



Catalysts for hydrotreating COED Pyrolysis Oil  
by Stephan Timothy Kujawa

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering  
Montana State University  
© Copyright by Stephan Timothy Kujawa (1978)

Abstract:

Commercial and developmental catalysts were screened in their ability to remove sulfur and nitrogen from COED Pyrolysis Oil. The catalysts were tested in both batch autoclaves and in trickle bed reactors operating at 415° C. and 800 psig.

Tests on commercial catalysts showed that nickel-molybdates were best for nitrogen removal. Of the nickel-molybdates tested, Shell 324, Cyanamid HDS 9A, and Harshaw HT 500 performed best. Sulfur removal was best effected by the cobalt-molybdate catalysts, Harshaw HT 400, Shell 344, and Cyanamid HDS-20A. Nickel tungsten catalysts did not perform well at the conditions of the test.

From the tests on commercial catalysts, it was concluded that nitrogen removal was limited by pore diffusion, that molybdenum was more active for nitrogen removal than tungsten, and that sulfur removal was quite possibly being controlled by film diffusion.

Developmental catalysts were prepared at Montana State University to test the effect of supports and of promoters on the heteroatom removal reaction. The larger pore size supports worked best. Of the ten catalysts developed to test promoter effects, the cobalt-nickel-molybdenum combination showed advantages over commercial catalysts in batch tests.

In extending the results from the batch reactor to continuous reactors, eight combinations of the cobalt-nickel-molybdate catalyses were fabricated and tested. The experimental conclusions, from a 24 factorial analysis were: 1. for nitrogen removal a) the more molybdenum and less cobalt on the support, the better, b) nickel was not found to have a significant effect 2. for sulfur removal a) the low cobalt, high molybdenum combination again was best, b) nickel again had no effect.

This seems to suggest that cobalt-molybdate catalysts are sufficient to hydrotreat the feed; however, none of the developmental catalysts worked as well in the continuous tests as the commercial nickel-molybdate catalysts.

CATALYSTS FOR HYDROTREATING COED PYROLYSIS OIL

by

STEPHAN TIMOTHY KUJAWA

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

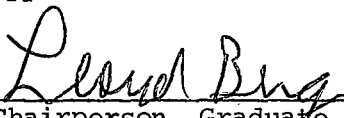
of

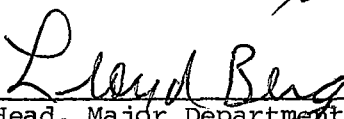
DOCTOR OF PHILOSOPHY


in

Chemical Engineering

Approved:

  
Chairperson, Graduate Committee

  
Head, Major Department

  
Graduate Dean

MONTANA STATE UNIVERSITY  
Bozeman, Montana

July, 1978

ACKNOWLEDGMENTS

The author would like to thank the Department of Energy for the financial support that made this research possible.

The moral support and encouragement of the staff of the Chemical Engineering Department, in particular Dr. Lloyd Berg, is gratefully acknowledged.

Much thanks and appreciation must go to Jim Tillery and the late Silas Huso, without whose help this project would have never gotten off the ground.

Finally, my appreciation goes to those people who did a major portion of the analytical work, namely, Danae Hass, Beth Hartz, Sharon Teigan, and Ron Novich.

A special thanks goes to Dr. Robert Taylor of the Industrial Engineering Department, who used much of his personal time in helping with the statistical analysis presented herein.

## TABLE OF CONTENTS

	<u>Page</u>
VITA . . . . .	ii
ACKNOWLEDGEMENTS . . . . .	iii
TABLE OF CONTENTS . . . . .	iv
LIST OF TABLES . . . . .	vii
LIST OF FIGURES . . . . .	ix
ABSTRACT . . . . .	xi
1. INTRODUCTION . . . . .	1
1.1. The Purpose of Coal Research . . . . .	1
1.2. Coal Liquefaction Processes . . . . .	2
1.3. Hydrotreating Studies of COED Pyrolysis Oil . . . . .	3
1.4. Statement of the Research Problem . . . . .	8
2. CATALYSTS . . . . .	10
2.1. Introduction . . . . .	10
2.2. Effects of Surface Area and Pore Size . . . . .	11
2.3. Effects of Metals and Promoters . . . . .	14
2.4. Effect of the Support . . . . .	15
2.5. Commercial and Conceptual Processes to Hydrotreat and Hydrocrack Heavy Feeds . . . . .	17
2.6. Catalyst Preparation Techniques . . . . .	19
2.7. Activation Procedures . . . . .	20
3. CHEMISTRY . . . . .	22
3.1. The Chemistry of Hydrotreating . . . . .	22
3.2. Desulfurization . . . . .	22
3.3. Hydrodenitrogenation . . . . .	25
3.4. Other Hydrotreating Reactions . . . . .	31
3.4.1 Demetalization . . . . .	31
3.4.2 Coking . . . . .	32
4. REACTION ENGINEERING . . . . .	34
4.1. Introduction . . . . .	34

	<u>Page</u>
4.2. Types of Activity Tests . . . . .	34
4.3. Activity Test Reactors . . . . .	36
4.3.1 Batch reactors . . . . .	36
4.3.2 The continuous trickle bed reactor . . . . .	36
4.4. Process Variable Effects . . . . .	37
4.4.1 Temperature . . . . .	38
4.4.2 Pressure . . . . .	42
4.4.3 Hydrogen to oil feed ratio . . . . .	43
4.5. Scale Up and Physical Aspects . . . . .	43
4.6. Conclusions . . . . .	44
5. EXPERIMENTAL EQUIPMENT AND PROCEDURES . . . . .	46
5.1. Reactors . . . . .	46
5.1.1 Trickle bed . . . . .	46
5.1.2 Operation . . . . .	48
5.1.3 Batch reactor . . . . .	50
5.2. Product Analyses . . . . .	50
5.2.1 Nitrogen . . . . .	50
5.2.2 Sulfur . . . . .	51
5.2.3 Product distillation . . . . .	51
5.3. Catalyst Preparation . . . . .	52
6. RESULTS - COMMERCIAL CATALYSTS . . . . .	54
6.1. Preliminary Continuous Runs . . . . .	54
6.2. Catalyst Screening Tests . . . . .	61
6.2.1 Cobalt molybdate catalysts . . . . .	61
6.2.2 Nickel tungsten catalysts . . . . .	65
6.2.3 Nickel molybdate catalysts . . . . .	67
6.2.4 Overall screening test results . . . . .	73
6.3. Batch Tests on Commercial Catalysts . . . . .	73
7. RESULTS - MSU CATALYSTS . . . . .	83
7.1. Batch Tests . . . . .	83
7.2. Continuous Tests . . . . .	87
7.2.1 Catalyst support studies . . . . .	87
7.2.2 Metal loading studies . . . . .	93
8. SUMMARY AND CONCLUSIONS . . . . .	100
9. RECOMMENDATIONS FOR FURTHER STUDY . . . . .	103

	<u>Page</u>
LITERATURE CITED . . . . .	105
APPENDIX I DATA TABLES . . . . .	109
APPENDIX II STATISTICAL ANALYSIS OF METALS LOADING RUNS . . . . .	116
APPENDIX III NOMENCLATURE . . . . .	128

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
I. Properties of Pittsburgh Filtered Oil . . . . .	3
II. Space Velocity for 80% Removal of Heteroatoms . . . . .	6
III. Liquid Product Distribution from ASTM Distillation - Cobalt Moly Catalysts . . . . .	64
IV. Liquid Product Distribution from ASTM Distillation - Nickel Tungsten Catalysts . . . . .	69
V. Liquid Product Distribution from ASTM Distillation - Nickel Molybdate Catalysts . . . . .	70
VI. Batch Run Data Summary - COED Feed . . . . .	75
VII. Batch Run Data Summary . . . . .	84
VIII. MSU Catalyst Batch Tests ASTM Distillation . . . . .	85
IX. Support Properties . . . . .	88
X. Catalyst Description . . . . .	89
XI. Cobalt-Nickel-Moly Catalyst Performance . . . . .	95
 <u>Appendix Tables</u>	
A-I. Cobalt Molybdate Catalyst Performance . . . . .	110
A-II. Nickel Tungsten Catalyst Performance . . . . .	111
A-III. Nickel Molybdate Catalyst Performance . . . . .	112
A-IV. Commercial Catalyst Description . . . . .	113
A-V. Cobalt - Nickel - Molybdate Catalyst Performance . . . . .	114
A-VI. Preliminary Run Data . . . . .	115
A-VII. Continuous Metal Loading Tests . . . . .	117

<u>Table</u>	<u>Page</u>
A-VIII. Weight Fraction Nitrogen in Product for 2 <sup>4</sup> Analysis . . . . .	123
A-IX. Weight Fraction Sulfur in Product for 2 <sup>4</sup> Analysis . . . . .	123
A-X. ANOVA Table for Coded Data . . . . .	124
A-XI. Modified ANOVA Table - Nitrogen . . . . .	125
A-XII. Nomenclature . . . . .	129



## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Project COED Pyrolysis Process . . . . .	4
2. Trickle Bed Reactor . . . . .	47
3. Weight Percent Sulfur vs Hydrogen Feed Ratio . . . . .	55
4. Weight Percent Nitrogen vs Hydrogen Feed Ratio . . . . .	56
5. Weight Percent Sulfur vs LHSV, Diffusion Tests . . . . .	58
6. Weight Percent Nitrogen vs LHSV, Diffusion Tests . . . . .	59
7. Weight Percent Sulfur vs LHSV, Co-Moly Catalysts . . . . .	62
8. Weight Percent Nitrogen vs LHSV, Co-Moly Catalysts . . . . .	63
9. Weight Percent Sulfur vs LHSV, Nickel Tungsten Catalysts . . . . .	66
10. Weight Percent Nitrogen vs LHSV, Nickel Tungsten Catalysts . . . . .	68
11. Weight Percent Sulfur vs LHSV, Nickel-Molybdate Catalysts . . . . .	71
12. Weight Percent Nitrogen vs LHSV, Nickel-Molybdate Catalysts . . . . .	72
13. ASTM D-86 Distillation, Harshaw W0801 . . . . .	77
14. ASTM D-86 Distillation, Harshaw Mo-1201 . . . . .	78
15. ASTM D-86 Distillation, Harshaw Ni-4303 . . . . .	80
16. ASTM D-86 Distillation, Shell 324 . . . . .	81
17. ASTM D-86 Distillation, Shell 344 . . . . .	82
18. Weight Percent Nitrogen vs LHSV, STK 5-2 Catalysts . . . . .	91

<u>Figure</u>	<u>Page</u>
19. Weight Percent Sulfur vs LHSV, STK 5-2 Catalysts . . . . .	92
20. Weight Percent Nitrogen vs Catalyst Metal Loading, MSU Catalysts . . . . .	97
21. Weight Percent Sulfur vs Catalyst Metal Loading, MSU Catalysts . . . . .	98

#### Appendix Figures

A-1. Weight Percent Nitrogen vs LHSV, MSU High Moly Catalysts . . . . .	119
A-2. Weight Percent Nitrogen vs LHSV, MSU Low Moly Catalysts . . . . .	120
A-3. Weight Percent Sulfur vs LHSV, MSU High Moly Catalysts . . . . .	121
A-4. Weight Percent Sulfur vs LHSV, MSU Low Moly Catalysts . . . . .	122

## ABSTRACT

Commercial and developmental catalysts were screened in their ability to remove sulfur and nitrogen from COED Pyrolysis Oil. The catalysts were tested in both batch autoclaves and in trickle bed reactors operating at 415 C. and 800 psig.

