	15.6
C-39-4*	2.0	10,000	82.8	79.2	46.5	13.1

* - Samples at 3 hour intervals

ASTM Distillations

C-39-1		C-39-2		C-39-3	
Vol %	Temp (°F)	Vol %	Temp. (°F)	Vol %	Temp. (°F)
IBP	229	IBP	239	IBP	269
10.1	359	12.0	425	13.0	425
20.2	425	20.3	447	20.4	467
30.3	470	30.4	449	30.6	499
40.4	501	40.6	535	40.8	536
50.5	535	50.7	572	51.0	572
60.6	577	58.8	600	59.5	600
66.6	600	71.0	654	71.3	648
70.7	621	84.1	700	83.2	690
80.8	642				
90.9	700				

C-39-4

<u>Vol %</u>	<u>Temp (°F)</u>
IBP	275
15.9	425
20.4	448
30.6	494
40.8	533
57.0	579
59.0	600
71.4	659
82.8	686

Notes to Appendix C:

- LHSV - Liquid Hourly Space Velocity
- % DeN - Weight percent denitrogenation
- % DeS - Weight percent desulfurization

Runs C-1 through C-8

Feedstock contained: .644% and 1.30% N

Runs C-9 through C-22

Feedstock contained: .72% S and 1.14% N

Runs C-23 through C-39

Feedstock contained: .72% S and 1.22% N

SRC Vacuum Flash Feed Distillation

<u>Vol %</u>	<u>Temp. (F°)</u>	
IBP	410	
9.0	480	
21.5	536	
30.5	578	
39.5	615	
44.9	641	
50.3	684	
52.1	694	wt% recovered 58.6%

APPENDIX D

Table D-I. Nickel-Cobalt-Molybdenum Catalyst Performance

Catalyst	LHSV	% N in Product	% S in Product
1003	1.0	.932	.275
	2.0	1.084	.385
2003	1.0	.827	.219
	2.0	1.030	.295
3003	1.0	.958	.235
	2.0	1.105	.295
4003	1.0	.944	.200
	2.0	1.054	.302
5003	1.0	.984	.300
	2.0	1.095	.290
6003	1.0	.939	.250
	2.0	1.120	.300
7003	1.0	.953	.321
	2.0	1.045	.270
8003	1.0	.914	.206
	2.0	1.120	.394

Table D-II. Derived Product Nitrogen Analyses of f (LHSV, Catalyst)

LHSV	Co	12%		Mo	18%	
		0.5%	Ni		.5%	Ni
1.0	1.5%	.914		.939	.944	.827
	3.0%	.953		.984	.958	.932
2.0	1.5%	1.120		1.120	1.054	1.030
	3.0%	1.045		1.095	1.105	1.084

The Table D-II data were coded by multiplying by 10 and then an analysis of variance was run assuming a 2^4 factorial design of one replicate as shown in Table D-III.

Table D-III. ANOVA Table for Coded Nitrogen Data

Source	df	SS	EMS
L	1	9.03	$6\phi_L + \alpha^2 E$
M	1	.35	$6\phi_M + \alpha^2 E$
C	1	.27	$6\phi_C + \alpha^2 E$
N	1	.04	$6\phi_N + \alpha^2 E$
NC	1	.14	$4\phi_{NC} + \alpha^2 E$
NM	1	.54	$4\phi_{NM} + \alpha^2 E$
CM	1	.36	$4\phi_{CM} + \alpha^2 E$
LN	1	.05	$4\phi_{LN} + \alpha^2 E$
LC	1	.24	$4\phi_{LC} + \alpha^2 E$
LM	1	0	$4\phi_{LM} + \alpha^2 E$
NCM	1	.01	$2\phi_{NCM} + \alpha^2 E$
LNC	1	.02	$2\phi_{LNC} + \alpha^2 E$
LMN	1	.12	$2\phi_{LMN} + \alpha^2 E$
LCM	1	.18	$2\phi_{LCM} + \alpha^2 E$
LCMN	1	.06	$\phi_{LCMN} + \alpha^2 E$
Error	0	unretrievable	
Total	15	11.40	

Notes:

L - LHSV
 M - Wt% MoO₃
 N - Wt% NiO₃
 C - Wt% CoO

As seen in the EMS column, the error can be determined if some of the interactions are assumed zero. It is felt that the interactions containing space velocity and metal content of the catalyst can be safely assumed to be zero. Therefore, these seven terms will be used for error as shown in the modified ANOVA Table D-IV.

