Effect of successive regenerations on catalysts used for hydrotreating SRC-II

by Muthuswamy Rameswaran

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

Abstract:
Three catalysts were fabricated with supports supplied by NALCO Chemical Company having 90Å, 220Å and 420Å median pore diameter for hydrotreating Solvent Refined Coal (SRC-II, Light End Column Feed) from Pittsburg and Midway Coal Mining Company. These supports were impregnated with 4.0% cobalt oxide (CoO), 8.0% molybdenum oxide (MoO_3), 1.0% nickel oxide (NiO) and 8.0% tungsten oxide (WO_3).

Ten runs were made with each catalyst in a batch reactor and regenerated after every one hour at run temperature. The denitrogenation effect and the pore volume after every regeneration were measured. There was no significant difference in the denitrogenation activity of the three catalysts. All three catalysts could be regenerated successively with compressed air without much damage to their pores.

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature Rameswaran.

Date May 11, 1982.

EFFECT OF SUCCESSIVE REGENERATIONS ON CATALYSTS
USED FOR HYDROTREATING SRC-II

by

MUTHUSWAMY RAMESWARAN

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemical Engineering

Approved:

Lloyd Berg

Chairperson, Graduate Committee

J.P. McCandless

Head, Major Department

Michael Malone

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

May, 1982

ACKNOWLEDGMENTS

The author wishes to thank the staff of the Chemical Engineering Department at Montana State University for their help and encouragement. A special thanks goes to Dr. Lloyd Berg, Dr. F. P. McCandless and Dr. W. P. Scarrah, for their guidance with this research.

The author wishes to extend his thanks to the United States Department of Energy for their financial support.

A special thanks goes to Mr. L. Fellows, for the help rendered during this research.

The author also wishes to thank Mr. A. Yeh and other members of this research team for their helpful suggestions and cooperation during this research.

Finally, the author thanks his parents for their encouragement and moral support during his stay in the United States of America.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Three catalysts were fabricated with supports supplied by NALCO Chemical Company having 90Å, 220Å and 420Å median pore diameter for hydrotreating Solvent Refined Coal (SRC-II, Light End Column Feed) from Pittsburg and Midway Coal Mining Company. These supports were impregnated with 4.0% cobalt oxide (CoO), 8.0% molybdenum oxide (MoO_3), 1.0% nickel oxide (NiO) and 8.0% tungsten oxide (WO_3).

Ten runs were made with each catalyst in a batch reactor and regenerated after every one hour at run temperature. The denitrogenation effect and the pore volume after every regeneration were measured. There was no significant difference in the denitrogenation activity of the three catalysts. All three catalysts could be regenerated successively with compressed air without much damage to their pores.

INTRODUCTION

Conversion of coal to fluid fuels is approaching a time when synthetic gasoline and pipeline gas will be manufactured in the United States of America (U.S.A.) on an enormous scale. Reasons include the growing needs for energy, the large reserves of coal and the limited reserves of petroleum and new technological advances in production of fluid fuels from coal.

There is a critical widening gap between supply and demand for petroleum in the U.S.A., although petroleum reserves are thought to be adequate for some time to come. However, reserves-to-consumption ratios are declining as new discoveries have not kept pace with the demands. Though nuclear power will play an important role in fulfilling the energy shortage, it will not be able to fulfill the growing demand for liquid fuel for the transportation sector of energy demand (1).

Over forty years ago, the concept of complete gasification of coal with oxygen under pressure was put into practice by the pioneering work of Drawe, Danulat and Hubmann (2). Later, during World War II, Germany had converted coal into gasoline in substantial amounts. One plant is currently in operation in South Africa.

There are three major ways to convert coal into liquid fuels. They are pyrolysis, direct hydrogenation and indirect hydrogenation. Of these, the direct hydrogenation process has captured the most attention due to economic considerations.

The United States Department of Energy (DOE) is currently encouraging the development of coal gasification and liquefaction processes. The gasification processes include BiGas, HYGAS and Synthane processes, and liquefaction processes include the Solvent

Refined coal process (SRC), the Exxon Donor Solvent process (EDS) and the Synthoil process. The SRC process is the oldest of these modern processes. The original SRC process is known as SRC-I and the modified version is called SRC-II.

The products of SRC-II cannot be used directly as a transportation fuel or as a feed stock acceptable to a conventional refinery. The nitrogen and sulfur content of the product is higher than the Environmental Protection Agency (EPA) specifications. Therefore, this product should be catalytically hydrorefined to be commercially available to the general public. This research is expected to give the SRC-II process technical advancement to improve the product and have an advantage over the other processes for commercialization.

BACKGROUND

The major problem met in conversion of coal to acceptable fuel is meeting the EPA air quality regulations; this can be resolved by removing the contaminants from coal before using it. The process begins with coal washing and preparation at the mines. The next major step is purifying coal via the solvent refining coal process (SRC process), which has been under development since the early 1970s and for which a 50 ton per day demonstration plant was built in Fort Lewis, Washington, by Pittsburg and Midway Coal Mining Company (P&M Company). This process produces a low sulfur low ash coal liquid.

The SRC process consists of the following major steps:

(1) Coal preparation and pulverizing to a fine particle size (approximately 200 mesh).