Tests on commercial catalysts showed that nickel-molybdates were best for nitrogen removal. Of the nickel-molybdates tested, Shell 324, Cyanamid HDS 9A, and Harshaw HT 500 performed best. Sulfur removal was best effected by the cobalt-molybdate catalysts, Harshaw HT 400, Shell 344, and Cyanamid HDS-20A. Nickel tungsten catalysts did not perform well at the conditions of the test.

From the tests on commercial catalysts, it was concluded that nitrogen removal was limited by pore diffusion, that molybdenum was more active for nitrogen removal than tungsten, and that sulfur removal was quite possibly being controlled by film diffusion.

Developmental catalysts were prepared at Montana State University to test the effect of supports and of promoters on the heteroatom removal reaction. The larger pore size supports worked best. Of the ten catalysts developed to test promoter effects, the cobalt-nickel-molybdenum combination showed advantages over commercial catalysts in batch tests.

In extending the results from the batch reactor to continuous reactors, eight combinations of the cobalt-nickel-molybdate catalysts were fabricated and tested. The experimental conclusions, from a  $2^4$  factorial analysis were:

1. for nitrogen removal
  - a) the more molybdenum and less cobalt on the support, the better,
  - b) nickel was not found to have a significant effect
2. for sulfur removal
  - a) the low cobalt, high molybdenum combination again was best,
  - b) nickel again had no effect.

This seems to suggest that cobalt-molybdate catalysts are sufficient to hydrotreat the feed; however, none of the developmental catalysts worked as well in the continuous tests as the commercial nickel-molybdate catalysts.

## 1. INTRODUCTION

### 1.1. The Purpose of Coal Research

G. Alex Mills, director of Fossil Energy Materials and Exploratory Research, of what was then called the Energy Research and Development Administration, and now is called the Department of Energy, stated in a recent paper that "In the absence of a national energy policy, present synfuels processes will not be economically competitive before the year 2000" [1]. He further stated in the article that the great need now in the coal to fuels and chemicals route is catalysts that will be able to snip apart the coal molecules at the proper places. Another government report states that for earlier commercialization, a new process will have to be developed that is considerably cheaper than those "first generation" processes now being developed [2]. Therefore, one of the major research needs in coal conversion research is catalyst studies.

The research which is the subject of this thesis is an attempt to study and improve a significant step in the overall fossil fuel conversion process. That step consists of the process whereby the heavy, tar-like substances produced in the primary coal liquefaction operation are hydrotreated (reacted in the presence of hydrogen at medium to high pressure and temperature) to remove objectional heteroatomic molecules (N,S,O) and improve the overall product. The reason for removing these compounds is two-fold. The first is to reduce

pollution from any eventual fuels made from the coal liquid. The second is to protect the catalysts in further refining steps.

### 1.2. Coal Liquefaction Processes

There are four basic processes to make liquids from coal that have received the majority of development in the last decade. The Synthoil process involves running coal, recycle oil, and hydrogen up-flow in an ebullating catalyst bed. Coal ash deactivation of the catalyst seemed to spell an early death for the project. Recently, however, the catalyst has been replaced by inert beads because it was found that either the ash actually catalyzed the conversion reaction or that the conversion reaction occurs mainly through a thermal process.

The Exxon Donor Solvent process and the Gulf Solvent Refined Coal process are similar in many respects. Both processes use a recycle oil to slurry coal which is then pumped into reactors in the presence of hydrogen. In the Exxon process, however, the recycle oil is hydrotreated prior to slurrying. This partially saturates the oil to tetralin type molecules. During the course of the liquefaction reaction, the multi-ring compounds donate this hydrogen to the coal and become more aromatic.

The feedstock used in this research was produced from Pittsburgh Seam bituminous coal in the FMC operated COED process (Char Oil

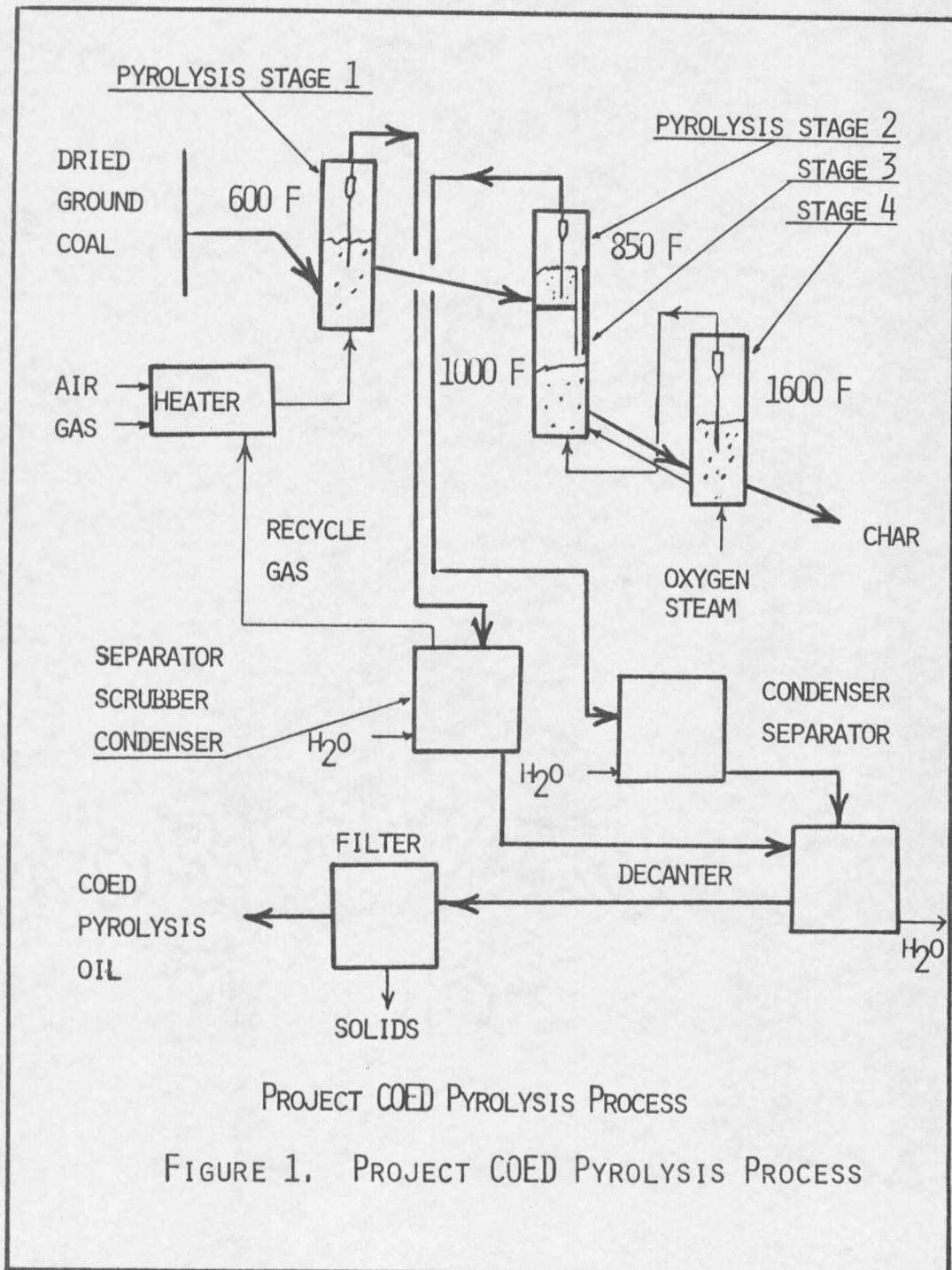
Energy Development process). This is a pyrolysis process where coal is fed into a series of fluidized bed reactors; each operated at a higher temperature. The volatiles are driven off by hot gases which are produced in the final reactor by partial combustion of the char. The process diagram is shown in Figure 1. Table I presents the physical and chemical properties of the feed [3].

Table I  
Properties of Pittsburgh Filtered Oil

Moisture	0.4 wt%
Quinoline Insolubles	7.0 wt%
API Gravity, 60°F	-7.4
Pour Point, °F	80
Flash Point, °F	240
Viscosity Cp @ 350°F	4.7
ULTIMATE ANALYSIS	
	wt % dry
C	82.9
H	7.3
O	5.9
N	0.9
S	2.3
Ash	0.7
HHV dry	15,900 BTU/lb

### 1.3. Hydrotreating Studies of COED Pyrolysis Oil

Two bench scale studies have shown the effects of processing conditions in hydrotreating COED Pyrolysis Oil. The first study [4] used a nickel-moly catalyst (American Cyanamid HDS-3A) to hydrotreat the oil at 3000 psig and hydrogen flow rates of 8000 and 12000 scf/bbl. Temperature and space velocity were varied in the study.



The study showed that the activation energies for the removal of oxygen and nitrogen from the feed were not constant and dropped sharply at temperatures of 730°F and 752°F, respectively. This was felt to be an indication of mechanism changes in the reactions and not due to diffusion control.

The product from the reactor was fractionated into naphtha, gas oil, and residual cuts. These were then evaluated for their ability to be processed in a commercial refinery. It was concluded that all of the cuts would have to be further hydrotreated to meet nitrogen specifications. The naphtha would then be a suitable reformer feedstock. The gas oil and residual fractions contain a large amount of refractory polynuclear aromatic molecules that coke cracking catalysts. These molecules would have to be selectively saturated and cracked before further processing. It would then be possible to make high octane gasoline blending stocks from these, but the severity of processes to saturate the feed precludes making diesel or jet fuel from them.

The second bench scale study used essentially the same set up as the first: 100 cc catalyst, 3000 psig, 8000-12000 scf/bbl, 650-800 F, and space velocities of 0.3 to 3 [5]. The temperature in the catalyst bed increased in the first few inches, then dropped again, so to correlate the data, the arithmetic average temperature of one inch increments of bed depth was used.



Two of the results of the study are very important. The first was that the severity of operation of the hydrotreater must be very high compared to conventional petroleum refining. Table II illustrates this.

Table II  
Space Velocity for 80% Removal of Heteroatoms @ 720 F,  
3000 psig, Pittsburgh Seam

Heteroatom	LHSV
Nitrogen	0.4
Oxygen	0.6
Sulfur	1.1

The second result had to do with the conversion of the feed to gas. The gas forming reaction directly correlates with the amount of coke deposited on the catalyst and thus the catalyst life. Making gas is also an inefficient use of the hydrogen present. The gas make was studied as a function of temperature. It was found that gas conversion was independent of space velocity. The gas yield increased at an enormous rate at bed temperatures above 780°F. It was concluded that it is necessary to keep the bed temperature below 780°F to produce oil and protect the catalyst.