Table D-IV. Modified ANOVA Table for Nitrogen Data

Source	df	SS	MS	$F_{1,7}$
L	1	9.03	9.03	94.3 ***
M	1	.35	.35	3.66*
C	1	.27	.27	2.82
N	1	.04	.04	.42
NC	1	.14	.14	1.46
NM	1	.54	.54	5.64**
CM	1	.36	.36	3.76*
NCM	1	.01	.01	.10
Error	7	.67	.0957	

*** $F_{1,7} = 12.2$ at $\alpha = .01$

** $F_{1,7} = 5.59$ at $\alpha = .05$

* $F_{1,7} = 3.59$ at $\alpha = .10$

Table D-V. Derived Product Sulfur Analysis as f (LHSV, Catalyst)

LHSV	Co	12%		Mo	18%	
		.5%	Ni		.5%	Ni
1.0	1.5%	.206		.250	.200	.219
	3.0%	.321		.300	.235	.275
2.0	1.5%	.394		.300	.302	.295
	3.0%	.270		.290	.295	.385

The Table D-V data were coded by multiplying by 10 and then an analysis of variance was run assuming a 2^4 factorial design of one replicate as shown in Table D-VI.

Table D-VI. ANOVA Table for Coded Sulfur Data

Source	df	SS	EMS
L	1	1.72	$6\phi_L + \alpha^2_E$
M	1	0.10	$6\phi_M + \alpha^2_E$
C	1	0.26	$6\phi_C + \alpha^2_E$
N	1	0.05	$6\phi_N + \alpha^2_E$
NC	1	0.18	$4\phi_{NC} + \alpha^2_E$
NM	1	0.23	$4\phi_{NM} + \alpha^2_E$
CM	1	0.13	$4\phi_{CM} + \alpha^2_E$
LN	1	0.04	$4\phi_{LN} + \alpha^2_E$
LC	1	0.60	$4\phi_{LC} + \alpha^2_E$
LM	1	0.19	$4\phi_{LM} + \alpha^2_E$
NCM	1	0.03	$2\phi_{NCM} + \alpha^2_E$
LNC	1	0.39	$2\phi_{LNC} + \alpha^2_E$
LMN	1	0.08	$2\phi_{LMN} + \alpha^2_E$
LCM	1	0.51	$2\phi_{LCM} + \alpha^2_E$
LCMN	1	0.09	$\phi_{LCMN} + \alpha^2_E$
Error	0	unretreivable	
Total	15	4.60	

Notes: L = LHSV N = Wt% NiO³
M = Wt% MoO₃ C = Wt% CoO

As can be seen from the EMS column, the error can be determined if some of the interactions are assumed to be zero. It is felt that the interaction containing space velocity and metal content of the catalyst can be safely assumed to be zero. Therefore, these seven terms will be used for error as shown in the modified ANOVA Table D-VIII.

Table D-VII . Modified ANOVA Table for Sulfur Data

Source	df	SS	MS	$F_{1,7}$
L	1	1.72	1.72	6.37*
M	1	0.10	0.10	.37
C	1	0.26	0.26	.96
N	1	0.05	0.05	.19
NC	1	0.18	0.18	.67
NM	1	0.23	0.23	.85
CM	1	0.13	0.13	.48
NCM	1	0.03	0.03	.11
Error	7	1.90	.27	