(2) Blending of fine coal with coalbased hydrocarbon solvent.

(3) Reaction at high temperature (480°C) and high pressure (about 2400 psig).

(4) Solvent recovery, utilizing high temperature vacuum flashing, and distillation for the separation of various hydrocarbon oil fractions.

(5) Removal of a gas containing the evolved sulfur compounds.

(6) Product collection.

Tests have indicated that coal of almost any quality except possibly anthracite is amenable to refining by the SRC process. A schematic flow sheet of the SRC process is given in Figure 1 (3).

Chemical and Physical Properties of SRC-II Product

The SRC-II product cannot be considered as single product process. Various products in the SRC-II oil are tabulated in Table 1 (4). Properties of P&M's SRC-II products (Light

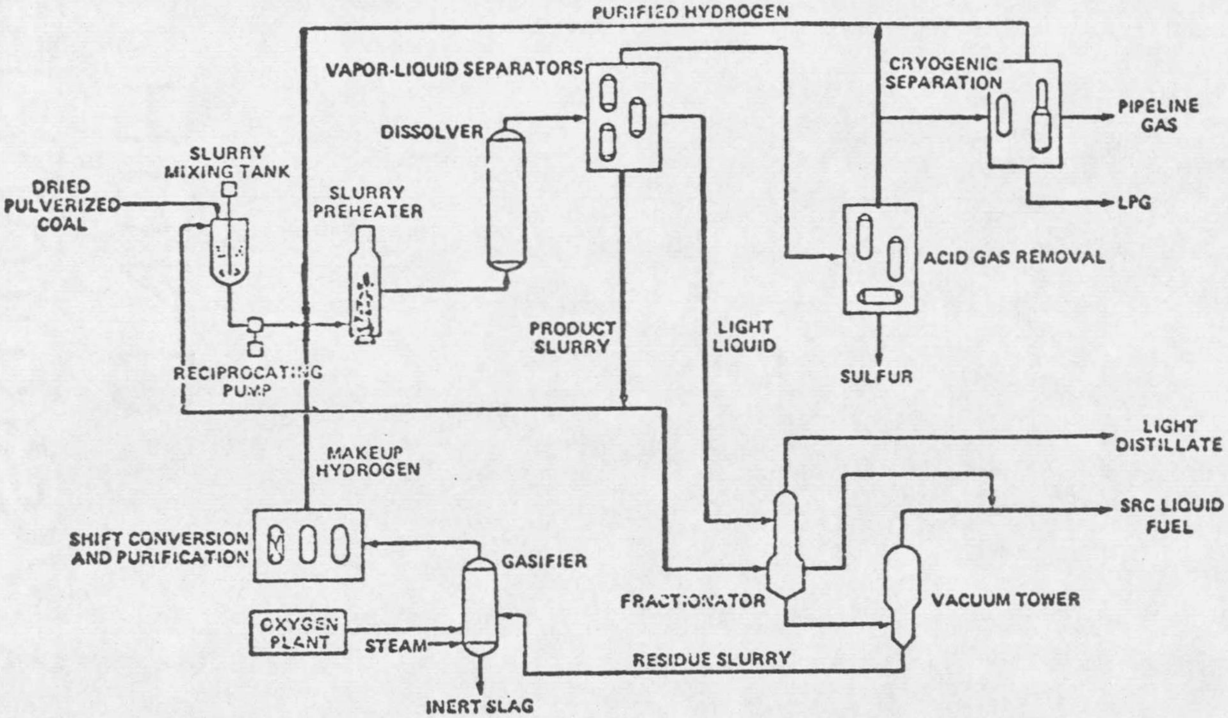


Figure 1. SRC-II Process (P&M's 50 ton pilot plant).

End Column feed) are shown in Table 2 (5). The SRC-II product used in this research was made from refining Kentucky #9 coal from the Colonial mines. The analysis of this coal is shown in Table 3 (6).

Chemistry of Coal Liquefaction

The term coal is applied to a wide range of substances. It is formed by metamorphosis of vegetable matter under pressure and heat, over a long period of time. According to Francis, coal is (7,8):

> . . . a compact stratified mass of mumified plants which have been modified chemically on varying degree, interspersed with smaller amounts of inorganic matter.

In the strict sense there is no such thing as a coal molecule. Yet scientists have identified many molecular subgroups in a so-called coal molecule. These subgroups are present in all coals, lignites and other similar products. The most prominent of these groupings is the benzene ring and condensed ring varieties such as maphthalene and anthracene. Larger ring compounds are also abundant.

Oxygen is one of the most common elements which is found in any typical representative molecule of coal besides carbon and hydrogen. The percentage of oxygen diminishes from 25% in lignite to almost 0% in anthracite (9). Other than oxygen, sulfur and nitrogen are also found in molecules of coal. These elements are scattered all over the coal molecules, either as part of heterocyclic rings or as a part of functional subgroups. Figure 2 (9) gives a typical representation of coal molecule.