The results from the hydrotreating process development unit at the COED pilot plant were presented to ERDA in 1975 [6]. The pilot hydrotreater processed 30 bbl/day of pyrolysis oil at 1400-1900 psig,

725-765°F, 0.22 to 0.31 LHSV (Liquid Hourly Space Velocity), and a recycle gas rate of 47,000 to 73,000 scf/bbl containing 93 to 96% hydrogen.

The ash in the feed became a problem because it plugged the catalyst pores causing rapid deactivation. This problem was solved by using a guard chamber upstream of the hydrotreaters. A high void volume combination of cobalt moly catalyst and Koch flexirings were used to trap the fines and to initiate demetalization reactions. The hydrotreating runs were terminated when the guard chamber plugged. The guard chamber decreased catalyst usage to 0.2 lb/bbl of oil processed.

Some of the major results of the P.D.U. (Process Development Unit) runs were that, as a function of pressure in the 1300 to 1900 psig range, sulfur removal was close to constant at about 93%; nitrogen removal increased from 45 to 75%; and hydrogen consumption increased from 1800 to 3800 scf/bbl. The projected cost of a barrel of syncrude from the process has recently been estimated to be between \$20 and \$30 [2, p. 143].

The necessary process improvements for syncrude production have been stated to be:

1. Develop selective catalysts to crack polynuclear aromatic molecules with minimum hydrogen production.

2. Reduce the necessary severity of hydrotreating by catalyst optimization thereby reducing equipment requirements which will in turn reduce capital costs.
3. Produce a syncrude refinable by conventional petroleum methods.
4. Be able to operate the entire coal to syncrude process at no less than a 70% overall thermal efficiency.

The above requirements must be met before an early commercialization of coal to fuels can be foreseen [2, p. 14].

#### 1.4. Statement of the Research Problem

From the above discussion, and from the requirements of ERDA contract number E(49-18)-2034, the following topics were addressed in the research presented in this thesis:

1. Commercial hydrotreating catalysts were screened in both batch and continuous trickle bed reactors. The purpose was two-fold:
  - A. determine the best commercial catalyst available.
  - B. determine why the catalysts effected the process as they did.
2. Develop catalysts that are an improvement on the commercial catalysts. Determine what facets of the catalyst make-up cause improvement.

The overall purpose of the project was not to come up with a one-step scheme to produce gasoline or other fuels or feedstocks. The purpose was to see the effect of the catalyst on the process used to upgrade the coal liquids to a point where downstream processes could produce the fuel or feedstock.

The following sections of the Introduction discuss some aspects of the catalyst, the reactions, and the reactor, that must be accounted for when doing a catalyst screening study and interpreting the data produced therein.

## 2. CATALYSTS

### 2.1. Introduction

This section will describe what some of the more conventional catalysts are; what they are made of; and what results when certain components are added to them. The section will also go into some of the methods of making catalysts, and some of the processes that use hydrotreating catalysts.

Traditionally, it was supposed that a hydrotreating catalyst consisted of an active component, usually a metal, that was deposited on a high surface area support. The support was considered inert and its only purpose was to disperse the catalyst. However, it has been shown that the support itself is catalytically active, and, in some processes, catalytic cracking, for example, the support is the only catalyst.

The catalysts for hydrotreating and hydrocracking have been found to be bi-functional. Some of the surface sites are active for hydrogenation; and other sites are active for cracking. The metal (actually an oxide or sulfide) promotes the hydrogenation reactions while the cracking activity is due to properties of the support (e.g., Bronsted and Lewis acid sites). The reactions that occur when a feedstock is desulfurized and denitrogenated include hydrogenation and cracking steps. These reactions will be explained in the next section.

Hydrotreating catalysts must be sulfur and nitrogen resistant. Traditional metal hydrogenation catalysts (Pt, Pd, Ni) are ruled out because of this [7]. The catalysts that are used for conventional whole crude and residual Oil hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) are usually made up of the oxides of group VIA and VIII metals on silica, alumina, or a combination of these supports. Some of the metal combinations are: Co-Mo, Zn-Mo, Ni-Mo, Cr-Mo, Fe-Co-Mo, Ni-Co-Mo, and Ni-W [8].

In most conventional petroleum refining, cobalt-molybdate catalysts are used for desulfurization; nickel-molybdate catalysts are used for denitrogenation; and nickel tungsten catalysts are used for severe denitrogenations and hydrogenations. The nickel tungsten catalyst is much more expensive, however, and usually its use cannot be economically justified [9].

## 2.2. Effects of Surface Area and Pore Size

As stated, the physical carrier has two functions:

1. Disperse the hydrogenation component over a large surface area.
2. Provide acid sites for cracking reactions.

The important surface area is not that measured by physical adsorption methods, but is the surface area active for the reaction in question. For the hydrogenation component, it is the area of the

metal crystallite that forms on the surface. The smaller the crystallite, the more surface metal atoms exposed, and the more active the catalyst. For the cracking reaction, the support provides a large number of acid sites of varying types and strengths.

The supports, primarily amorphous solids, are very porous. If the catalyst is intrinsically very active, there is a possibility that the rate of the reaction will be limited by the rate of the molecules diffusing through the pores to the active sites. This is especially true in the case of resid and syncrude desulfurization where very large molecules are reacting. Since, in a catalyst particle, the surface area and pore volume (hence, pore size distribution) are inversely related, there will be a trade off between surface area and pore size. An optimum of the two factors must therefore be found [9, p. 84].

In one study of resid desulfurization, it was found that the activity could be related by [10],

$$\%DS = K + 0.0589A + R(6.6A \times 10^{-4} + .012)$$

K = constant

A = S.A. of catalyst

R = Avg. pore radius

%DS = percent desulfurization

The above shows that both an increase in surface area and pore size would increase activity.

Generally speaking, pure silica supports will be characterized by very high surface area (300-450 m<sup>2</sup>/gm), and the pore size will be small. Silica aluminas and aluminas will have surface areas of 100 to 250 m<sup>2</sup>/gm and have correspondingly larger pore sizes. Molecular sieves, which are crystalline supports of silica-alumina, have uniform pore sizes of up to 9 Å and very high surface areas.

There is generally an attempt to characterize catalysts by what is called an average pore size [11]. The calculation assumes that the pore size distribution is mono-disperse; the pores are straight, cylindrical, not interconnected, and have the same radius,  $\bar{a}$ , and length,  $\bar{l}$ . The average pore size is obtained by writing equations for the surface and volume of the particle, giving finally,

$$\bar{a} = 2 Vg/Sg$$

$Vg$  = cc/gm of catalyst

$Sg$  = surface area per gram

$\bar{a}$  = average pore radius

The major assumption of the above equation is that the pore system has a normal or skewed normal distribution. Aluminas and silica aluminas, however, have pore systems that generally consist of small particles containing micropores ( $a < 100 \text{ \AA}$ ) interconnected by macropores ( $a > 100 \text{ \AA}$ ). Since the pore size distribution will usually have two most common pore sizes, a single value of average size will not describe the catalyst adequately.



### 2.3. Effects of Metals and Promoters

The most common metals responsible for the hydrogenation-dehydrogenation function of a hydrotreating catalyst are molybdenum and tungsten. Molybdenum has been found to be active for denitrogenation on a support even without additional promoters present [12]. "Metal" is used here, keeping in mind that under reaction conditions the active species is a sulfide or oxy-sulfide.

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 heteroatom removal reaction [13].

If the sulfided catalyst, prior to use, is visualized as having a surface monolayer of molybdenum sulfide species, it is believed that, for a cobalt-moly catalyst, the cobalt displaces aluminum into the active monolayer. This stabilizes the monolayer by binding it more strongly with the alumina surface. As the catalyst is used, cobalt ions diffuse back and forth into and out of the monolayer. This causes the molybdenum crystallites to become smaller, thereby exposing more molybdenum ions to the molecules and maintaining activity. Nickel supposedly has a similar effect differentiated slightly by coordination [13, p. 298].

Studies have established the optimum ratio of promoter to hydrogenation component. For cobalt-molybdate catalysts, the ratio is about 1:3. This has been found to be independent of support and material [9].

#### 2.4. Effect of the Support

As stated above, the purpose of the support is not only to disperse the metal component, but also to provide acid sites to initiate the carbonium ion mechanisms of the cracking reactions. The acid sites are of both the Bronsted and Lewis type and are a function of the support preparation temperature [14].

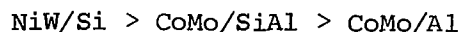
The acid sites are weak or strong and can be manipulated depending on the purpose of the process. Generally, pure silica is less acid than alumina, which is less acid than silica-alumina. The metals on the support also influence acidity. It was found that NiO on alumina reduces the acidity, while MoO<sub>3</sub> increased it [9, p. 276]. This was given as the reason unsulfided HDS catalysts of the cobalt-moly type exhibit uncontrolled cracking when put on stream with feed that is too hot.

The acid sites on a catalyst are subject to nitrogen poisoning. One study found that, when treating a feedstock low in nitrogen, the desulfurizing activity of three catalysts was in the order:



This trend exactly follows acid strength.

When the above catalysts were run on a high nitrogen feed, the order of activity became,



Essentially, the nitrogen had neutralized the strong acid sites of the CoMo catalysts; and the stronger hydrogenation activity of the Ni-W catalyst, which tends to keep the acid sites clean, overcame the support effects.

Hydrocracking occurs along with hydrotreating at the severe conditions usually present in resid and syncrude processes. By varying the relative strengths of the hydrogenation component and the cracking function, the product distribution can be changed [14]. For example, to hydrocrack to middle distillates, moderate acidity with high hydrogenation ability is needed along with high porosity to allow the large molecules to adsorb and desorb. The moderate acidity would allow the larger molecules to desorb sooner; the high hydrogenation ability would reduce aromatics and increase the saturated molecules desired for diesel and jet fuel.

To process to gasoline, strong acid sites are needed to keep the molecule on the support, increasing cracking and isomerization. Low hydrogenation ability is wanted, however, to keep from saturating the high octane alkyl-aromatic molecules.

For polycyclic aromatic cracking, high hydrogenation ability is not wanted, because it would use up hydrogen in saturating the aromatic rings. Selective cracking of the center rings is the desired reaction. Both CoS/SiAl [14] and  $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$  [7] catalysts have been found to be selective for this reaction.

In any of the hydrocracking processes, the sulfur and nitrogen content of the feed streams must be in the range of 7-100 ppm depending on the process. The sulfur in the feed poisons the hydrogenation function if it is a noble metal; the nitrogen, as stated above, poisons the acid centers.

The effects of pore size must also be accounted for. When heavy feeds are treated, large molecules cannot get into the pores of molecular sieves and high silica catalysts and therefore, silica-alumina and alumina supports must be used for at least the initial hydro-treating step to remove the heteroatoms from the large, aromatic structures.

#### 2.5. Commercial and Conceptual Processes to Hydrotreat and Hydrocrack Heavy Feeds

There are several commercial processes that give clean, lighter products from heavy feeds. Characteristic to almost all is two stage processing. The first stage hydrotreats the high nitrogen containing feeds, while the second stage hydrocracks to the desired products. Examples of operating processes are the U.O.P. - Chevron Isomax, and

the Union Oil - Exxon Unicracking JHC processes. Molecular sieves are used in the second stages of these processes where the operating conditions are 400-800°F and 500 to 1500 psig.

