



Catalytic hydrotreating of solvent refined coal (SRC-II)  
by An-Gong Yeh

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

Solvent Refined Coal (SRC-II) from Pittsburg and Midway Coal Mining Company's pilot plant was hydrotreated with commercial and Montana State University developed catalysts. Twenty-two batch autoclave runs and twenty-five continuous trickle bed reactor runs were performed.

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Nitrogen and sulfur content was decreased to meet the requirements, 0.3wt%. The catalyst lasted three hours before carbon laid down on the preheat section caused shut-down.

The study of catalyst- base properties and metal loading was performed to determine the effects of pore diameter, pore volume, surface area, and MoO<sub>3</sub> concentration on the nitrogen removal. The higher surface area gave the better nitrogen removal. However, the smallest surface area with a large median pore diameter was not the poorest performer. An optimum combination of proper surface area and pore diameter seems important. The effect of MoO<sub>3</sub> concentration on nitrogen removal is dependent on the catalyst base used, but it is insignificant compared with the effect of catalyst base. The larger pore volume base gave the higher liquid product yield.

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November 28, 1979

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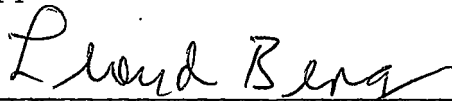
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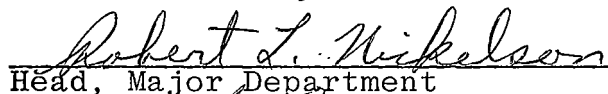
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Chairperson, Graduate Committee



Head, Major Department



Graduate Dean

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## ABSTRACT

Solvent Refined Coal (SRC-II) from Pittsburg and Midway Coal Mining Company's pilot plant was hydrotreated with commercial and Montana State University developed catalysts. Twenty-two batch autoclave runs and twenty-five continuous trickle bed reactor runs were performed.

The liquid products were analyzed for sulfur and nitrogen content, and the extent of hydrocracking was determined by ASTM-D86 distillation test.

Nitrogen and sulfur content was decreased to meet the requirements, 0.3wt%. The catalyst lasted three hours before carbon laid down on the preheat section caused shut-down.

The study of catalyst base properties and metal loading was performed to determine the effects of pore diameter, pore volume, surface area, and MoO<sub>3</sub> concentration on the nitrogen removal. The higher surface area gave the better nitrogen removal. However, the smallest surface area with a large median pore diameter was not the poorest performer. An optimum combination of proper surface area and pore diameter seems important. The effect of MoO<sub>3</sub> concentration on nitrogen removal is dependent on the catalyst base used, but it is insignificant compared with the effect of catalyst base. The larger pore volume base gave the higher liquid product yield.

## INTRODUCTION

In view of energy crisis and national energy policy, it seems clear that sooner or later the United States will come to rely much more on coal as a resource of energy than it has over the past few decades. It is estimated that coal accounts for 80 percent of the fossil-fuel resources in the U.S.(1). In contrast, for the past decade or so the sources of energy in the U.S. have been predominantly oil and gas (44 and 31 percent respectively), with coal accounting for 21 percent(2). Coal is not the ideal fuel both because it is not a fluid and causes air pollution. Therefore, the development of a technology that will convert the U.S.'s abundant reserves of coal to clean fluid fuels is needed.

Coal conversion processes include gasifications and liquefactions. Since the shortage of domestic liquid hydrocarbons has caused the balance-of-payments problem in the U.S., coal liquefaction schemes are being examined closely. There are three major ways to turn coal into liquid fuels : pyrolysis, indirect liquefaction and direct hydroliquefaction. So far, most pyrolysis

processes haven't been too suitable for making liquid fuels. Although indirect coal technology is in a more advanced state of development, direct hydroliquefaction offers, at least in theory, better economics and higher efficiency in terms of liquids per ton of coal. Therefore, most federal support is going to the direct processes.

Several direct hydroliquefaction processes have been developed such as the Solvent Refined Coal (SRC) process, the Exxon Donor Solvent (EDS) process and the H-Coal process. SRC process is the oldest of these modern processes dating back to 1962. Its original process is known as SRC-I, a later modified version is SRC-II process. Conceivably, its commercial scale plant could be in operation by 1989 or 1990(1).

The product of SRC-II process still cannot be used as a clean fuel at present costs, it must be catalytically upgraded or hydrorefined(3). This research is the second step of SRC-II process. The SRC-II product must be catalytically hydrotreated in a trickle bed reactor to remove unfavorable heteroatom molecules, sulfur and

especially nitrogen, and to improve the overall product. This research is expected to provide the technology for the rapid commercialization of the SRC-II process and give the SRC-II process greater advantages over other processing schemes.