* $F_{1,7} = 5.59$ at $\alpha = .05$

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Klass, D.L., "Synthetic Crude Oil From Shale and Coal," Chemtech, August 1975, pp. 499-510.
2. Stewart, R.W., "How to Finance Synthetic Pipeline Gas," Abstracts of 29th Annual Meeting of Institute of Gas Technology, November 19, 1970, Chicago, Ill.
3. Mills, G.A., "Alternate Fuels From Coal," Chemtech, July 1977, pp. 418-423.
4. Walsh, J., "Problems of Expanding Coal Production," Science, 184, 336-9, April 19, 1974.
5. Jones, J.F., "Project COED Char Oil Engery Development," in Symposium Paper "Clean Fuels from Coal" of Institute of Gas Technology, Chicago, Ill., Sept. 10-14, 1973, pp. 383-402.
6. Greene, M.E. et al. "Low Sulfur Synthetic Crude Oil From Coal," ACS Div. Fuel Chem. Prepr, 19(1): 215-35, April 1-5, 1974.
7. Carlson, F.B. et al., "The Toscoal Process Coal Liquefaction and Char Production," in Symposium Papers, "Clean Fuels From Coal," pp. 367-381, Institute of Gas Technology, Chicago, Ill., Sept. 10-14, 1973.
8. Sass, A., "Garrett's Coal Pyrolysis Process," Chemical Engr. Progress, 70(1): 72-73, January 1974.
9. Hoogendoorn, J.C., "Experience With Fischer-Tropsch Synthesis at Sasol," in Symposium Papers, "Clean Fuels From Coal," pp. 353-65, Institute of Gas Tech., Chicago, Ill., Sept. 10-14, 1973.
10. _____, "South Africa Lets Contract for Big Coal SNG, Liquefaction Facility," Oil and Gas Journal, p. 85, March 17, 1975.
11. Brum, T., "Direct Conversion Technology Not Ready," Oil Daily, No. 5, 598, pp. 1,2, Feb. 26, 1974.
12. _____, "They Dig Coal Projects," Chem Week, 114, 10, March 20, 1974.
13. Johnson, C.A. et al., "Present Status of the H-Coal Process," ibid. no. 9, pp. 549-75.

14. _____, "Energy Newsmakers of 73, Hydrocarbon Research," Oil Daily, No. 761, Jan. 3, 1974.
15. _____, "Washington Newsletter, Coal Liquefaction is Getting New Government Backing," Chem Week, 114, 14, Aug. 7, 1974.
16. Yavorsky, P.M., "Synthoil Process Converts Coal to Clean Fuel Oil," ibid. no. 9, pp. 539-47.
17. _____, "When Will Synthetic Fuels Begin Flowing From Coal," Chem. Week., 114, p. 35,36, Jan. 9, 1974.
18. Frank, M.E., Schmid, B.K., "Economic Evolution and Process Design of A Coal-Oil-Gas (COG) Refinery," ibid no. 9, pp. 577-600.
19. _____, "Solvent Refined Coal (SRC) Process," Quarterly Technical Progress Report, Jan. 1978, The Pittsburg & Midway Coal Mining Co., Contract EX-76-C-01-496.
20. _____, "Gulf, Pursuing Coal to Gas Research, Begins Constructing One-Ton Pilot Unit," Chem. Marketing Report, 205(24): 4,18, June 17, 1974.
21. Phinney, J.A., "Clean Fuels Via the CSF Process," ibid no. 9, pp. 525-8.
22. _____, "Dormant COG Plant Comes to Life With a New Mandate," Chem. Eng, 81(13): 97, June 24, 1974.
23. Office of Fossil Energy, "Coal Liquefaction--Quarterly Report," June 1975, ERDA-76-33-2, pp. 9-13.
24. Ralph M. Parsons Co., "Coal Conversion and Utilization-Liquefaction: Solvent Refined Coal," Prepared for ERDA, FE-1234-6, May 1976.
25. Higginson, G.W., "SRC Could Provide Three-Way Approach to More Energy," Oil and Gas Journal, Aug. 1, 1977, pp. 89-93.
26. U.S. Energy Research and Development Administration, Scientific Resources Relevant to the Catalytic Problems in the Conversion of Coal, Part III, pp. 301-351.
27. Exxon Research and Engineering, U.S. Patent no. 3,928,176.