The solvent refined coal process (SRC-II) eliminates almost all mineral matter. The products are practically ash free. Yet the nitrogen and sulfur content is too high to be used as a substitute alternate for refinery feed stock or gasoline. Before it can be used for the

Table 1. SRC Process Gas and Liquid Yields.*

C_1-C_4 gas, Scf**	3130
CH_4 gal	2100
C_5-350°F, gal	32
bbl	0.762
350-750°F distillable, gal	38
bbl	0.094
Total liquid, gal	70
bbl	1.666

**Approximate analysis of C_1-C_4 gas cut:

	Vol. %	BTU Value/ft³ of Total Gas
CH_4	67.0	680
C_2H_6	19.3	340
C_3H_8	10.0	260
C_4H_{10}	3.7	120
	100.0	1400

*Per ton of SRC.

Table 2. Properties of SRC-II Light Ends Column Feed.

	Light Ends Column Feed
% Carbon	–*
% Hydrogen	–*
% Nitrogen	0.88
% Sulfur	1.21
% Oxygen	–*
% Ash	0.02
Sp. Gravity 60/60°F	0.983
ASTM D-86 DISTILLATION	
IBP	122
5%	217
10%	288
20%	381
30%	446
40%	488
50%	541
60%	577
70%	611
80%	660
90%	727
95%	795
End Point	956

*Data not available.

Table 3. Properties of Kentucky #9 Coal.*

Average Raw Coal Analysis (Wt %)	
Ash	9.55
Moisture	6.14
Average Dried Pulverized Coal Analysis (Wt %)	
Carbon	70.76
Hydrogen	5.18
Nitrogen	1.53
Sulfur	3.57
Oxygen (by difference)	8.60
Ash	9.97
Moisture	6.39
Average Analysis of Forms of Sulfur (Wt %)	
Pyritic Sulfur	2.03
Sulfate Sulfur	0.27
Organic Sulfur	1.27
Total Sulfur	3.57

*Analyzed in June, 1979.

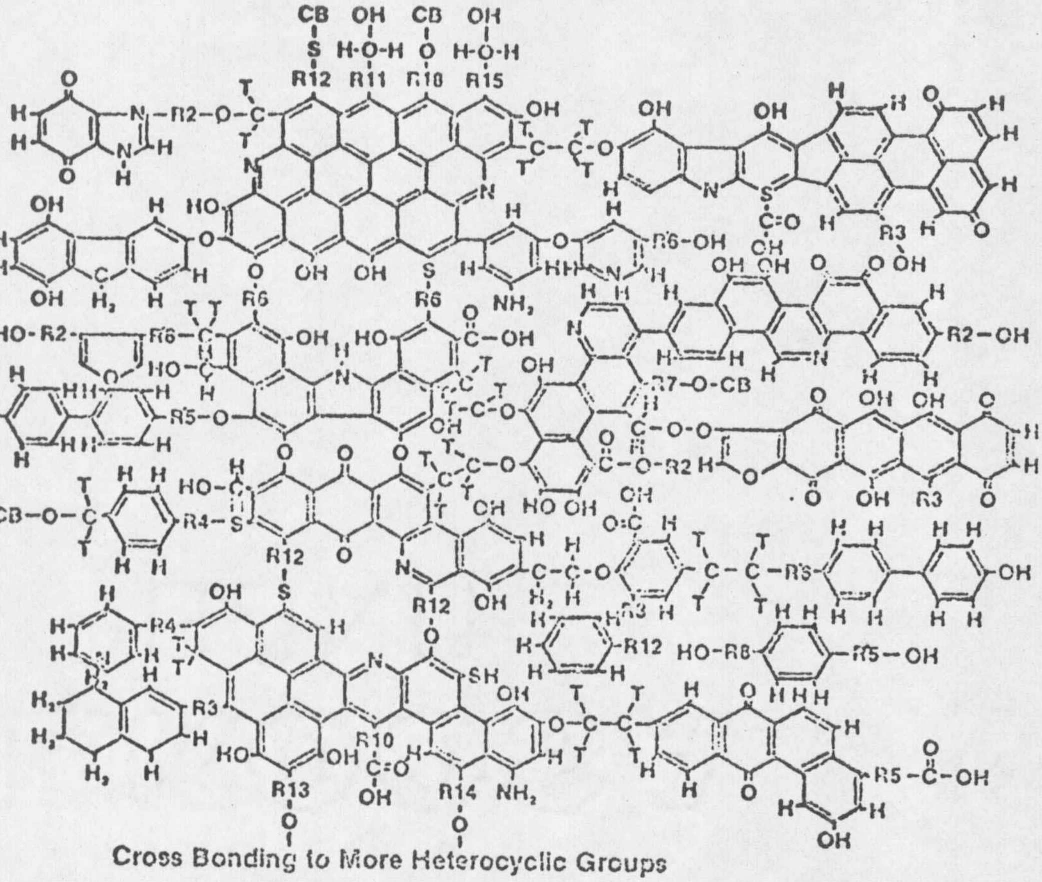


Figure 2. A Typical Coal Molecule.

above mentioned purposes, SRC-II has to be catalytically upgraded by removing the nitrogen and sulfur and increase hydrogen to carbon ratio. Saturating the unsaturated bonds with hydrogen is also accomplished. The processes of hydrogenation, denitrogenation and desulfurization play an important role in this research.