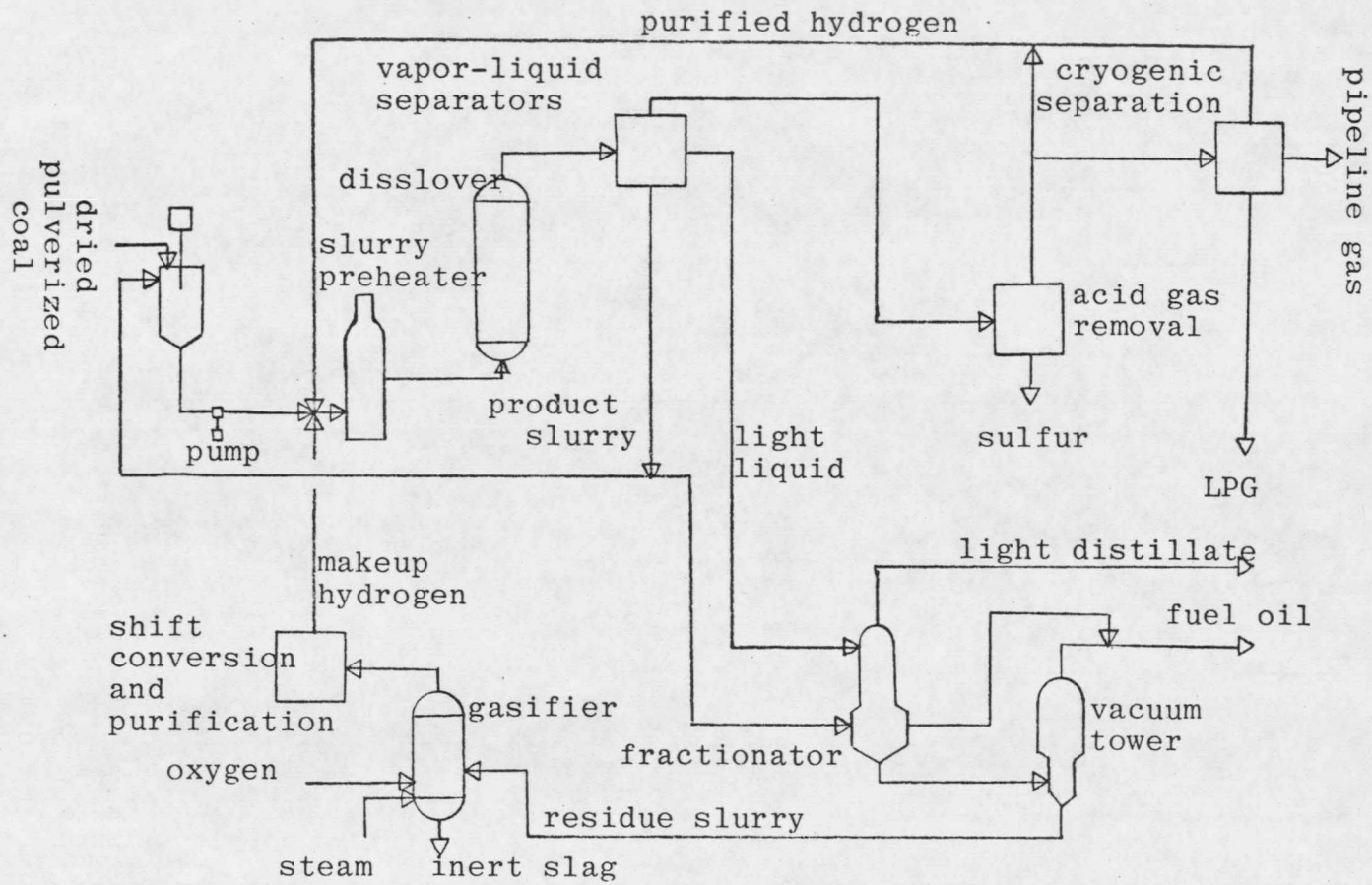
## BACKGROUND

### SRC-II Process

Of major concern to this research is the SRC-II process operated by Pittsburg and Midway Coal Mining Company. A fifty ton per day pilot plant is being operated at Fort Lewis, Washington. Pulverized raw coal is mixed with a process-derived slurry product and hydrogen at high temperature and pressure. The coal dissolves; most of its ash and much of its sulfur settle out and can be removed by filtration. Most of the coal is converted to liquids; naphtha, boiler fuel and vacuum residue. This residue contains heavy oil, ash, and undissolved organic material from coal(4). A schematic diagram of the SRC-II process is shown in Figure 1(5).

### Chemical Properties of SRC-II Products

The SRC process is not defined as a single product process. The gas and liquid yields per ton of Solvent Refined Coal is shown in Table I(6). Table II(7) presents the analysis of SRC-II product obtained in this research. The SRC-II product shown was made from



5

FIGURE 1. SRC-II PROCESS SCHEMATIC

TABLE I  
SRC Process Gas and Liquid Yields\*

C <sub>1</sub> - C <sub>4</sub> gas, scf	3130
CH <sub>4</sub> gas	2100
C <sub>5</sub> - 350°F gal	32
bbl	0.762
350-750°F distillate, gal	38
bbl	0.904
Total liquid, gal	70
bbl	1.666

Approximate analysis of C<sub>1</sub> - C<sub>4</sub> gas cut:

	<u>Vol. %</u>	<u>BTU value/ft<sup>3</sup></u>
CH <sub>4</sub>	67.0	680
C <sub>2</sub> H <sub>6</sub>	19.3	340
C <sub>3</sub> H <sub>8</sub>	10.0	260
C <sub>4</sub> H <sub>10</sub>	3.7	120
	<u>100.0</u>	<u>1400</u>

\* Per ton solvent refined coal

TABLE II  
 SRC-II Vacuum Flash Feed as Received

=====

Sampled 1-24-77

% Carbon	87.43
% Hydrogen	7.15
% Nitrogen	1.17
% Sulfur	0.72
% Oxygen	3.72
% Ash	0.249

ASTM D-86 Distillation @ 640 mmHg

<u>Volume, ml</u>	<u>Temperature, °F</u>
IBP	408
5	445
10	485
15	544
20	598
25	642
30	684
33.5	Final

wt% recovered 69.2; Volume% recovered 69.7

=====

Kentucky #9 from the Colonial Mine. The analysis of Kentucky #9 coal is shown in Table III.

### The Chemistry of Catalytic Hydrotreating

Catalytic hydrotreating of petroleum and coal liquids consists of two main parts: the hydrogenation of unsaturated hydrocarbons and the hydrogenolysis of heteromolecules. Usually hydrocracking also occurs at some of the more severe process conditions. The hydrogenation, desulfurization and denitrogenation play important roles in this research.