Catalyst development in recent years has concentrated on two stage processes to treat heavy feeds. The catalysts in the first stage characteristically concentrate pore volume in the macropore region. This allows large asphaltene molecules to enter the pores and react. In one recent patent [15], the first stage catalyst consisted of gamma-alumina impregnated with either cobalt-moly, nickel-moly, or nickel tungsten. The surface area varied from 250 to 400 m<sup>2</sup>/g, and 50 to 75% of the pore volume was concentrated in the 200 to 300 Å range; less than 20% consisted of pores smaller than 100 Å. The operating conditions of the first stage were 700 to 800°F; 2000 to 5000 psig, 3000 to 10,000 scf-H<sub>2</sub>/bbl; and LHSV of 0.5-1.

The second stage of the process contained a catalyst with greater than 99% of its pore volume in pores between 15 and 100 Å diameter. Nickel moly and aluminum phosphate were contained in the catalyst make-up. The operating conditions were 700°F; 1500 to 3000 psig; 2000 to 4000 scf-H<sub>2</sub>/bbl; and LHSV of 0.5 to 2. The small pores excluded the large molecules that bypassed the first stage which would tend to coke and poison the second catalyst.

Other recent patents have essentially stated the same: two stage processes with large pore catalysts in the first stage for hydrotreating; small pore catalysts in the second stage for hydrocracking [16].

## 2.6. Catalyst Preparation Techniques

Again, hydrotreating catalysts consist of a support that sets the acidity and physical properties of the catalyst; and the metal oxide precursor to the sulfide or oxy-sulfide hydrogenation component. Preparing the catalyst consists of somehow dispersing the metals on the support. Sometimes this is done by gelling from a solution of support material and catalytic metals. The final product is small catalyst particles that are pelleted or extruded to the final physical catalyst.

A more traditional way, and the approach used in this research, is called the incipient wetness technique of support impregnation. The silica, alumina, or combination support is already in a pelleted or extruded form. The ways to prepare these are described in a recent report [7]. The physical properties are set by the manufacturing technique and are varied by the producer.

Using prepared supports, the problem becomes that of dispersing the metals on it. The incipient wetness technique involves impregnating the support with soluble metal salts, the volume of which is

equal only to the pore volume of the support. After a soaking period, the catalyst is dried; calcined in air, hydrogen, or inert gas; and then the procedure is repeated until the desired metal loading is obtained. The final product is a support containing oxides of the impregnated metals.

### 2.7. Activation Procedures

The catalyst is generally not in its most active form as an oxide. The activated catalyst is a sulfide or oxysulfide of the hydrogenation metals. There are several methods to obtain the sulfide form. The first method consists of pretreating the catalyst in the reactor with a hydrogen stream containing from one to ten percent hydrogen sulfide. The catalyst should be free of water, and the initial temperature should be less than 100°C. If pure hydrogen contacts the catalyst at this temperature, irreversible reduction of the oxides to metals occurs with activity loss of the catalyst. The most common method of sulfiding in the commercial reactors is to spike the feed with easily degraded compounds such as carbon disulfide or dimethyl sulfide, and operate at mild conditions until the sulfiding is complete.

Thomas suggests methods of presulfiding catalysts [10]. He states that cobalt-moly catalysts are usually not presulfided commercially, but should be in pilot plants. Ketjen catalyst company

suggests that all catalysts used for hydrotreating should be presulfided so that maximum activity can be reached quickly [17].

Nickel tungsten catalysts are sulfided similarly to cobalt-moly catalysts. Nickel-moly catalysts should first be steam treated, and then sulfided as above.



### 3. CHEMISTRY

#### 3.1. The Chemistry Of Hydrotreating

The purpose of this section is to illustrate some of the reactions that occur during the hydrotreating of petroleum and coal liquids. Some model reactions will be shown along with supposed molecule-catalyst interactions as reported in the literature.

Hydrotreating is a broad process that involves not only desulfurization and denitrogenation, but also demetalization reactions and aromatic saturation. Hydrocracking also occurs at some of the more severe processing conditions.

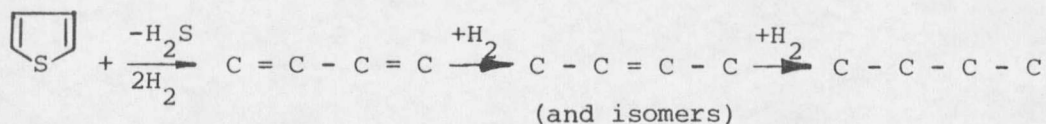
#### 3.2. Desulfurization

The first reaction to be discussed is also the one most historically important and the one most studied. The reaction is the process of desulfurization. Shuit and Gates [18] state that the two primary reasons to remove sulfur are,

1. To prevent sulfur poisoning of cracking and reforming catalysts used in gasoline manufacture.
2. The removal of sulfur from fuels to reduce SO<sub>2</sub> pollution.

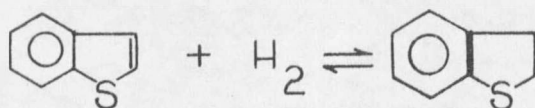
Also stated in the same article is that at the usual industrial conditions (600-800°F, up to 3000 psig) the hydrodesulfurization reactions are irreversible, exothermic, and have heats of reaction of about 50 to 100 BTU per standard cubic foot of hydrogen consumed.

The most common sulfur compounds in coal liquids are thiophene and its substituted derivatives. The order of most to least difficult to decompose are dibenzothiophene, benzothiophene, and naphthobenzothiophene [19]. The proposed mechanism for thiophene desulfurization is,



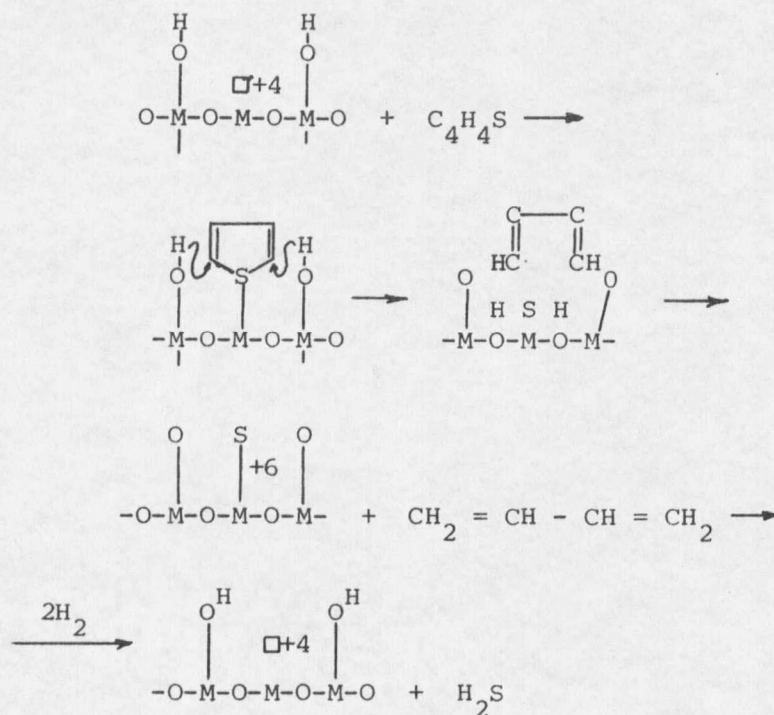
In the above reaction, the rate determining step is C - S bond cleavage to form 1-3 butadiene, and not saturation of the aromatic bonds in thiophene.

In the hydrodesulfurization of benzothiophene, however, it was found that hydrogenation of the double bond in the thiophene ring took precedence over the removal of sulfur.



It was found that the two compounds above 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 [18].

The thiophene desulfurization reaction mechanism on the catalyst surface is proposed to be the following for a cobalt-molybdate catalyst: [18]



The square ( $\square$ ) denotes an anion vacancy; M is the molybdenum cation.

The kinetic analysis of the desulfurization of petroleum would be extremely difficult because of the presence of many different classes of compounds reacting simultaneously. The sulfur compounds, however, are usually concentrated in a very reactive fraction, and a very unreactive fraction. A kinetic expression can be written that considers each fraction in a first order expression. Adding the two expressions will model the total sulfur removal, which will then appear as a second order reaction.

For high sulfur removal industrial reactions, the easily removed fraction can be ignored, using just the expression for the unreactive fraction to explain desulfurization at high conversions. The expression is, [5]

$$R_{\text{HDS}} = \frac{\alpha_2 k_2 P_{\text{H}_2} C_{\text{S}}}{(1 + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{H}_2\text{S}} P_{\text{H}_2\text{S}})}$$

$\alpha_2$  = the fraction of unreactive molecules in the feed.

The equation shows that increasing the partial pressure of hydrogen increases conversion up to a point where it cancels in the rate expression; at that point further pressure increase has no effect and kinetics become first order in sulfur. Hydrogen sulfide is shown to inhibit the rate if it is present in quantities more than a few mole percent.

Other workers have found that the rate of desulfurization is first order with respect to sulfur at high partial pressures of hydrogen [7]. They also found that  $\text{H}_2\text{S}$  inhibits the reaction and the rate of desulfurization decreases with increasing molecular weight of the sulfur containing compounds.

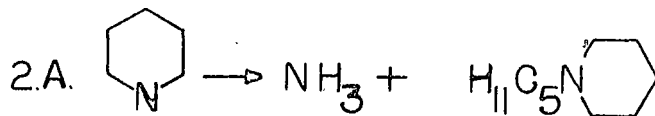
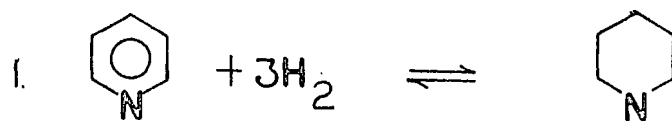
### 3.3. Hydrodenitrogenation

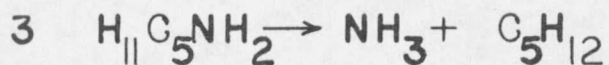
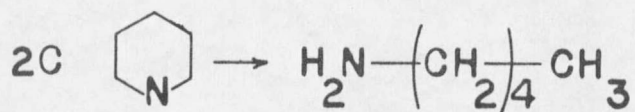
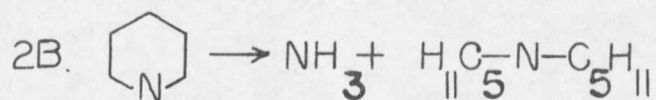
The three reasons to remove nitrogen from coal liquids are to protect acid sites on cracking and reforming catalysts in downstream

processing, to reduce nitrogen oxides pollution when the final products are used, and to remove nitrogen compounds which cause harsh performance and varnish in many fuel applications.