Hydrodesulfurization (HDS)

Hydrodesulfurization processes are those of the following class:

Organic					desulfurized
Sulfur	$+ H_2$	$\rightarrow$	H_2S	$+$	organic
Compound					compound

The following is a listing of important reactions occurring in hydrodesulfurization processes. Those reactions which result in cleavage of C-S bonds are known as hydrogenolysis. For example:

$$R - SH + H_2 \rightarrow RH + H_2S$$

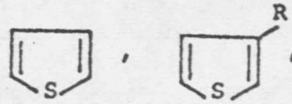
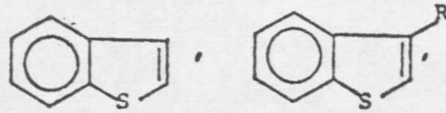
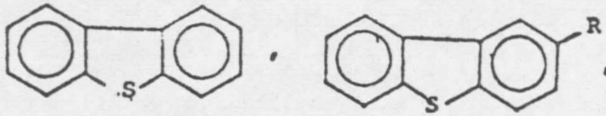
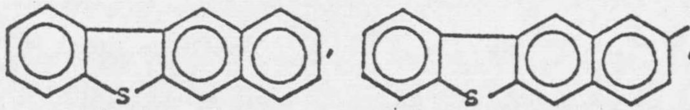
Under severe conditions, hydrogenolysis reaction which would result in breaking of C-C bonds (hydrocracking) also occur, for example:

$$R - CH = CH - R' + H_2 \rightarrow R - CH_2 - CH_2 - R' \xrightarrow{+H_2} R - CH_3 + R' - CH_3$$

The cracking reactions are important, since large molecules break up to produce low molecular weight compounds.

Some of the most commonly found sulfur containing compounds in coal liquids are shown in Table 4 (10). A typical example of the hydrodesulfurization reaction of benzothiophene is shown in Figure 3 (10).

Table 4. Some Sulfur Containing Compounds in Coal Liquids.

Thiols (Mercaptons)	R-SH
Disulfides	R-S-S-R'
Sulfides	R-S-R'
Thiophenes	 , etc
Benzothiophenes	 , etc
Dibenzothiophenes	 ,etc
Benzonaphtho- -thiophenes	 ,etc

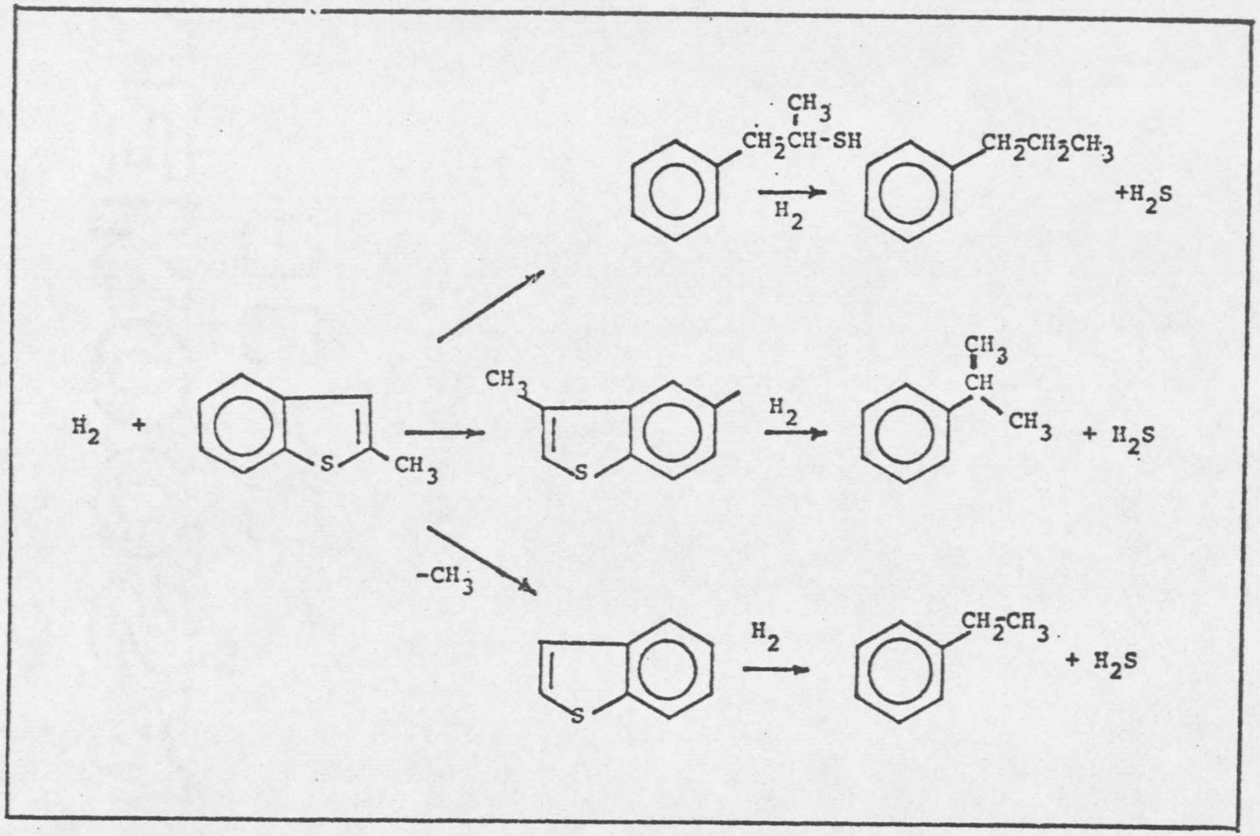


Figure 3. Hydrodesulfurization Reaction.