If SRC-II product is to be used as a boiler fuel; a hydrogen to carbon atoms ratio of about 2:1, and nitrogen, sulfur and mineral level below 0.5 wt% is required. The sulfur level is determined from the current Environmental Protection Agency (EPA) Standards(8). If the SRC-II product is to be a feed stock for a conventional catalytic cracker, the nitrogen requirement is much more stringent. Catalysts in catalytic cracking operations provide acid sites which facilitate cracking of hydrocarbon feeds. If nitrogen is present, it neutralizes these acid sites

TABLE III

SRC Feed Coal Analysis, January 1977

=====

## Kentucky #9 Coal

	<u>wt%</u>
Carbon	71.35
Hydrogen	5.07
Nitrogen	1.44
Sulfur	3.50
O <sub>2</sub>	7.55
Ash	10.12
Moisture	0.97

Sulfur Forms (wt% on Coal)

Pyritic sulfur	1.63%
Sulfate Sulfur	0.09%
Organic Sulfur	<u>1.76%</u>
Total	3.48%

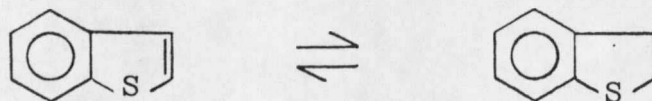
Average Mineral Residue Analysis (wt%)

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

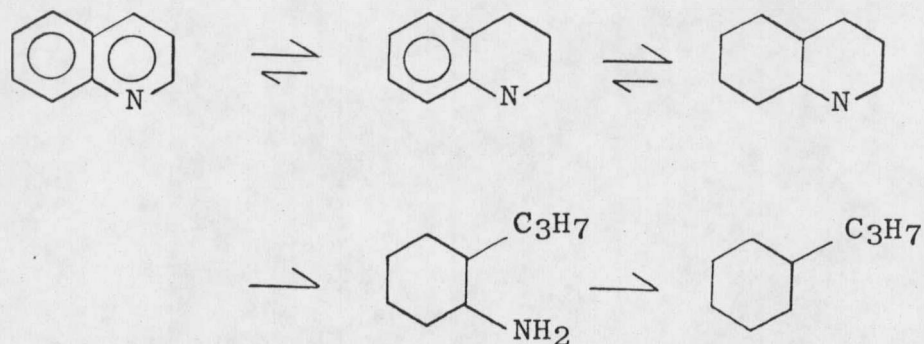
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and acts as a poison. Deactivation of the catalyst progresses in direct proportion to the duration of operation and in proportion to the amount of nitrogen in the catalytic cracker feed. The preferred nitrogen level of catalytic cracker feed is in the range of 100-400 ppm(9). Several hydrocracking processes can tolerate nitrogen levels of 0.3 wt% in the feedstock. Examples of these processes are Standard Oil's Ultracracking process and Union Oil's Unicracking process(10,11).

Several sulfur and nitrogen compounds such as benzothiophenes and quinolines, which make it more difficult for the desulfurization and denitrogenation of coal liquids, have been studied in microreactors to give an insight into the mechanisms(12-16). In the hydrodesulfurization of benzothiophene, it was found that the hydrogenation of the double bond in the thiophene ring took precedence over the removal of sulfur.



Benzothiophene and benzohydrothiophene desulfurized at the same rate when both were reacted separately, so it is not certain whether one is an intermediate of the other in the reaction(12,13). Methyl substitution near the sulfur atom in dibenzothiophenes greatly reduces the hydrogenation activity, believed to be caused by steric effects which restricts the interaction of the sulfur atom and the surface of the catalyst(12,14,15). Usually nitrogen is more difficult to remove than sulfur from hydrocarbon streams. Conditions which reduce excess nitrogen content to a satisfactory level will usually effectively remove excess sulfur. It has been shown that the total rate of hydrodenitrogenation shows a maximum with respect to hydrogen partial pressure. However, the only individual reaction which decreases in rate with increasing hydrogen partial pressure is the conversion of 1,2,3,4-tetrahydroquinoline to ortho-n-propylaniline. This rate determining step dominates the overall network at high temperature(14,15,16).



### Hydrotreating Catalysts

Since petroleum hydrotreating processes are governed by fairly well established kinetics, the most important factor for further progress in the coal liquefaction is the catalyst. Traditionally, a hydrotreating catalyst consists of an active component, usually a metal, that is deposited on a high surface area support. The support is considered inert and its purpose is not only to disperse the metal component, but also to provide acid sites to initiate the carbonium ion mechanisms of cracking reaction(17). Generally, pure silica is less acid than

alumina, which is less acid than silica-alumina. The metals on the support also influence acidity. It was found that NiO on alumina reduces the acidity, while MoO<sub>3</sub> increases it(18).

In catalytic hydrotreating, one of reasons for catalyst deactivation is the deposition of carbonaceous materials(19). It is believed that the Solvent Refined Coal has a high asphaltene content with an average size of 40-50 Å per molecule and smaller pores of the catalyst tend to plug up. The large molecule causes the problem of pore diffusion limitation. Therefore, the effects of surface area and pore size must be accounted for. Theoretically, the higher surface area gives the higher initial activity of catalyst and the larger pore diameter obtains a longer catalyst life(20). In an attempt to develop a satisfactory catalyst, high surface area and/or large pore diameter bases were used in this research.

The most common metals responsible for the hydrogenation-dehydrogenation function of a hydrotreating

catalyst are molybdenum and tungsten. The metals Ni, Co, Fe, Zn, and Cr are usually described as promoters. The function of the promoter is believed to increase the number of exposed molybdenum or tungsten ions—the active centers for the hetro-atom removal reaction(21). For cobolt-moly catalysts, the ratio is about 1:3. This has been found to be independent of support and material(22). The fabrication of catalysts with Mo, W, Ni, and Co or these combinations is the basis of this research.