28. _____, Hydrocarbon Processing, Vol. 55, No. 9, pp. 121-128, Sept. 1976.
29. Cheadle, G.D. et al., "Unicracking--JHC Process Extends Commercial Applications," Oil and Gas Journal, pp. 76-82, July 18, 1966.
30. Ahuja, S.P. et al., "Acidity and Selectivity of Hydrotreating Catalysts," Ind. Eng. Chem. Prod. Res. Develop., Vol. 9, No. 3, 1970, pp. 272-281.
31. Technical Service Report, Ketjen Catalyst Co., No. HDS68/27.
32. _____, "Upgrading of Coal Liquids for Use as Power Generation Fuels," Mobil Research and Development, EPRI Report #361-1, (1966).
33. Yakahayashi, E., Japan Prtr. Inst. Journal, 16, 651 (1973).
34. Schmit, G.G., and Gates, B.C., "Chemistry and Engineering of Catalytic Hydrodesulfurization," AIChE Journal, Vol. 19, No. 3, pp. 417-438 (1973).
35. Qader, S.A., Journal of the Inst. of Petrol., 59, 178 (1973).
36. _____, and Hill, G.R., Amer. Chem. Soc., Div. Fuel Chem., Prepr., 16, 93 (1972).
37. Flinn, R.A. et al., Ind. Eng. Chem., 52, 153 (1960).
38. Sullivan et al., J. Amer. Chem. Soc., 83, 1156 (1961).
39. _____, J. Catal., 3, 183 (1964).
40. Wiser, W.H. et al., Ind. Eng. Chem., Prod. Res. Div., 9, No. 3, 350 (1970).
41. Gates, et al., Dept. of Chem. Eng. and Chem., Delaware, Univ., ERDA report FE-2028-8 Nov. (1977).
42. Ibid No. 26, pp. 122-139.
43. Satterfield, C.N., "Trickle Bed Reactors," AIChE J., Vol. 21, No. 2, 1975, pp. 209-228.

44. _____, Mass Transfer in Heterogeneous Catalytic, MIT Press, 1970.
45. Pelessof, A.A., Satterfield, C.N., Sherwood, T.K., "Mass Transfer Limitation in Trickle Bed Reactors," AIChE J., Vol. 15, p. 226 (1969).
46. Hutchinson, P. and Luss, D., "Lumping of Mixtures with Parallel First Order Reactions," Chem. Eng. J., 1, 129 (1970).
47. Luss, D. and Hutchinson, P., "Lumping of Mixtures of Many Nth Order Reactions," Chem. Eng. J., 2, 172 (1971).
48. Sata, Y. et al., "Performance of Fixed Bed Catalytic Reactor With Cocurrent Flow," Pacific Chem. Eng. Conf., Session 8, Paper 8-3, p. 187 (1972).
49. Weekman, V.W. Jr., and Myers, J.E., "Fluid Flow Characteristics of Cocurrent Gas-Liquid Flow in Packed Beds," AIChE J., 10, 951 (1964).
50. Porter, K.E., "Liquid Flow in Packed Columns, I. The Rivulet Model," Tr. Inst. Chem. Engrs., 46, T69 (1968).
51. Porter, K.E., "II. The Spread of Liquid Over Random Packings," ibid, 46, T74 (1968).
52. _____, "III. Wall Flow," ibid, 46, T86 (1968).
53. Acres, G., "Trickle Column Reactors," Platinum Metals Rev., 11 (3), 86 (1967).
54. Mears, D.E., "Tests for Transport Limitations in Experimental Catalytic Reactors," Ind. Eng. Chem., Proc. Des. Develop., Vol. 10, No. 4 (1971).
55. Montagne, A.A. and Shah, Y., "The Role of Liquid Holdup, Effective Catalyst Wetting, and Backmixing on the Performance of a Trickle Bed Reactor for Residue Desulfurization," Ind. Eng. Chem., Proc. Des. Develop., Vol. 14, No. 4 (1975).
56. Smith, J.M., Chemical Engr. Kinetics, McGraw-Hill Co., New York, 1970, pp. 473-76.