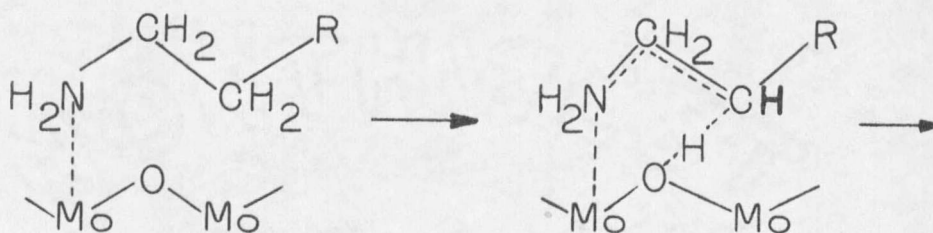
The differences between coal liquids and petroleum were explained in a recent article [20]. The coal liquids have a "higher degree of aromaticity and a more condensed ring structure . . . The most striking difference is in heteroatom content." "The nitrogen content is usually much higher than in petroleum with 40 to 70% of it being basic nitrogen." The implication is that petroleum processing methods will have to be modified to adequately hydrotreat coal liquids to synthetic crude oils.

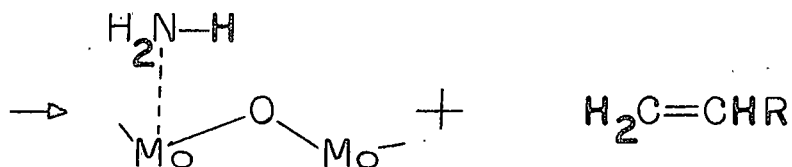
Model nitrogen compounds that are present in coal liquids are pyridines and substituted pyridines (quinoline); and pyrroles and substituted pyrroles (indole) as the basic nitrogen heterocyclics. The non-basic compounds are the saturated derivatives of the above [7, p. 124]. Pyridine will be used to illustrate the proposed mechanism of hydrodenitrogenation [7, p. 125]:





In the above, Step 1 is in equilibrium; Steps 2A and 2B further react to pentylamine. The rate determining steps are the hydrocracking of the bases. The surface mechanism on a cobalt-moly catalyst was suggested as, [7, p. 126]





It was stated in the cited article that the C-N hydrogenolysis occurs at the molybdenum site. The cobalt adds to the hydrogenating activity, but high ratios of Co/Mo reduce denitrogenating activity. It was concluded that if the above mechanism is true, then increasing the molybdenum-nitrogen surface interaction should increase the amount of denitrogenation.

Cocchetto and Satterfield discuss the possibility of a thermodynamic limitation to the rate of denitrogenation [21].

The limitation would exist depending on the rate determining step of the reaction. If the mechanism is saturation followed by ring opening at the C-N bond, calculations performed for the steps show that the equilibrium constants for the saturation step are favorable only at low temperatures (below 200°C for pyridine; 100°C for acridine).

The article concludes "If the initial saturation reaction is rate limiting, the hydrogenated heterocyclic compound reacts as soon as it is formed, and the position of the hydrogenation equilibrium for the initial step does not affect the overall rate of hydrodenitrogenation. If the cracking step determines the rate, the initial reaction will achieve equilibrium.

If the cracking step does limit the rate, the rate constant for the step will increase with temperature. With an increase in temperature, however, the equilibrium constant for the saturation reaction will decrease, thus lowering the amount of saturated compound present. Since the rate of the cracking step depends also on the concentration of the saturated molecules, the rate will drop. Since the overall rate depends on temperature both directly and inversely, an optimum rate of denitrogenation as a function of temperature will show up if the second step is rate limiting.

The position of equilibrium is also a function of pressure. Since a reduction in the number of moles occurs in the saturation step, an increase in pressure will shift the equilibrium to the saturate, thus increasing the number of molecules available to crack, hence increasing the rate.

Typical denitrogenation conditions in industrial reactors are similar to those for desulfurization: 600 to 800°F, up to 3000 psig. The nitrogen removal reaction is much more difficult, however, so



usually two or three reactors in series must be used. The nitrogen content must be lowered to 5-100 ppm for further processing depending on the process.

To specifically remove nitrogen, nickel molybdate and nickel tungsten catalysts are traditionally used. Cobalt-moly catalysts are sometimes used if only a small removal is needed. It has been found that some hydrogenation function is needed no matter what catalyst is used; strictly acidic cracking catalysts do not remove nitrogen [11, pg. II-B-31].

Desulfurization occurs along with denitrogenation. The  $H_2S$  has been found to increase the rate of denitrogenation, especially at higher temperatures [11, p. II-B-45]. It is generally stated that if a reactor is designed to remove nitrogen down to specifications, sulfur will be well below the process limits.

In summary, for hydrodenitrogenation, temperature and pressure are very important to the chemistry, and there will probably be an optimum of both. The hydrogenation component of the catalyst seems to be the most important factor in the reaction if the molecule can reach the surface. Nitrogen removal is generally the most difficult hydro-treating operation.

### 3.4. Other Hydrotreating Reactions

3.4.1 Demetalization. Coal liquids and residual fuels contain compounds that incorporate heavy metals. Also, ash from previous processes is suspended in the feed. Coal liquids contain many iron and calcium compounds along with nickel and vanadium as in resids.

The metals and ash are deposited on the catalyst surface during hydrotreating. Eventually, the pores of the catalyst are plugged, thereby permanently deactivating the catalyst. The catalyst then cannot be regenerated and must be discarded. Resid hydrodesulfurization is one process where this type of deactivation ends the hydrotreating cycle.

The "guard chamber" concept has been successfully used during coal liquid hydrotreating. The feed is pumped through the guard chamber prior to the hydrotreaters. As stated above, the use of the guard chamber in the COED process to remove ash greatly reduced catalyst usage.

3.4.2 Hydrocracking. Hydrocracking processes take large molecules and turn them into small ones. The actual process is a separate technology from hydrotreating, but hydrocracking reactions do occur to some extent at the condition of severe hydrotreating. Ideally, these reactions would take the large, polynuclear aromatic molecules and

break them into smaller, substituted aromatics and saturates with a minimum of hydrogen consumption.

The cracking reaction occurs through both a thermal, free radical mechanism, and a catalytic carbonium ion mechanism which is initiated by the acid sites. The carbonium ion, in the second case, cracks or isomerizes until the products are hydrogenated by the metal sulfide part of the catalyst. Since the purpose of this thesis is to study hydrotreating, hydrocracking will not be discussed further.

3.4.3 Coking. Catalysts are deactivated reversibly by coke formation. The reaction has two mechanisms: In the first, hydrogen is abstracted from carbonium ions forming increasingly unsaturated compounds on the catalyst surface. The second reaction mechanism is by the polymerization of the carbonium ions.

All catalysts coke when contacted by hydrocarbon feeds. Coking is controlled by the hydrogenation component of the catalyst. The component "heals" the cracked compounds and thus keeps the acid sites clean by hydrogenating the coke precursors. Research has shown that on a steady state catalyst, only the acid sites that are near the hydrogenation sites are still active and functioning [11, p. II-D-20]. Coked catalysts are usually regenerated by controlled combustion with very low (2-3%) oxygen concentrations. Care has to be taken to keep the temperature below that which sinters the catalyst support. After

regeneration, the oxide catalyst must again be presulfided before being put on stream.

## 4. REACTION ENGINEERING

### 4.1. Introduction

When attempting to set up a test to screen catalyst activities for a specific reaction and feedstock, several aspects of the engineering and operation of the test reactor must be kept in mind. This is because the results that are obtained could possibly be clouded by effects that are not due to the catalyst, but due to the influence of the processing variables. The three subjects to be discussed in this section are, the type of activity test being attempted; the type of reactor used in the test; and the possible influences of the processing variables.

### 4.2. Types of Activity Tests

The purpose of the activity test determines what type it is and how precise it needs to be. If the test is used to distinguish between reaction mechanisms, then it must be of a more precise nature than a test used to establish whether a catalyst will or will not accelerate a reaction.

The conditions for the ideal activity test would be, "to ensure isothermal conditions with a particle size which eliminates intraparticle diffusion." "Likewise . . . would try to run the reaction under fluid dynamic conditions so that mass transfer to the catalyst surface presented no resistance." ". . . would try to design the reactor to prevent bypassing and to obtain rate data before the

catalyst had aged" [22]. The article further states that it is impossible to eliminate all potential activity disguises, but the ones that are present when the reactor is operated must be kept in mind and the results interpreted in the light of these.

There are a number of ways to set up and interpret activity experiments; several are,

- which catalyst gives the required conversion at the lowest temperature.
- what space velocity is required to give a given conversion at a given temperature.
- what catalyst gives the highest rate.
- what catalyst has the largest rate constant.

The second two tests involve much more work than the first two. They require that the flow and diffusional effects be uncoupled in the reaction expression if intrinsic chemical kinetics are to be determined [22].

There are both coarse and fine tests to rate the performance of a catalyst. Coarse tests are used to see if a catalyst will work at all for the reaction. Fine tests must closely model the actual process itself if catalysts are to be ranked. Fine tests can give data on activity as above, and, if designed and controlled precisely, can give data on controlling mechanisms and chemical kinetics [23].

### 4.3. Activity Test Reactors

#### 4.3.1 Batch reactors

The type of reactor is dictated by the type of test. For coarse testing, the batch reactor is often used. The advantage of the batch autoclave is that high temperatures and pressures can be used with low equipment cost. The disadvantage is, "the long heat up time makes it impossible to obtain rate data or determine the effects of varying the reaction time. Such a test would not be very discriminating between catalysts since most reactions would be driven to equilibrium" [7, p. II-15]. New batch systems are being developed to eliminate the disadvantages of the batch reactor [7, p. II-16]. These involve developing methods of almost instantaneous heating up and quenching of the reactor.

4.3.2 The continuous trickle bed reactor. To rank catalyst activity, a flow reactor is needed, and what is usually used when heavy feeds are processed at relatively high pressure and temperature is the trickle bed reactor. The reactor is tubular and filled with catalyst. Of the liquid hydrocarbon feed, usually no more than five percent, at the conditions in the reactor, exist in the vapor state; the other feed component is gaseous hydrogen. According to Satterfield [24], there are three possible flow mechanisms in the reactor:

1. Low liquid and gas flows: liquid trickles over the packing in laminar flow; gas flows continuously through the voids in the bed. This is called gas continuous flow; is encountered in laboratory and pilot scale reactors.
2. Increasing gas and/or liquid flows: rippling, slugging, or pulsation occurs. This is characteristic of petroleum processing.
3. High liquid and low gas flows: the liquid is continuous and the gas is dispersed in bubbles. This flow is characteristic of chemical processing.

The analysis of data obtained from a trickle bed reactor is complex because the reactors do not operate isothermally. Plug flow of the feed usually cannot be assumed either. The reactors operate somewhere between adiabatic and isothermal; external and pore diffusion must be accounted for; and holdup, dispersion, and wetting of the particles are affected by the process variables of temperature, pressure, space velocity, and gas to liquid ratio; as well as the physical aspects of the system such as bed length and particle diameter.

#### 4.4. Process Variable Effects

The effects of process variables and physical aspects on the data will now be discussed. During the course of experimental work, some of the variables will be held constant with the hope that the



effect of the particular variable on the reaction system for each catalyst will be similar. It must be recognized that some of the data obtained could possibly be due to the effects and interactions of the processing variables, and not due to the catalyst itself.