#### Operation Conditions of Trickle Bed Reactor

In the simplest terms the conversion of coal into oil or gas calls for adding hydrogen. The ratio of hydrogen atoms to the carbon atoms in coal is about 0.87:1. The consumption of hydrogen is a major cost in the conversion of coal into oil. An optimal hydrogen flow rate of 10,000 scf/bbl investigated by Runnion(23, 24) was used in all catalyst tests in this research.

In trickle bed reactors the catalyst is fixed, the flow pattern is close to plug flow, and liquid to

catalyst ratio is much lower thus limiting side reactions. In the petroleum industry, typically less reactive, higher boiling-viscous feeds are operated at low liquid flow rates. The liquid hourly space velocity (LHSV-Volume of Liquid Feed/(Volume of Catalyst x Hour)) of 1.0 usually was used in this research. Generally speaking, higher space velocities will give lower conversions.

Representative operating conditions for the reactors are a pressure range of 500-2,500 psig and a temperature range of from 345 °C to 425 °C. In most fixed bed reactors, as the run progresses, it is necessary to raise the temperature to compensate for the loss in catalyst activity in order to increase reaction rate and maintain conversion levels. It was found that the higher temperatures give the higher conversions, however, the conversion of hydrocarbon to coke(25) also increases. So there is no good reason to operate at a higher reactor temperature. In the petroleum industry, it is understood that most of the carbon is laid down

in the initial running period, so starting at a lower temperature and then increasing the temperature gradually should prevent the reactor from coking up. However, it was found in coal research(26) that a longer packed bed reactor and higher feed flow rates will give a higher pressure drop caused by carbon lay down on the packed bed. It also has been shown that a spherical support is able to prevent reactor bed plugging(27). A study of effect of pressure on the activity of the catalyst reported that better results can be obtained by using a higher pressure, but 1,000 psig is the limiting working pressure of the equipment in this research(28,29).

## RESEARCH OBJECTIVE

This research is an attempt to upgrade the SRC-II product to a feedstock suitable for a conventional refinery or a boiler fuel. The SRC-II product is a tar-like substance received from Pittsburg and Midway Coal Mining Company.

The amount of sulfur and nitrogen are to be reduced and the amount of product yield in ASTMD-86 distillation is to be improved. The reasons for the removal of sulfur and nitrogen is to prevent the catalyst poisoning in further refining steps and to reduce pollution from any eventual fuels made from the SRC-II process. Catalysts, either self-fabricated or commercial manufactured, were to be evaluated in a batch autoclave reactor and continuous trickle bed reactor in this research. The purpose is to determine the best catalyst and the best operation condition for trickle bed reactor.

## MATERIALS, EQUIPMENT AND PROCEDURES

### Feedstock

The Pittsburg and Midway Coal Mining Company provided the SRC-II product that was used as feed in this research. SRC-II product was made from Kentucky #9 Coal from the Colonial Mine. The analysis of this coal is listed in Table III. SRC-II product analyses are listed in Table II.

### Catalyst Fabrication

All catalysts fabricated at Montana State University were prepared by impregnating commercial supports with metal salts using the incipient wetness technique. The procedure used was as follows :

1. Oven dry the supports at 110 °C for 8 hours
2. Calcine the supports at 450 °C for 8 hours
3. Cool to room temperature in a dessicator
4. Record weight of the support
5. Impregnate the support in a slowly rotating jar with a specific metal solution, the concentration of which is calculated by the formulation(30) :

$$\begin{aligned} & \text{metal oxide percent in the support} \\ & = \text{conc. of solution} \times \text{pore vol.} / \\ & (1 + (\text{pore vol.} \times \text{conc. of solution})) \end{aligned}$$

The concentration of solution is further adjusted by experience.

6. Air dry in an air stream of 3 psig
7. Oven dry the impregnated supports at 110 °C for 8 hours
8. Calcine the impregnated supports at 450 °C for 8 hours
9. Cool to room temperature in a dessicator
10. Record the weight and calculate the weight percent of metal oxide impregnate.

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

#### Catalyst Pretreatment

All catalysts were pretreated by sulfiding. This procedure is used to activate the catalyst and to prevent the reduction of catalyst activity by hot hydrogenation(31,32). The catalyst was treated with a

10% hydrogen sulfide in hydrogen mixture for 12 hours in order to sulfide the metal oxides into the metallic sulfides. The stream of hydrogen sulfide was passed through the pipe reactor at approximately atmospheric pressure. Exit gas from the apparatus was scrubbed with 20% sodium hydroxide-water solution before venting to the hood. Temperature was maintained at 325 °C by use of a powerstat to control an electric pipe heater. Extreme caution should be taken whenever handling hydrogen sulfide because it causes coma and death within a few seconds after a few inspirations. Hydrogen sulfide is extremely hazardous because it fatigues the sense of smell in high concentrations; therefore, it gives no warning(33).

#### Batch Autoclave Runs

Batch runs were made in Parr Series 4,000 pressure reaction apparatus(34). The apparatus was heated in a rocking autoclave heater. The Parr autoclave and heater-rocker are shown in Figure 2.