57. Carberry, J.J., Chemical and Catalytic Reaction Engr., McGraw-Hill Book Co., New York, 1976, pp. 519-616.
58. Product Data Bulletin, Ketjen Catalyst Co., No. 76-4 (1971), p. 3-4.
59. SRC Process Quarterly Report, ERDA Contract #EX-76-C-01-496, Pittsburg and Midway Coal Mining Co., March 1977.
60. Stecher, P.G., Merck Index, 8th ed., Merck & Co., Inc., Rahway, N.J., pp. 545-46.
61. Parr Instrument Co., Instructions for the Series 4000 Pressure Reaction Apparatus, Parr Manual No. 141.
62. Haskell Engineering and Supply Company, Operating and Maintenance Instructions for Haskell Air Drive Gas Booster Compressor.
63. Goop Lubricants, Idaho Valve and Fitting Company Catalog, P.O. Box 2946, Idaho Falls, Idaho 83401.
64. Norton Denston Catalog, Norton Company.
65. Cole Parmer 1976 Catalog, pp. 137-140, Cole Parmer Instrument Co., 7425 North Oak Park, Chicago, Ill. 60648.
66. Instructions for Operation of Brooks Thermal Mass Flowmeter, Brooks Instrument Division, Emerson Electric Co., Hatfield, PA 19440, April 1975.
67. Bloedel, W.J. and Meloche, V.W., Elementary Quantitative Analysis, 2nd Ed., Harper and Row, Publishers, New York, 1963.
68. Peters, E.D., "Determination of Sulfur and Halogens, Improved Quartz Tube Combustion Apparatus," Analytical Chemistry, Vol. 24, No. 4, April 1952, pp. 710-714.
69. American Society for Testing and Materials, "Standard Method of Testing for Sulfur in Petroleum Oils (Quartz Tube Method)," 1974 Annual Book of ASTM Standards, Part 23, ASTM Designation D1551.
70. Fritz, J.S., and Schenk, G.H., Quantitative Analytical Chemistry 3rd Ed., Boston, 1974, pp. 44-69, 191-193.

71. Lake, G.R. , Effects of Digestion Temperature on Kjeldahl Analyses, Analytical Chemistry, Vol. 23, No. 11, Nov. 1951, pp. 1634-1638.
72. American Society for Testing and Materials, "Standard Method of Testing for Nitrogen in Organic Materials by Modified Kjeldahl Method," 1974 Annual Book of ASTM Standards, Part 30, Designation E258.
73. American Society for Testing and Materials, "Standard Test for Distillation of Petroleum Products," 1974 Annual Book of ASTM Standards, Part 23, Designation D86.
74. U.S. Patent No. 3,928,176 Exxon Research and Engineering.
75. U.S. Patent No. 3,891,539 Texaco, Inc.
76. Kujawa, S.T., "Catalytic Hydrogenation of Coal-Derived Liquids," ERDA report FE-2034-6, Feb. 1977.
77. Runnion, K.N., "Catalytic Hydrogenation of Synthoil," Master's Thesis, Montana State University, March 1977.
78. Hicks, Charles R., Fundamental Concepts in the Design of Experiments, 2nd Ed., Holt, Rinehart, and Winston, Inc., New York, 1973, pp. 86-120.

NOMENCLATURE

$\text{\AA}$	angstrom
bbl	barrel
DN, Den, DeN	weight percent denitrogenation
DS, Des, DeS	weight percent desulfurization
LHSV	Liquid Hourly Space Velocity
MAF	Moisture and Ash Free
P.D.	pore diameter
P.V.	pore volume
S.A.	surface area
scf	standard cubic feet



Catalytic hydrogenation
of solvent refined coal

D378
H276
cap. 2