Hydrodenitrogenation (HDN)

Nitrogen compounds are undesirable in processing of coal liquids as mentioned elsewhere in this thesis. It is also probable that the conditions required to reduce the nitrogen will effectively remove sulfur in coal liquids.

Some previous research in HDN proves that complete hydrogenation of unsaturates is required before the C-N bond is broken. Thus HDN requires a large consumption of hydrogen before the nitrogen atom is removed from the hydrocarbon backbone (11). The following is an example reaction for hydrodenitrogenation.

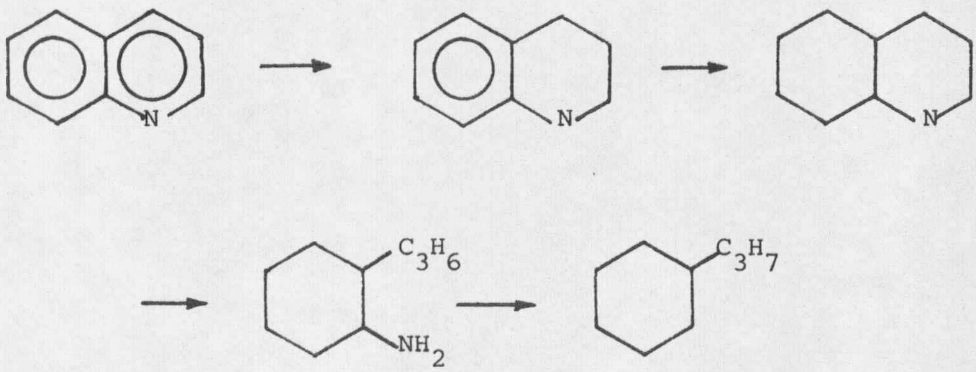


Figure 4. Hydrodenitrogenation Reaction.

Catalysts

Further developments in upgrading coal liquids depend mainly on searching for the optimum catalyst. Traditionally hydrotreating catalysts used for hydrocarbon processes are metal oxides impregnated on high surface area inert supports.

Commercially many catalysts are available for hydrotreating petroleum products. These catalysts contain various combinations of oxides of cobalt, molybdenum, tungsten and nickel, impregnated on supports made of aluminum oxide, silicon oxide or a combination of both. These catalysts can also be used for upgrading process.

The most common metal oxide found in hydrotreating catalyst are molybdenum and tungsten. The other oxides, such as Co, Ni, Fe, Zn and Cr are known as promoters. These promoters are said to expose the active centers of the cobalt and molybdenum ions for the hetroatom removal reaction (12).

Deactivation of these catalysts under hydrotreating conditions is the greatest problem faced by researchers involved in synthetic fuel. The deactivation of the catalysts are due to the following reasons:

(1) Carbonaceous material deposits

(2) Catalyst walls collapsing and reducing the actual surface available for reaction

(3) Deposits of mineral matter (ash)

Among the above three, the most common are the deposits of carbonaceous material in the pores. It is believed that Solvent Refined Coal has a high asphaltene content which has an average size of 40-50 Å per molecule (13). Pores which are smaller in size than that of the asphaltene molecules tend to plug up. This problem can be, to some extent, avoided by using catalyst supports whose pore dimensions are larger than 50 Å after impregnation and yet have high surface areas.

These carbonaceous materials can be burned off by passing controlled amount of oxygen at a temperature around 550°C, and regain the loss in activity due to these deposits. This process is known as regeneration. Temperatures above 600°C were avoided in this research by carefully controlling the oxygen supply in order to save the catalyst supports from sintering. Cause for such deactivation due to high temperature may be due to collapsing of pore walls and reduction of the active centers available to reactions.

The last form of deactivation, which is deposition of mineral matter (ash) on the surface, is a serious problem encountered in coal liquefaction catalysts SRC-II process Light End Column Feed (LECF), the feed used in this research, has practically no ash (refer to Table 2). So, in this research ash was not considered as a serious problem.

It has been reported earlier in this thesis that the impregnated catalyst should have pore diameters larger than the size of asphaltene molecules (50 Å). Very large pore diameter may allow most of the asphaltene molecule to pass through the pores without ever contacting the active centers and smaller diameter supports may plug up and deactivate the catalyst. The purpose of this research is to select a catalyst support which will give the best denitrogenation and yet last through successive regenerations.

RESEARCH OBJECTIVES

This research is a part of a larger project which is to develop a unique catalyst which would be used for upgrading coal liquids. The feed stock used in this research was Light End Column feed, a product obtained from SRC-II process pilot plant of Pittsburg and Midway Coal Mining Company (P&M Company).

A catalyst should be developed which will upgrade the SRC-II product into a clean distillate fuel and/or a feed stock acceptable to a conventional refinery. The objective of this research is to find a support with optimum pore diameter which would last through successive regenerations.

It is hoped that this research would help to narrow the range of investigation of pore diameters of supports.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental procedure for this research consisted of the following major steps.

(1) Catalyst Preparation

(2) Batch Run

(3) Regeneration

(4) Analysis of Product

Catalyst Preparation

Three catalysts were fabricated here at Montana State University with Nalco bases. The properties of the three bases are tabulated below.