The autoclave was charged with 25 ml of catalyst

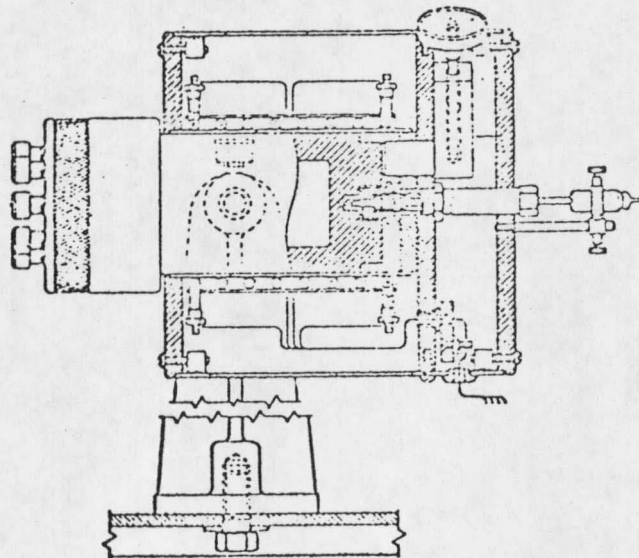
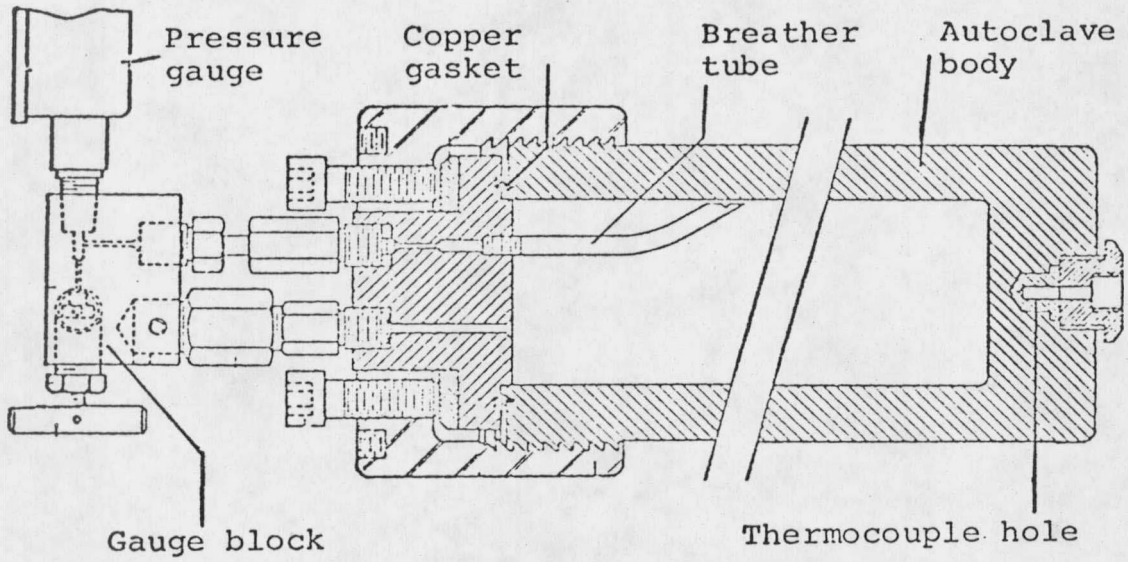


FIGURE 2. ROCKING AUTOCLAVE ASSEMBLY DETAILS

and 200 ml of SRC-II product. The copper head of autoclave and copper gasket were secured using a torque wrench. A new copper gasket was torqued to 60 ft-lb with subsequent 10 ft-lb increases per run. The copper gasket was replaced when a torque of 100 ft-lb was reached. After the head of reactor was secured, the pressure gauge and gauge block was attached to the autoclave head. The autoclave was pressurized with hydrogen to  $2,500 \pm 50$  psig using a Haskel gas booster air-driven compressor(35) and checked for leaks. The autoclave was then heated up to  $425 \pm 5$  °C in the heater-rocker(34), which usually took 1.5 hours. The residence time of a run was 1.5 hours. Silver Goop(36) was used on all threaded autoclave connections to prevent bolt seizure at high temperature. An iron-constantan thermocouple, placed in the base of the autoclave, connected to a single point Micromax recorder(37) monitored the temperature of reaction. Reaction temperature was controlled by manual adjustment of a powerstat variable transformer. Pressure and

temperature were recorded at 15 minute intervals during each run. Upon completion of the run, the autoclave was removed from the heater-rocker and allowed to cool to room temperature. Then the hydrogen consumption (measured by the difference in cold loading pressure and the final pressure at room temperature) was recorded. The gas in the autoclave was then vented in a hood by opening the needle valve in the autoclave gauge block. After the autoclave head and gauge block were removed, the liquid product was then filtered from the catalyst and analyzed.

#### Continuous Trickle Bed Reactor

The trickle bed reactor was designed and constructed by the Chemical Engineering Department at Montana State University prior to this research. The schematic diagram of the trickle bed reactor is shown in Figure 3.

Two different lengths of reactor were used in this research. One was forty inches long, the other thirty-six inches. Both of them are made by 1-inch