4.4.1 Temperature. For a homogeneous, non-catalytic reaction, the effect of temperature on the rate can usually be accounted for by the Arrhenius equation:

$$k = k_0 \exp. (-E_A/RT)$$

$E_A$ ,  $k_0$  are constants, and  $k$  is the rate constant in the expression:

$$\text{rate} = k \cdot f(\text{concentration})$$

For a catalytic reaction, however, not only is there a chemical reaction to account for, but also the diffusion of both the reactants and the products from both the bulk stream to the catalyst exterior surface, and from the exterior surface to the active sites within the catalyst must be accounted for. The Arrhenius expression is still used to describe the temperature effect, but, in this case, the activation energy is not constant and is a function of temperature.

As illustrated in Satterfield [25], for porous catalysts, as the temperature of reaction increases, the activation energy, as determined by an Arrhenius plot, will go through three distinct regimes:

1. At low temperatures, the rate will be controlled by the chemical reaction step occurring on the surface. This is because the conversions are so low that the diffusion rates are much faster than the rate of reaction. The rate constants obtained and the activation energies will be those values for the intrinsic chemical reaction. Usually, the activation energy will be in the range of 20 to 100 Kcal/mole.
2. With an increase in temperature, the chemical rate approaches the rate of pore diffusion and both phenomena control the overall rate in parallel. If power law kinetics for the chemical step can be assumed, the activation energy from an Arrhenius plot will be approximately half of the intrinsic activation energy because the average of the activation energies for the two steps is found; and the activation energy for diffusion is about 5 Kcal/mole which is usually negligible compared to the reaction activation energy.
3. As the temperature increases further, a concentration gradient is set up in the film surrounding the catalyst particle because reactants are being consumed at a rate faster than diffusion through the film can supply them. The global rate is then limited by this film diffusion effect.

It is of major importance not to be in a regime of film diffusion control when screening catalysts. This is because the rate of diffusion is a first order phenomena and all reactions occurring would appear to be first order, thus, all catalysts would appear to have the same activity. Any differences in the observed activities would be due to differences in the diffusion coefficients of the molecules rather than the characteristics of the surface reaction. The observed activation energies would be very low and equal to 4 to 5 Kcal/mole for heavy hydrocarbon feeds.

Finally, if a homogeneous reaction is possible in conjunction with the catalytic process (for example, thermal cracking occurring at severe hydrocracking conditions), it will occur with the catalytic reaction. The reaction observed will be the inherently faster reaction.

To obtain data for an Arrhenius plot, and therefore obtain activation energies, requires an isothermal reactor that operates in ideal plug flow. Data is obtained at a series of space velocities and at a series of temperatures. If power law kinetics hold (rate =  $kC^N$ ), then rate constants can be obtained and then plotted as  $\log k$  vs  $1/T$  to obtain the Arrhenius activation energy.

Most trickle bed reactors cannot meet the isothermal and plug flow assumptions. The best that can be done is to use some average temperature to determine a pseudo-activation energy. The number of

runs necessary to determine the activation energies and thereby determine controlling regimes is probably not justified in a catalyst screening experiment. There are, however, experimental techniques to qualitatively determine the controlling resistances at the test conditions. Perry [26] illustrates two of these tests for film and pore diffusion.

To test for film diffusion, runs are made at constant space velocity with different amounts of catalyst. If the conversion in the runs at higher superficial velocity (runs with the most amount of catalyst) is higher, then there is an indication of film diffusion being present. This test will show the minimum velocity required to induce sufficient turbulence to keep the reactant concentration at the catalyst surface negligibly close to the bulk concentration.

Pore diffusion tests are made by making a series of runs with decreasing catalyst particle size. If pore diffusion is present, the smaller size particles will show a higher conversion. A point will be reached where a further decrease in particle size will not increase the rate, this signifies that another mechanism is now controlling the reaction.

The above test might give the wrong impression of what is controlling in the light of recent articles [24,27,28]. Instead of mass transfer effects, what might be showing up are results of axial dispersion (deviation from ideal plug flow), bed holdup, or incomplete

particle wetting. A longer bed will increase holdup, increase the contacting effectiveness of the catalyst, and therefore increase the rate. Smaller catalyst particles improve wetting, therefore more catalyst is being used, and again the rate increases. The conclusion is that there can be several reasons for the increase in rate that are due not to diffusional effects, but due to the small scale reactor not operating in an ideal manner.

Ketjen division of ARMAK has done much work on making bench scale reactors model industrial situations [17]. They state that "in small reactors of 1" I.D. with a 1/4" O.D. thermowell, severe deviations from plug flow occur by channeling or axial dispersion, especially for heavier feedstocks." They found by diluting the catalyst bed with inert particles in a 1:1 ratio, the above effects can be largely cancelled. They conclude that, for the above diffusion tests, any remaining activity differences noticed after dilution are probably due to film and pore diffusion.

4.4.2 Pressure. The effects of pressure on the hydrodenitrogenation reaction have already been discussed. For the overall hydrotreating process, pressure increases will increase conversion up to the point where the liquid in the catalyst pores becomes saturated with hydrogen. A pressure increase above this will generally have no effect on conversion. Higher pressures do have an effect on catalyst life,

however. The coke precursors are more easily saturated at high pressure so less coke is laid down, allowing a longer cycle life. Essentially, when higher temperatures are used and hydrocracking begins, pressures must be increased to a point where coking will not appreciably poison the catalyst.

4.4.3 Hydrogen to oil feed ratio. As the above ratio is increased, an optimum will be found for each reaction. The rate of reaction will first increase due to having more  $H_2$  available to react, and due to the faster gas flow breaking up rivulets and stagnant areas.

After the optimum ratio is reached, higher gas rates will decrease conversion. The drag exerted on the liquid by the gas pulls it off of the catalyst and decreases the contacting time experienced by the liquid.

#### 4.5. Scale Up and Physical Aspects

It was found that industrial reactors operated much better than pilot reactors when operating on the same feed with the same catalyst. This was because the superficial flow rates in the industrial reactors were much higher than in the pilot reactors; the catalyst was being used much more effectively. The hold up or wetting was increased in the industrial reactors and accounted for the better performance.

Satterfield states [24] that the Mears equation developed to explain trickle bed performance and based on particle wetting realistically explains the scale-up effects. The equation is,

$$\log \frac{C_{in}}{C_{out}} \propto (h)^{-0.32} (\text{LHSV})^{-.68} dp^{.18} v^{-.05} \left(\frac{\sigma C}{\sigma}\right)^{.21} N$$

C = concentration

h = catalyst bed depth

LHSV = liquid hourly space velocity

dp = particle diameter

v = kinematic viscosity

$\sigma$  = surface tension

N = catalyst effectiveness factor

This equation gives the effects of catalyst size and bed depth. For example, halving the catalyst size will increase the outlet concentration by a factor of 3.5; and doubling the bed depth will increase the concentration by a factor of 3.1, if all other variables can be held constant.

#### 4.6. Conclusions

As stated above, there are many aspects of reactor operation that can affect the results when screening hydrotreating catalysts. To study all of the factors along with many catalysts would require an

inordinate number of experiments. Therefore, to reduce the number of experimental runs, some of the factors will be held constant assuming that their effects on the performance of the reactor would be similar for each catalyst. The variables that will be held constant are:

- Pressure, which assumes that there will be no pressure-catalyst interaction.
- Temperature, at a value which is not in the film diffusion region.
- Hydrogen to oil feed ratio, once the optimum is found for the reaction.
- Particle size, whenever possible. Bed volume and bed dilution ratio.



## 5. EXPERIMENTAL EQUIPMENT AND PROCEDURES

### 5.1. Reactors

5.1.1 Trickle bed. A schematic flow diagram of the trickle bed reactor is shown in Figure 2. The construction of the system and then its operation will be described in turn.

The reactor is a one-inch i.d. schedule 80 inconel pipe, 32 inches long. There is inserted from the top a 1/4" O.D. concentric thermowell the entire length of the packed section that contains four thermocouples. At the top of the reactor there is also an inlet for the externally mixed hydrogen and liquid feedstock, plus an exit to a rupture disk. The reactor is heated by an aluminum block wrapped with nichrome heating wires. There are three heating coils, and power input and control is by manual variable transformers. The system is easily capable of attaining a temperature of 450°C with an eight hour heatup time.

Liquid feed was accomplished with a Milroyal packed plunger pump of 1.25 gal/hr maximum capacity at 3000 psig. The pump head and all feed lines and feed reservoirs are heated with electric heating tapes from Cole-Parmer. The pumping rate was measured by using a heated 100 ml buret. Feed was normally taken from a 1000 ml graduated reservoir, but, when the stopcock on this was closed, the level began dropping in the small buret; and the rate could be measured with a stopwatch.