Table 5. Properties of Catalyst Bases.

Support	Surface Area (m^2/g)	*Pore Volume (m^1/g)	Medium Pore dia. (Å)	**Ave. Pore dia. (Å)
Nalco 78-6008A	323.2	0.7183	90 Å	88.9
Nalco 80-6477	280.6	0.9313	220 Å	132.8
Nalco 78-6008E	146.95	0.684	420 Å	186.2

*Evaluated and reported by Nalco (14).
**Ave. Pore Dia. = 40,000 * Pore Vol./Surface Area.

The supports were impregnated with 4.0% CoO, 8.0% MoO_3, 1.0% NiO and 8.0% WO_3, in the same order (all percentages were by weight). This combination of metal oxides was reported by Yeh to have the best HDN activity (15).

The impregnation of metal oxide on the supports was carried as follows:

(1) Oven dry the supports at 110°C for 8 hours.

(2) Calcine the support at 450°C for eight hours.

(3) Cool to room temperature in a desiccator.

(4) Record weight of the calcined support.

(5) Prepare salt solution for impregnation

i. calculate the amount of metal oxide to be impregnated to get the desired percentage.

ii. calculate the concentration of salt solution to be used for impregnation by the formulation:

metal oxide percent in support = conc. of solution × pore volume/(1 + (pore vol. × conc. of solution))

The concentration was further adjusted by experience. The volume of solution should be at least the same as the volume of support

(6) Mix the weighed support and the solution in a jar.

(7) Rotate the jar with the help of a motor at 7 to 9 rpm and pass air through at 3 psig.

(8) When the support is dry, remove from the jar and oven dry for 8 hours at 110°C.

(9) Calcine the salt impregnated support at 450°C for 8 hours.

(10) Cool the support to room temperature in desiccator.

(11) Weigh the impregnated support.

(12) Increase in weight gives the amount of oxide impregnated and hence the weight percent.

The procedure was repeated until all the required salt was impregnated to within desired accuracy. This method is known as incipient wetness technique.

The salts used in impregnation were

(1) Cobaltous Nitrate ($Co(NO_3) \cdot 6\, H_2O$)

(2) Ammonium Molybdate ($(NH_4)_6 \cdot Mo_7O_{24} \cdot 4H_2O$)

(3) Nickelous Nitrate ($Ni(NO_3)_2 \cdot 6\, H_2O$)

(4) Ammonium Tungstate ($(NH_4)_6 \cdot H_2W_{12}O_{40} \cdot H_2O$)

Hydrodenitrogenation and hydrodesulfinization catalysts are usually sulfided (8,16 , 17). It is speculated that adsorption of small amounts of H_2S modified the surface energy balance and led to higher catalytic activity. Also, it reduces cracking activity which leads to high surface concentrations of unsaturated carbon species which polymerize and coke up the pores (18).

The calcined metal oxide catalyst was placed in a one inch diameter tube and placed in a heating block. The tube had a concentric thermowell for temperature measurement. The temperature was controlled using a powerstat and maintained at 350 ± 10°C. Ten percent H_2S in hydrogen was passed through the tube for at least 10 hours at the rate of 3 to 4 ml per min. The exit H_2S was scrubbed by using a series of flasks containing 10% solution of sodium hydroxide (Fig. 5). Since H_2S is a highly dangerous gas, extreme caution was taken while handling. High concentration of H_2S cannot be smelled and exposure to such concentration could be fatal (19).

A small sample of unsulfided catalyst was taken for measuring pore volume. The pore volume was measured by the method of titration (20). The procedure adopted was as follows:

(1) Dry approximately 1 gram of sample at 110°C for one hour.

(2) Weigh the sample on a glass plate.