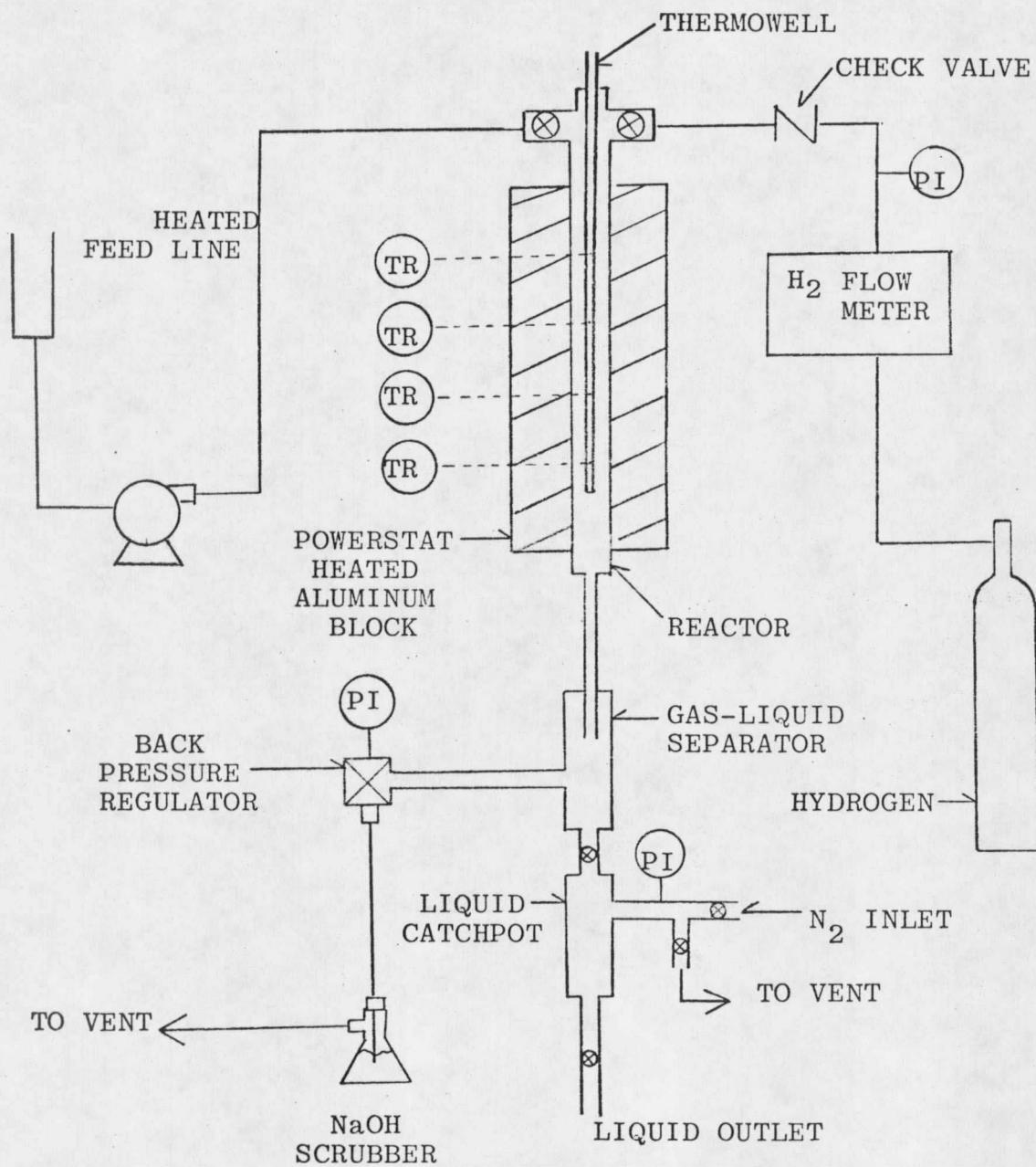


FIGURE 3. TRICKLE BED REACTOR

I.D. schedule-80 Inconel pipe. The top of the reactors are fitted with a 1/4-inch stainless steel cross. This allows the fitting of a 36-inch, or 32-inch, stainless steel tubing, which serves as a thermowell, and the fitting of two feed ports, one for SRC-II feed and one for hydrogen.

The reactors are placed into the 1-inch bore hole of a 6-inch O.D. aluminum block which is about three feet long. The longer reactor extends 6-inch outside the top of aluminum block, the top of shorter reactor and aluminum block are about of equal length. The aluminum block is wrapped with three sets of nichrome wire heating coils encased in ceramic beads. Each heating coil is connected to a Powerstat variable transformer which is manually controlled for temperature. Four iron-constantan thermocouples were placed in the thermowell at six inch intervals. These four thermocouples allow the monitoring of two temperatures in the preheat section of the reactor and two temperatures in the catalyst section of the bed. In the

preheat zone, the longer reactor and shorter reactor were loaded at the top with 175 c.c. and 125 c.c. of 1/4" Denstone support(38) respectively, then followed by 25 c.c. of 1/8" Denstone inert support. The sixty cubic centimeters of catalyst mixed with 60 c.c. of 1/8" inert support was loaded into the catalyst zone. The bottom section of the reactor was filled with 1/8" Denstone inert support. Then a cone of stainless steel screen was inserted as a plug support above the 1/4-inch I.D. reactor closure that was threaded into the pipe. The threaded connection was sealed with Teflon tape and Silver Goop to prevent leakage.

SRC-II product was pumped into the top of the reactor by use of a Milton Roy Model MR-1-49 Simplex packed piston pump through a 1/8" stainless steel feedline. The pump is equipped with a manually controlled micrometer adjustment for feed rate control. All feedlines and reservoirs were wrapped with Cole-Parmer flexible heating cords(39) to prevent the feed from freezing up. Technical grade hydrogen is fed

through a regulator, a micrometer valve, a Brooks Thermal Mass Flowmeter(40), and a ball check valve to the top of the reactor.

Gases and liquids passed through the reactor to a gas-liquid separator. The gases pass through a condenser and through a Grove back pressure regulator. The Grove back pressure regulator was equipped with a Teflon diaphragm to handle the corrosive gases. The exit gases passed through a 20% NaOH-water solution and then was vented. A wet test meter can be connected before the gas is vented in order to calibrate the Brooks Thermal Mass Flowmeter. The liquids passed from the gas-liquid separator into a pressurized catchpot. When a liquid sample was taken, the valve between the separator and the catchpot was closed. The catchpot was then depressurized and the sample was drained from the bottom of the catchpot. The catchpot was then repressurized with nitrogen and the valve was reopened.

#### Continuous Trickle Bed Runs

After the reactor was loaded as previously des-

cribed, it was placed in the aluminum block. The catch-pot system, and the liquid and hydrogen feedlines were attached. The thermocouples, connected to a Leeds and Northrup Multipoint recorder, were then placed in the thermowell. The whole system except the pump was pressurized and checked for leaks. If no leaks were found, the system was depressurized. The variable Powerstats were then turned on and the system was allowed to heat for ten hours.

When the reactor reached run temperature, the SRC-II product, all liquid feedlines, reservoirs and pump jacket were preheated. The feed reservoir was filled and SRC-II product was pumped through the feed lines. Then the pump was stopped and the feed line connected to the top of the reactor. If the feed line is not filled first, the pump will tend to cavitate on the pressurized system.