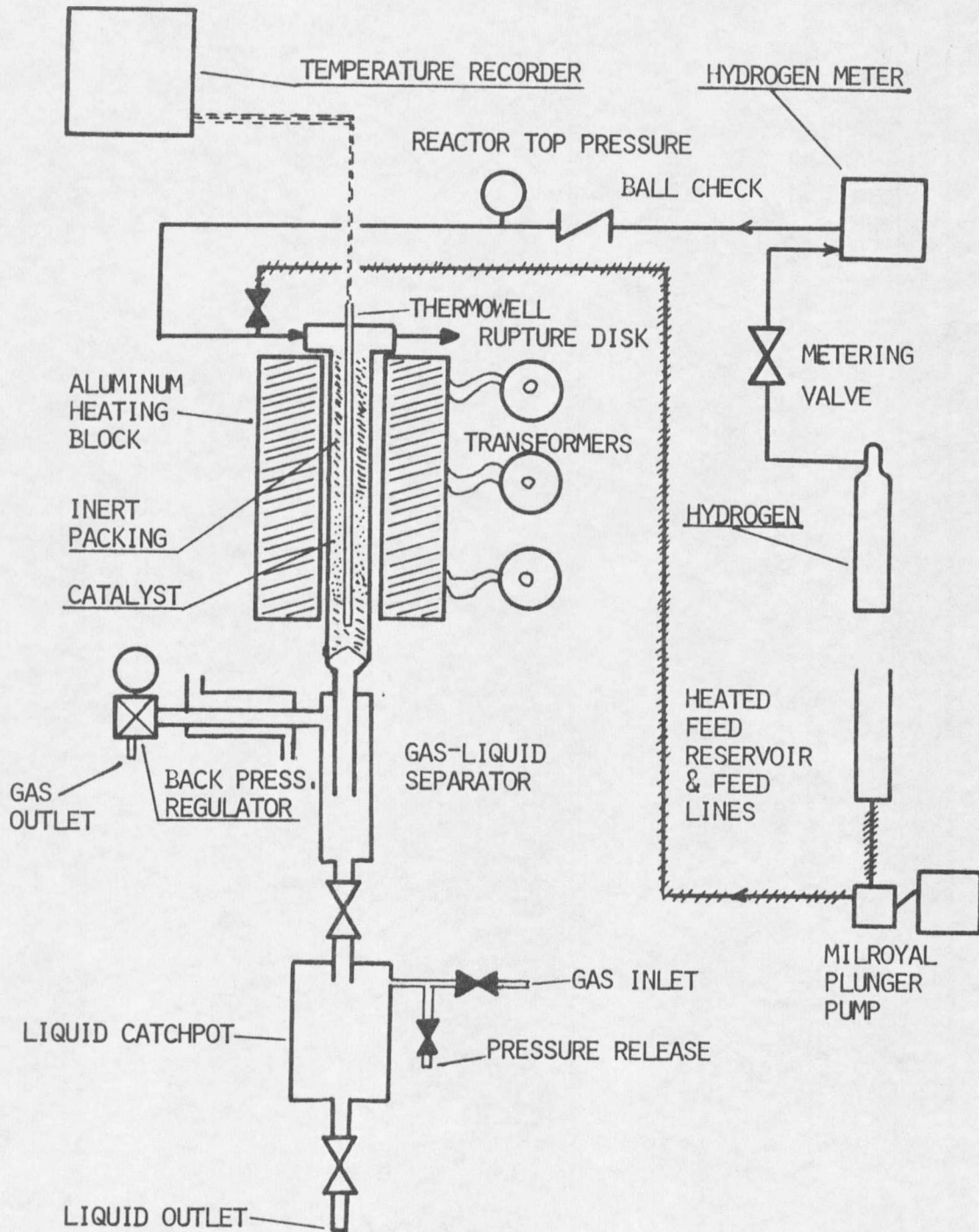


FIGURE 2 TRICKLE BED REACTOR

Hydrogen feed from a 2000# cylinder was controlled by a Whitey micrometering valve, and measured with a Brooks Model 5811 mass flow meter. The range of the meter was 0-10 standard liters per minute at an operating pressure of 1500 psi. The meter was calibrated with a wet test meter when lower pressures were used.

Pressure in the reactor was controlled by a Grove Valve Company back pressure regulator. This was constructed of stainless steel and had a teflon diaphragm. The regulator was rated for control up to 3000 psig.

The gas was separated from the liquid products in a phase separator; the liquid continuing downward into a catch-pot which was dumped intermittently. The procedure to dump the liquid was to close the inlet ball valve to the catch-pot; release the pressure through the side valve; and dump the liquid through the bottom valve. The catch-pot was then repressurized with nitrogen through the side valve; then the top ball valve was reopened to the phase separator.

5.1.2 Operation. The reactor was filled with 20 ml of 1/4" Norton Denstone ceramic bed support; 100 ml of 1/8" Denstone; 160 ml of catalyst bed consisting of 80 ml of catalyst mixed with 80 ml of 1/8" Denstone; and then 1/4" Denstone to fill the tube. A stainless steel screen was placed at the bottom of the bed to support it. The reactor was then placed in the heater; the catch-pot connected; and the

reactor pressurized to check for leaks. If no leaks were found, the reactor was depressurized and the heaters turned on to bring the reactor up to run temperature. This usually took overnight.

The startup procedure consisted of bringing the reactor up to pressure with hydrogen. The liquid feed line was then disconnected from the reactor, and the pump was run until feed exited the reactor end of the line; this was to ensure that the pump was operating. The line was then reconnected; the reactor side valve opened, and the pump restarted to begin the run.

In most runs, three to five hundred milliliters of feed were run to age the catalyst and to bring the system to steady state. Then 150 to 200 ml of feed was pumped at the set space velocity; the conditions were then changed, and another 200 to 300 ml of feed were used to steady the reactor before taking a sample. Three or four space velocities were usually taken in each run, and the total amount of feed was usually under 1500 ml.

The reactor was shut down by turning off the liquid feed and disconnecting the liquid feed line. Hydrogen was allowed to flow through the reactor while motor oil was pumped through the feed line to clear out the tar. Once it was apparent that the pump and feed line contained only oil, the hydrogen was shut off, the reactor depressurized, and the catchpots disconnected. The liquid feed line was reconnected, and oil was pumped through the catalyst bed. This

served to clear the unreacted tar from the reactor and loosen the catalyst. After the reactor and pump had cooled to room temperature, acetone was pumped through the system to further clean it. After this the catalyst would fall out of the reactor when it was dismantled, otherwise the catalyst would be fused by the solidified tar and had to be drilled out.

5.1.3 Batch reactor. A Parr Rocking Bomb Autoclave was used for batch catalyst tests. It is a standard reactor and will not be completely described here. When catalysts were tested, the bomb was charged with 100 ml of feed, 25 ml of catalyst, and, after assembly, approximately 2000 psig of hydrogen.

The bomb took about an hour to heat to 450°C, and then was held there for thirty minutes. The pressure would first rise as the temperature increased, and then would fall as reaction began. After the run, the bomb was removed from the rocker-heater and allowed to cool in air.

## 5.2. Product Analyses

5.2.1 Nitrogen. The analysis for nitrogen in the feed and products was by the Kjeldahl method as described in reference [29]. The method is standard and was modified only by increasing the  $K_2SO_4$  from 20 g to 40 g; increasing the amount of  $H_2SO_4$  to 35 ml; and decreasing the

amount of sample to 1/2 g. The digestion and distillation procedure were followed exactly as stated in the reference.

To determine the accuracy and the precision of both the method and the analysts, nitrogen determinations were run on the feedstocks with known nitrogen contents. Once repeatability was achieved in the feedstock analysis, it was felt the product analyses would also be accurate and repeatable. N-Point<sup>R</sup> indicator was used in the final titration step.

5.2.2 Sulfur. The analysis of sulfur was accomplished using a Shell-Braum Sulfur analyzer and using the exact technique described in reference [30]. The sample was burned in air and oxygen and the resulting SO<sub>2</sub> and SO<sub>3</sub> was absorbed in hydrogen peroxide. The amount of sulfur was determined by titration using standard NaOH and methyl purple indicator.

5.2.3 Product distillation. Products were distilled using the ASTM D-86 method. This is a simple distillation that provides the data of the volume percent of the initial charge distilled versus the boiling temperature. This distillation was used to obtain a gross idea of how much the product boiling temperature was reduced as compared to the feed.

The distillation end temperature was 700°F. About 53% of the feed had come over at that temperature. The products boiled about 80%

over at 700°F. Finally, since the distillations were performed at 640 mm, slightly more product boiled over than would have at the standard pressure. No attempt was made to correct the data to standard pressure because it was only being used to compare products.

### 5.3. Catalyst Preparation

The catalysts prepared at Montana State were made using commercial supports and impregnated with metal salts using the incipient wetness technique as described in the Introduction. To make a nickel-moly catalyst, for example, the following procedure was followed.

1. The support, say, Norton 6176 alumina, was calcined overnight to 450°C, and then cooled in a dessicator and weighed.
2. A solution of ammonium heptamolybdate tetrahydrate of about .3 gm/ml was made up and cooled to or below room temperature (AHM =  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ).
3. The catalyst support was placed in a slowly rotating jar, and the AHM solution was slowly dripped onto it using a separating funnel. Usually, it took about two hours to complete this step.
4. After all the solution was used, the jar was sealed and the catalyst was allowed to soak, with frequent stirring, for about eight hours.

5. The next step involved drying the catalyst by directing a stream of air into the rotating jar. This was allowed to continue overnight.
6. The catalyst was next dried at 110°C in air from four to six hours.
7. The catalyst was then calcined in air with a six hour heat up to 400°C, then a slower heatup to 450°C for twelve hours.
8. The catalyst was then cooled in a dessicator and weighed to determine the amount of molybdenum oxide added to the support.

Nickel (or other promoter) impregnation then followed using nickelous nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and following the same procedure.

No attempt was made to determine the form of the oxides on the support. The composition was reported as the weight percent of the metal oxide on the support irregardless of the form.

All catalysts used were sulfided externally to the reactor using the same procedure. The catalyst was placed in a 1" tube placed in a furnace. A gas mixture of 10%  $\text{H}_2\text{S}$  in  $\text{H}_2$  was begun as the furnace was turned on; it took about 4 hours to reach the temperature of 340°C and then this was held for twelve hours. The catalyst was removed from the tube after cooling, and sealed in glass jars until it was used.



## 6. RESULTS - COMMERCIAL CATALYSTS

### 6.1. Preliminary Continuous Runs

(a) Establishment of a hydrogen flow rate. Data from runs three, four and six were used to determine a hydrogen to oil ratio that would be used throughout the catalyst screening tests. Runs three and four used a cobalt-molybdate catalyst (C.&C.I. C20-6-E-1/16") while run six used a nickel tungsten catalyst (Harshaw 4401-E-1/12"). The reactor was run at the nominal pressure and temperature of 800 psig and 450°C; liquid space velocity was varied along with hydrogen rate during the runs.

The effect of hydrogen feed ratio on percent sulfur in the product is shown in Figure 3. The hydrogen ratio varied from 1600 to 7000 scf/bbl. It appears that at flow rates over about 5000 scf/bbl, the effect of the variable levels out.

Figure 4 shows the percent nitrogen versus the H<sub>2</sub> feed ratio for both the cobalt-moly and nickel tungsten catalysts. The sparse data presented appears to show that the effect for nitrogen has leveled off also.

As was stated in the Introduction, the original bench scale hydrotreating tests had used hydrogen flow ratios of between 8000 and 12000 scf/bbl. Using this, and the data presented in Figures 3 and 4, it was decided to use 10,000 scf/bbl (1781 NL/liter) as the ratio of hydrogen to liquid feed in the catalyst screening tests.