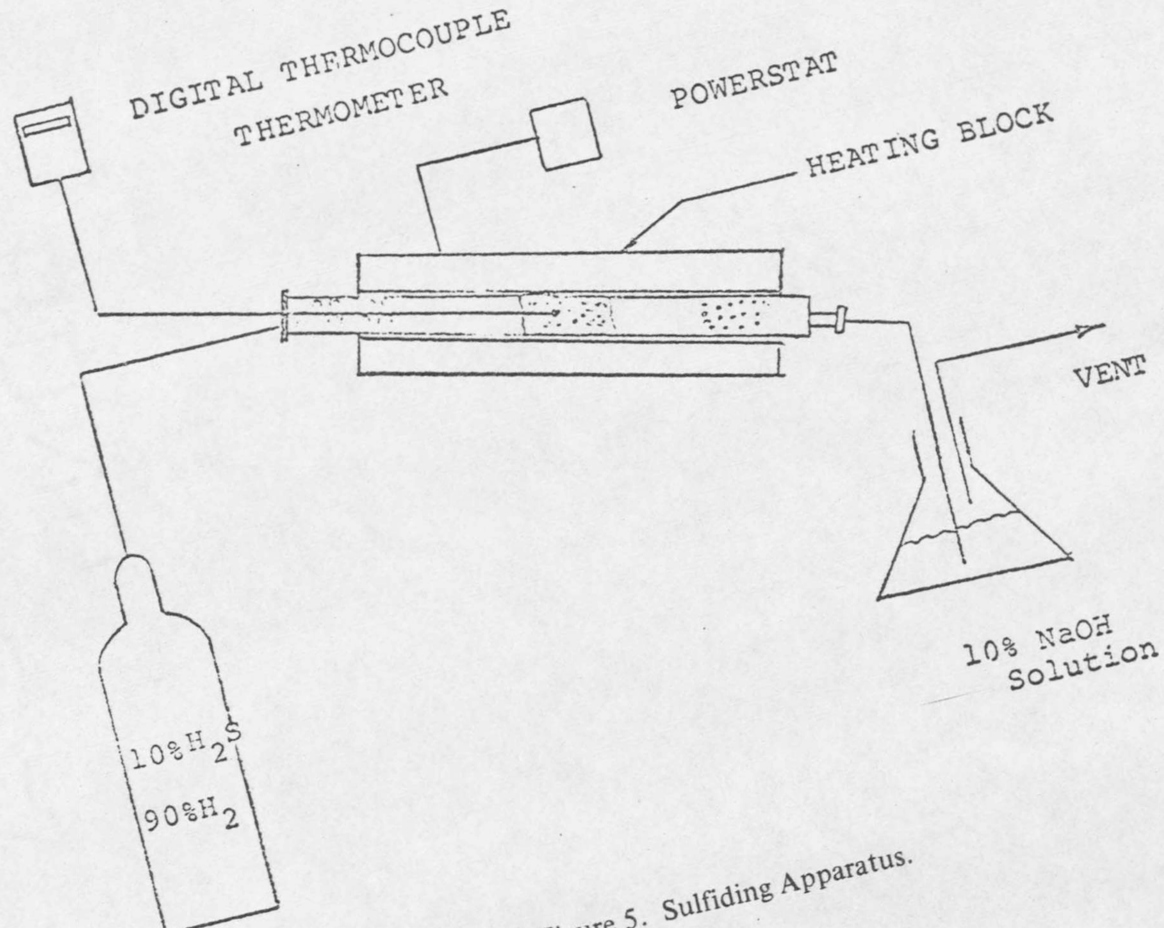


Figure 5. Sulfiding Apparatus.

(3) Titrate the sample on glass plate with water, while rubbing the catalyst with a finger against the glass plate, enabling the catalyst particles to absorb all the water.

(4) The end point was when all the catalyst particles had changed to a darker color and there was no wetness felt on the glass plate.

(5) The end point gave the volume of water absorbed hence the pore volume.

The Run

The catalysts were tested in a Parr series 4,000 pressure reaction apparatus (21). The reaction vessel (which will be referred to as the bomb) was heated in a rocker heating block. The heat input was controlled by a powerstat to maintain at a desired temperature. The bomb and heating block assembly are shown in Figure 6 (19).

The bomb was charged with 25 ml of sulfided catalyst in a wire basket together with 250 ml of Light End Column Feed (LECF) from SRC-II process. The copper gasket and the head of the bomb was secured using the eight Allen screws. The new copper gasket was torqued by fastening the screws to 60 ft.-lb with subsequent increase of 10 ft.-lb for every three runs. When the torque was in excess of 100 ft.-lb, the gasket was rejected. After the head and gasket were secured, the pressure gauge and gauge block assembly was mounted on the bomb. Silver or copper antiseize compounds were used on all the eight screws of the bomb to prevent high temperature seizing (22,23). The bomb was then pressurized with 1000 ± 50 psig of hydrogen from a high pressure cylinder or using a Haskel gas booster air-driven compressor (24).

The pressurized bomb was then placed in the rocker heater and heated. A Chromel-Alumel thermocouple was placed in the thermowell of the bomb, shown in Figure 6.