The reactor was slowly pressurized with hydrogen. When the system had reached the desired pressure, the by-pass valve on the flowmeter was closed and the micro-

metering valve was adjusted to keep the desired hydrogen flow rate, 10,000 standard cubic feet per barrel (scf/bbl). The valve of the feed line was then opened and the pump started. The liquid flow rates were measured by using a stop watch and timing the flow from a graduated side-arm attached to the main feed reservoir. The flow rate was checked frequently to maintain an even flow and the average flow rates was reported. The flow rates for all runs were kept at a liquid hourly space velocity (LHSV) of one except Run A-2 which was 0.5 LHSV.

For Runs A-1 to A-4, samples were taken every three hours for 12 hours. In Runs A-5 to A-21, only two hour samples or a little longer were collected. Runs A-22 to A-25 were shut down when the reactor pressure reached 1,300 psig. In Runs A-5 to A-25, unless specifically noted, samples were taken as follows :

Time on Stream

minutes :	30	45	60	75	90	105	120	150	180	210	240
sample :	1	2	3	4	5	6	7	8	9	10	11

The amount of samples in Runs A-21 to A-25 were measured by volume. The ratio of sample volume to the volume of feed was reported as the yield of oil. Gaseous products and hold-up in the reactor were not part of the yield.

After the last sample was taken, the pump was shut off, the valve between the feed line and reactor was closed and the feed line was removed. The excess SRC-II product was then drained.

The hydrogen flow and heaters were shut off and the reactor was depressurized. The catchpot system was removed and cleaned thoroughly with acetone. The hydrogen inlet valve at the top of reactor was then closed. The reservoirs were filled with 30 W motor oil, which was pumped through the feed line while the reactor was still hot. The motor oil was to loosen catalyst particles and flush the system of reactants. The smoke from hot motor oil is very hard to tolerate and the room must be vented thoroughly during cleaning. After flushing with motor oil, the reactor was removed from the aluminum block with asbestos gloves. The feed

line and reservoir were cleaned with acetone. After the reactor was cooled to room temperature, catalyst and inert supports were knocked or drilled out. Then the reactor was cleaned with acetone to be used in the next run.

#### Analytical Procedure

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

Sulfur analysis was done on all samples for continuous Runs A-1 to A-4, and for all batch runs. Sulfur analysis on selected samples was done for continuous Runs A-5 to A-25. The analyses were performed by the quartz tube combustion method using a Bico-Brown Shell design sulfur apparatus(41,42,43). Sulfur content of the feed, SRC-II, is 0.72 wt%. Weight percent desulfurization (% DS) was calculated as follows :

$$(0.72\% - \text{wt\%}) / 0.72\% = \%DS$$

Nitrogen content was determined by Macro-Kjeldahl method(43,44,45) using 0.5 grams of samples and 40 grams of potassium sulfate. SRC-II contains 1.17% nitrogen. Weight percent denitrogenation (%DN) is calculated similarly to %DS.

The extent of cracking was determined by ASTM D-86 atmospheric distillation(46). This technique measures the cumulative amount of product which boils below 700 °F or when decomposition begins, whichever occurs first. The amount of the sample used for the distillation was 50 ml whenever possible.

## RESULTS AND DISCUSSION

Twenty-two batch autoclave runs and twenty-five continuous trickle bed runs were performed. Four commercial catalysts and twenty-nine catalysts that were fabricated at Montana State University were tested in these runs. The data for each run are presented in the appendices. Appendix A contains the data from the batch runs which are specified the prefix B. Appendix B contains the data from the continuous runs which are specified the prefix A. All samples taken from all runs were analyzed for nitrogen content and the amount of distillable liquids. Sulfur analyses, for Runs A-5 to A-25, were done only on periodic samples to reduce the load of analytical work. A few samples in Runs A-7 and A-14 were missed due to the inadvertant handling in the process of analysis.

Commercial catalysts used are shown in Table IV. A variety of pore diameter bases in Table V were received from Nalco Chemical Company. Three major effects were to be investigated:

- (1) the effect of the base; pore diameter, pore

TABLE IV

## COMMERCIAL CATALYST DESCRIPTION

Catalyst*	Chemical Combination	Surface Area, m <sup>2</sup> /g	Pore Volume, ml/g	Ave. Pore Diameter, Å <sup>**</sup>
HARSHAW HT-400E 1/16"	15%MoO <sub>3</sub> , 3%CoO	220	.5	91
CYANAMID HDS-20A 1/16", Trilobe	16.2%MoO <sub>3</sub> , 5%CoO	230	.52	90
NALCO NM 502 1/16"	14%MoO <sub>3</sub> , 4%NiO	240	.53	88
NALCO MO 477 1/16"	14%MoO <sub>3</sub> , 3.3%CoO	250	.55	88
HARSHAW HT-400E 1/16" 720A-2-1-1	14.8%MoO <sub>3</sub> , 2.8%CoO	222	.51	110

\* Catalysts are on alumina bases

\*\* Ave. Pore Diameter(Å) =  $40,000 \frac{\text{Pore Volume}}{\text{Surface Area}}$

TABLE V  
 PROPERTIES OF CATALYST BASES

Sample No.	Composition	Surface Area, m <sup>2</sup> /g	Pore Vol. ml/g	Median Pore Dia. Å	Average* Pore Dia., Å
NALCO-78-6008A-1/32"	4%SiO <sub>2</sub> , 96%Al <sub>2</sub> O <sub>3</sub>	323.2	.7183	90.2	88.9
NALCO-78-6008B-1/16"	100%Al <sub>2</sub> O <sub>3</sub>	232.4	.7215	137.3	124.2
NALCO-78-6008C-1/32"	2%SiO <sub>2</sub> , 98%Al <sub>2</sub> O <sub>3</sub>	214.57	.8397	161	156.5
NALCO-78-6008D-1/16"	9%P <sub>2</sub> O <sub>5</sub> , 91%Al <sub>2</sub> O <sub>3</sub>	211.39	.7943	190	150.3
NALCO-78-6008E-1/16"	17%P <sub>2</sub> O <sub>5</sub> , 83%Al <sub>2</sub> O <sub>3</sub>	146.95	.6841	420.2	186.2
NORTON-6176-1/16"	99.85%Al <sub>2</sub> O <sub>3</sub> , .12%SiO <sub>2</sub> , .014%Na <sub>2</sub> O	250	.70		152