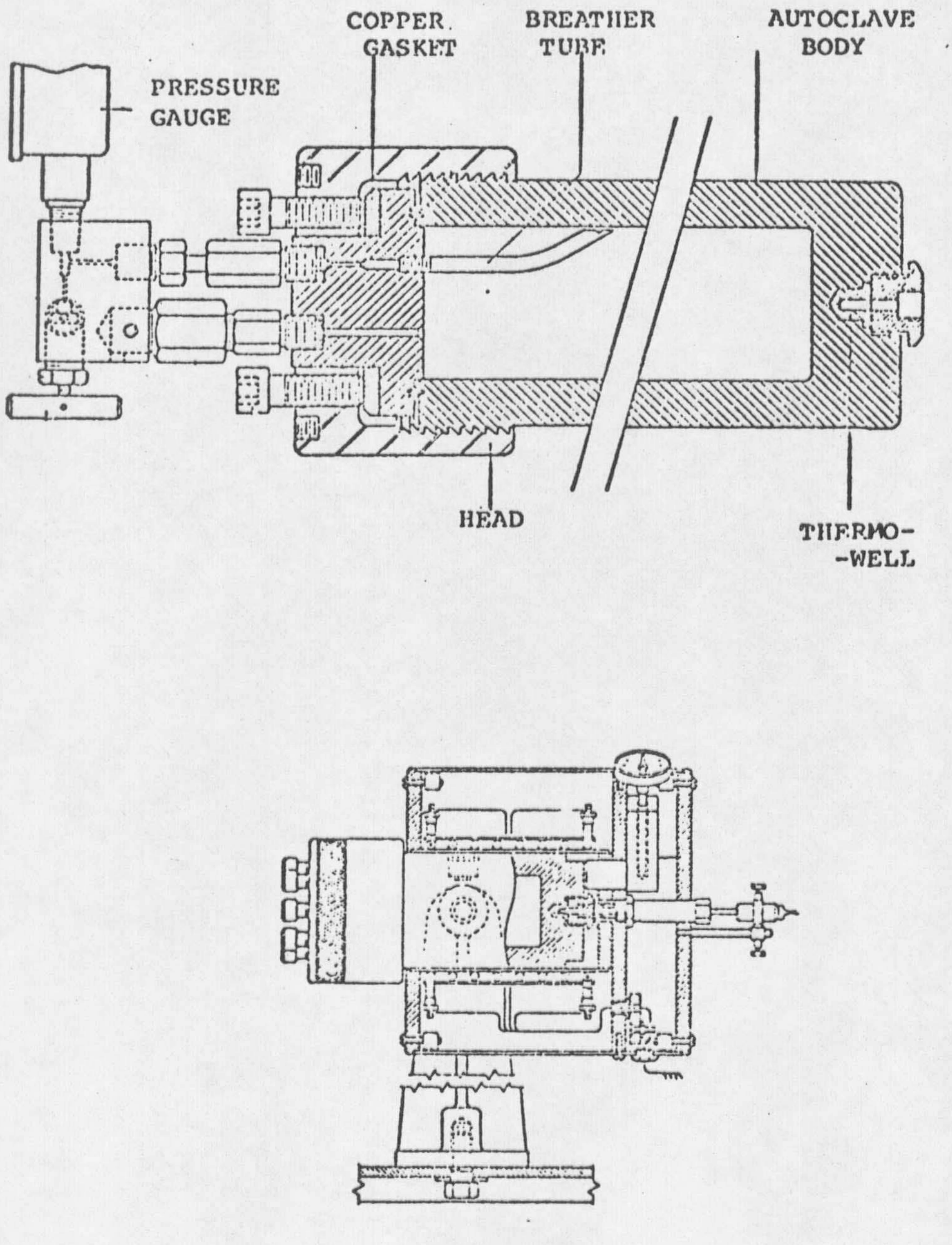


Figure 6. Rocking Autoclave Assembly.

Temperature was controlled manually using the powerstat and temperature was noted using a Cole-Palmer thermocouple thermometer (25) every 15 minutes during heat up period and every 10 minutes during the run, along with the pressure. Sixty to 75 minutes were required to heat up the reactor to 425°C. The run time, 60 minutes, was calculated from the time the reactor reached the temperature of 425°C. The reactor was rocked continuously from the time addition of heat began until the run was over.

After the run time was over, power for heating was shut and the rocker was stopped. The bomb was allowed to cool to a temperature when it could be pulled out of the heater without any difficulty. The mixture of gases remaining in the bomb was vented by opening the needle valve provided on the gauge block.

The catalyst in the basket was pulled out and the product was stored in an air tight bottle. The reactor head and the gauge block were washed with either acetone or toluene and dried for further use.

Regeneration

The burn off process had to be carried out at temperatures around 550°C. It was feared that if the catalyst was exposed to temperatures above 600°C for a long time, it may cause the pore walls of the support to collapse.

The regeneration was carried out in a one inch diameter inconel tube, 36 inches long (the same as the one used for sulfiding). The tube was filled with about 175 ml of 0.25 inch Denstone inert support (26) followed by a thin layer of approximately 15 ml of 0.125 inch inert supports were mixed. The position of this mixture was marked outside the reactor with a piece of chalk. The rest of the volume of the reactor was filled with 0.125 inch support. A wire gauze was placed on top to prevent the particles from slipping out. The reactor was closed. Teflon tape was used on all the threaded connections of the reactor. This packed tubular reactor was provided with a concentric thermowell to note the temperature. A Chromel-Alumel thermocouple was placed initially at the top of the catalyst zone of the packed bed. Then the whole assembly was placed in an aluminum heating block. Input of heat was controlled manually using the power stats.

The inlet for air or oxygen was at the top of the reactor. The exit was connected to two glass jars of water for scrubbing the exit gas and connected to the vacuum outlet. For the first five runs (R-90-1 to 3 and R-220-1 and 2), 40% oxygen in nitrogen was used and for the rest compressed air was used for regeneration. A schematic flow diagram is shown in Figure 7.

Once the temperature of the reactor reached about 500°C, the supply of air (or 40% oxygen) was flushed in for a period of not more than a minute to initiate the burnoff process. When an increase in temperature was seen, the supply was cut down to the lowest possible flow. Meanwhile the thermocouple was positioned at various points within the catalyst zone to find the hottest spot. With thermocouple fixed at that position, the oxygen supply was slightly increased in such a way that temperature was maintained within 550 ± 25°C. For a period of at least 2 hours, the position of the thermocouple was changed to the hottest spots, and oxygen supply was controlled accordingly. The burnoff was assumed to be complete when no rise in temperature was seen when oxygen supply was increased. It took at least 3.5 hours to reach this stage. However, oxygen supply was continued with minimum possible flow rate for another period of at least 3 hours to ensure