\* Average Pore Diameter, Å = 40,000(Pore Vol./Surface Area)

volume and surface area specifically

(2) the effect of  $\text{MoO}_3$  content

(3) the effect of additional  $\text{WO}_3$

by impregnating the same or nearly the same amount of metal oxides on to each base as well as different metal compositions on to the same base. Table VI presents the actual analyses of the amount of metals loaded and the base carrier material. All catalysts fabricated at Montana State University were designated the prefix MSU. NiO and CoO were kept as constant as possible, the objective content of NiO and CoO, prior to MSU-C24-E, being 0.5% and 0.8% respectively. Catalysts MSU-C25-A to MSU-C29-E were impregnated the same metal composition of 13% $\text{MoO}_3$  3.0%NiO 7.0%CoO 10.0% $\text{WO}_3$ .

#### Batch Autoclave Runs

Batch tests were performed on SRC-II product to evaluate the activity of catalysts. As continuous runs had been very long, it was thought that the batch runs could provide relatively fast catalyst testing. In an attempt to investigate the activity of catalysts influenced by the base,  $\text{MoO}_3$  content and additional  $\text{WO}_3$ , twenty-two

TABLE VI  
MSU CATALYST DESCRIPTION

Catalyst	%MoO <sub>3</sub>	%NiO	%CoO	%WO <sub>3</sub>	Base
MSU-C1-A	19.4	.1	.43	-	NALCO-78-6008A-1/32"
MSU-C2-A	12.0	.48	.1	-	NALCO-78-6008A-1/32"
MSU-C3-A	10.4	1.16	.11	-	NALCO-78-6008A-1/32"
MSU-C4-A	9.1	.37	1.38	8.2	NALCO-78-6008A-1/32"
MSU-C5-B	18.6	.26	.45	-	NALCO-78-6008B-1/16"
MSU-C6-B	14.8	.19	1.17	-	NALCO-78-6008B-1/16"
MSU-C7-B	14.6	.13	5.8	-	NALCO-78-6008B-1/16"
MSU-C8-B	9.8	.45	.43	-	NALCO-78-6008B-1/16"
MSU-C9-B	8.3	.57	1.55	8.8	NALCO-78-6008B-1/16"
MSU-C10-C	20.6	.1	1.08	-	NALCO-78-6008C-1/32"
MSU-C11-C	11.1	.1	1.56	-	NALCO-78-6008C-1/32"
MSU-C12-C	9.5	.44	1.77	-	NALCO-78-6008C-1/32"
MSU-C13-C	9.05	.79	1.6	9.0	NALCO-78-6008C-1/32"
MSU-C14-D	20.7	1.86	1.2	-	NALCO-78-6008D-1/16"
MSU-C15-D	13.7	.78	.1	-	NALCO-78-6008D-1/16"

TABLE VI(continued)

Catalyst	%MoO <sub>3</sub>	%NiO	%CoO	%WO <sub>3</sub>	Base
MSU-C16-D	11.8	.1	1.9	-	NALCO-78-6008D-1/16"
MSU-C17-D	9.3	.17	1.76	8.8	NALCO-78-6008D-1/16"
MSU-C18-E	29.3	.1	.1	-	NALCO-78-6008E-1/16"
MSU-C19-E	18.9	.1	3.5	-	NALCO-78-6008E-1/16"
MSU-C20-E	13.0	.1	.3	-	NALCO-78-6008E-1/16"
MSU-C21-E	9.5	.37	1.89	-	NALCO-78-6008E-1/16"
MSU-C22-E	9.8	.3	1.4	9.2	NALCO-78-6008E-1/16"
MSU-C23-B	23.0	.2	1.4	-	NALCO-78-6008B-1/16"
MSU-C24-E	15.5	.15	2.3	-	NALCO-78-6008E-1/16"
MSU-C25-A	12.5	2.66	6.65	9.66	NALCO-78-6008A-1/32"
MSU-C26-B	13.2	3.0	6.7	9.45	NALCO-78-6008B-1/16"
MSU-C27-C	11.54	3.16	6.6	9.5	NALCO-78-6008C-1/32"
MSU-C28	12.6	2.87	6.48	7.75	NORTON-6176-1/16"
MSU-C29-E	14.4	3.1	4.5	9.1	NALCO-78-6008E-1/16"

catalysts were tested in the batch autoclave runs, which are designated B-1 to B-22. The detailed data from these tests are presented in Appendix A. Table VII summarizes the catalyst activity on denitrogenation, desulfurization, and distilled yield at 650 °F. Unfortunately, it is hard to determine which base is the best or to obtain a general expression for the effect of composition of catalyst effectiveness from these data. Figures 4, 5, 6, and 7, 8 help to show the tendency of each base for the different amounts of MoO<sub>3</sub> impregnated. Nevertheless some important information still can be obtained from these figures : (1) a better catalytic activity for both desulfurization and denitrogenation can be obtained by increasing the content of MoO<sub>3</sub> on base B (2) increasing the concentration of MoO<sub>3</sub> on base A or decreasing it on bases C and D might yield a better catalyst for desulfurization (3) there is no significant improvement in denitrogenation with additional WO<sub>3</sub>. The distillation results of batch





















































































































































