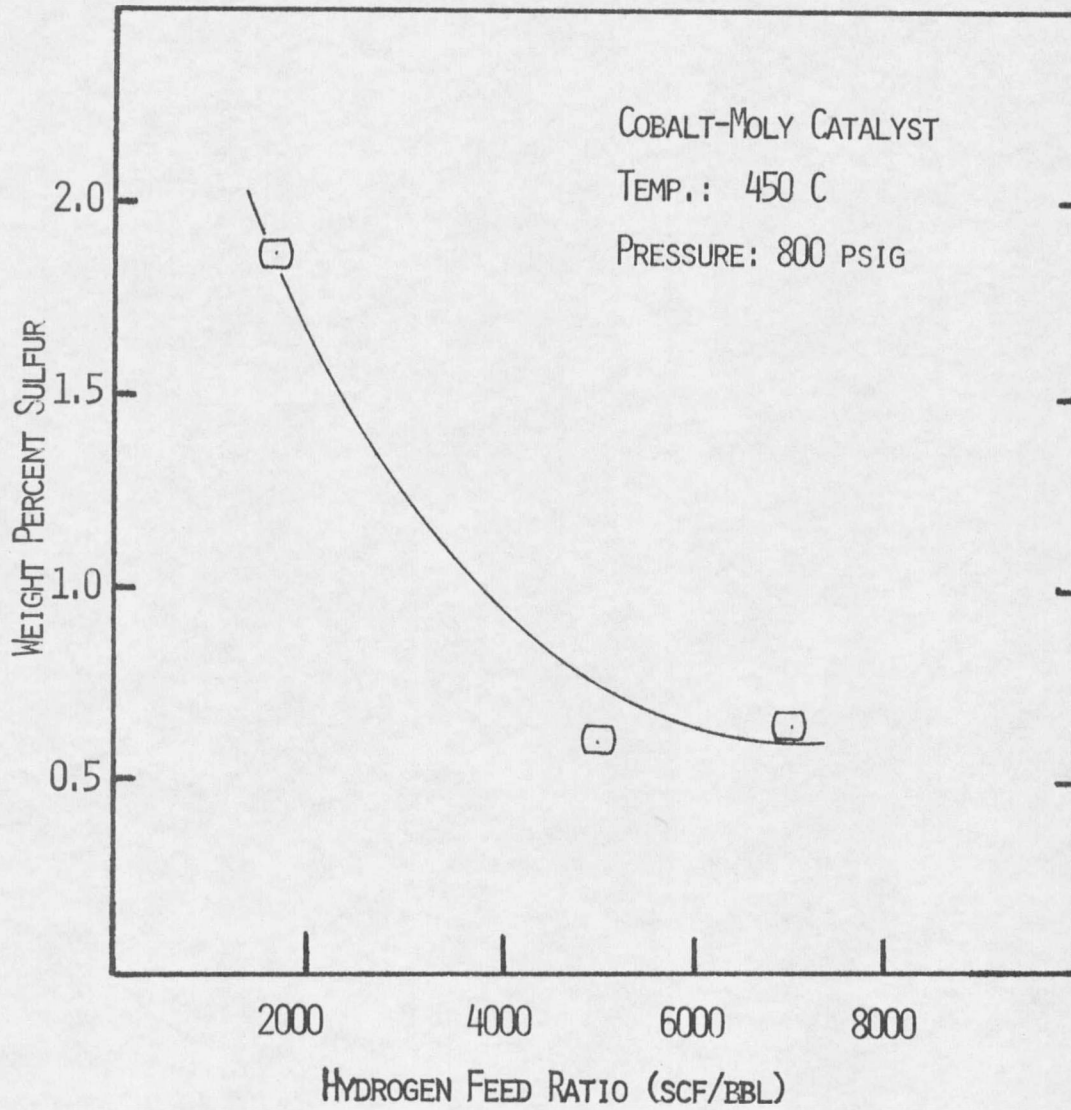


FIGURE 3. WEIGHT PERCENT SULFUR VS HYDROGEN FEED RATIO

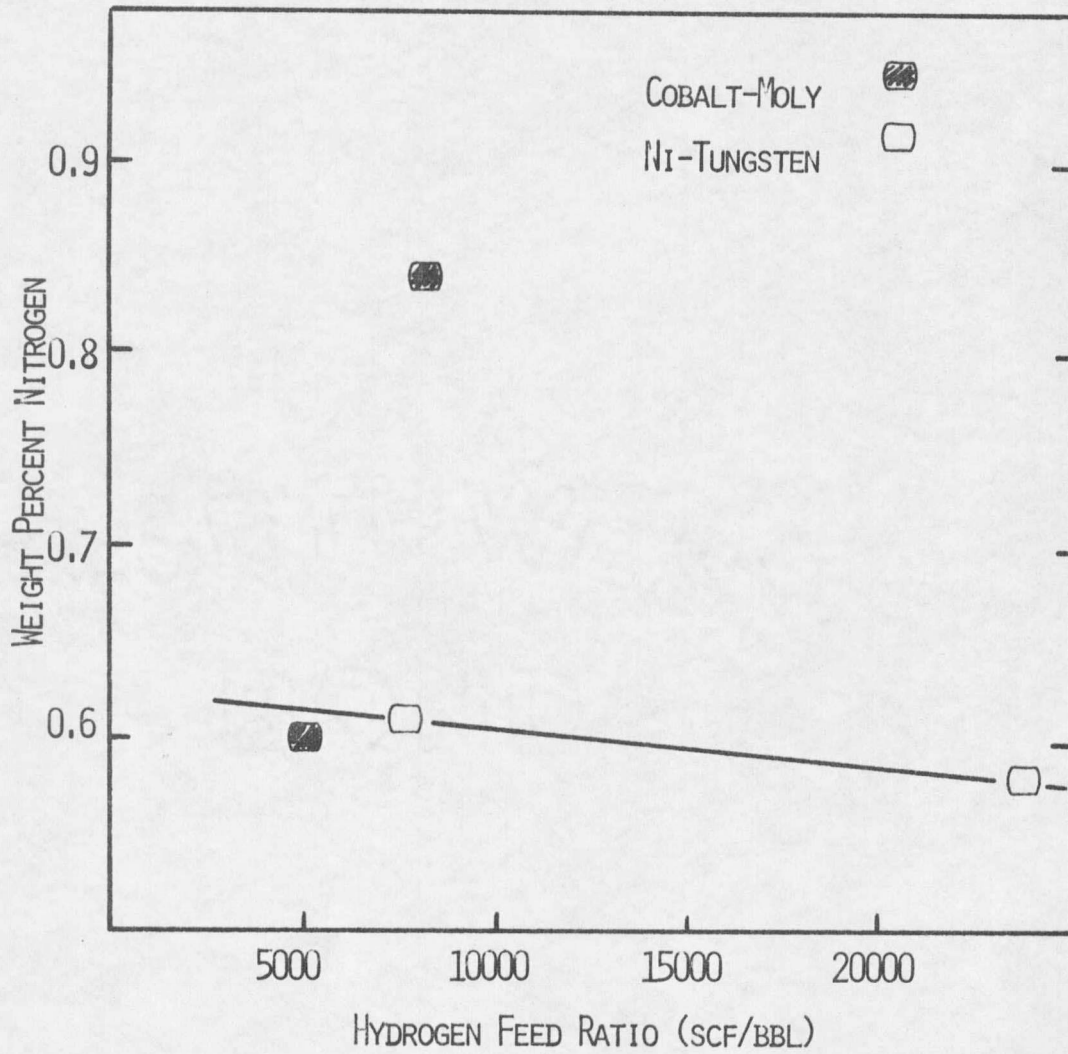


FIGURE 4. WEIGHT PERCENT NITROGEN VS HYDROGEN FEED RATIO

(b) Establishment of a test temperature. The test for film diffusion from Perry's Handbook as described in the Introduction was made using a cobalt-molybdate catalyst (Harshaw 0401-T-1/8"). Three runs were made, the first with 60 ml of catalyst diluted with 60 ml of 1/8" Denstone, and the second and third with 35 ml of catalyst diluted with 35 ml of Denstone. As stated before, if conversion increases for the test at higher liquid superficial velocity, mass transfer resistance is indicated as long as the catalyst bed is diluted. The results of the tests are shown in Figures 5 and 6.

The sulfur analyses versus space velocity is plotted in Figure 5 for the test. There appears to be a difference in conversion in the middle space velocities. This seems to indicate that at the test conditions, film diffusion possibly controlled the rate of sulfur removal. This is reasonable in light of the discussion in the Introduction which states that as the rates of surface reaction and pore diffusion increase with temperature, film diffusion can possibly control the rate of reaction. The conversions of sulfur were very high, indicating that the rates are high, and therefore, it appears that film diffusion could be controlling the rate of hydrodesulfurization.

The results of the tests for nitrogen are shown in Figure 6. Only a single curve could be drawn through the points indicating that film diffusion probably did not control the rate of reaction. Since the reaction rates were very low (since more nitrogen actually was in

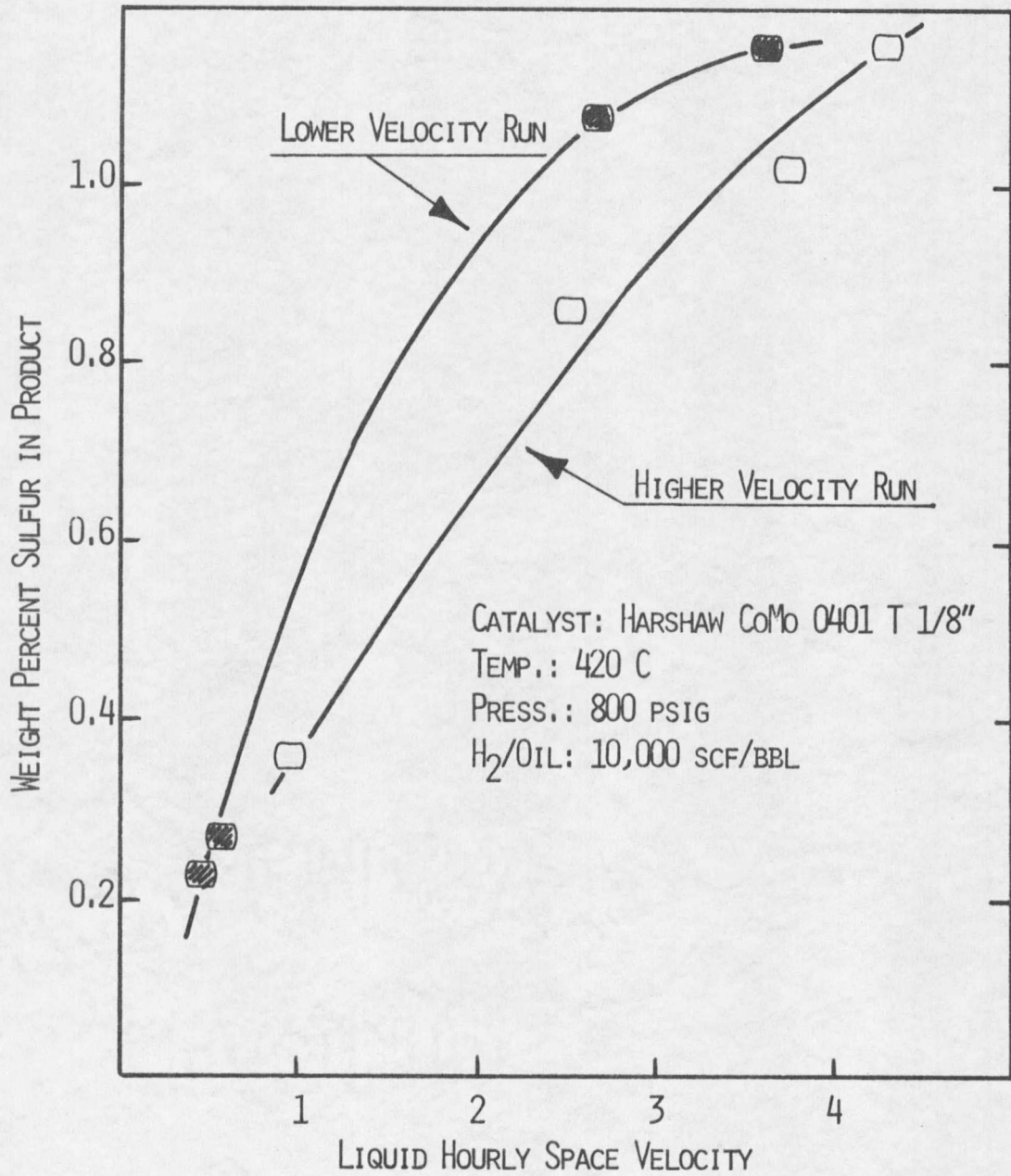


FIGURE 5. WEIGHT PERCENT SULFUR VS LHSV, DIFFUSION TESTS



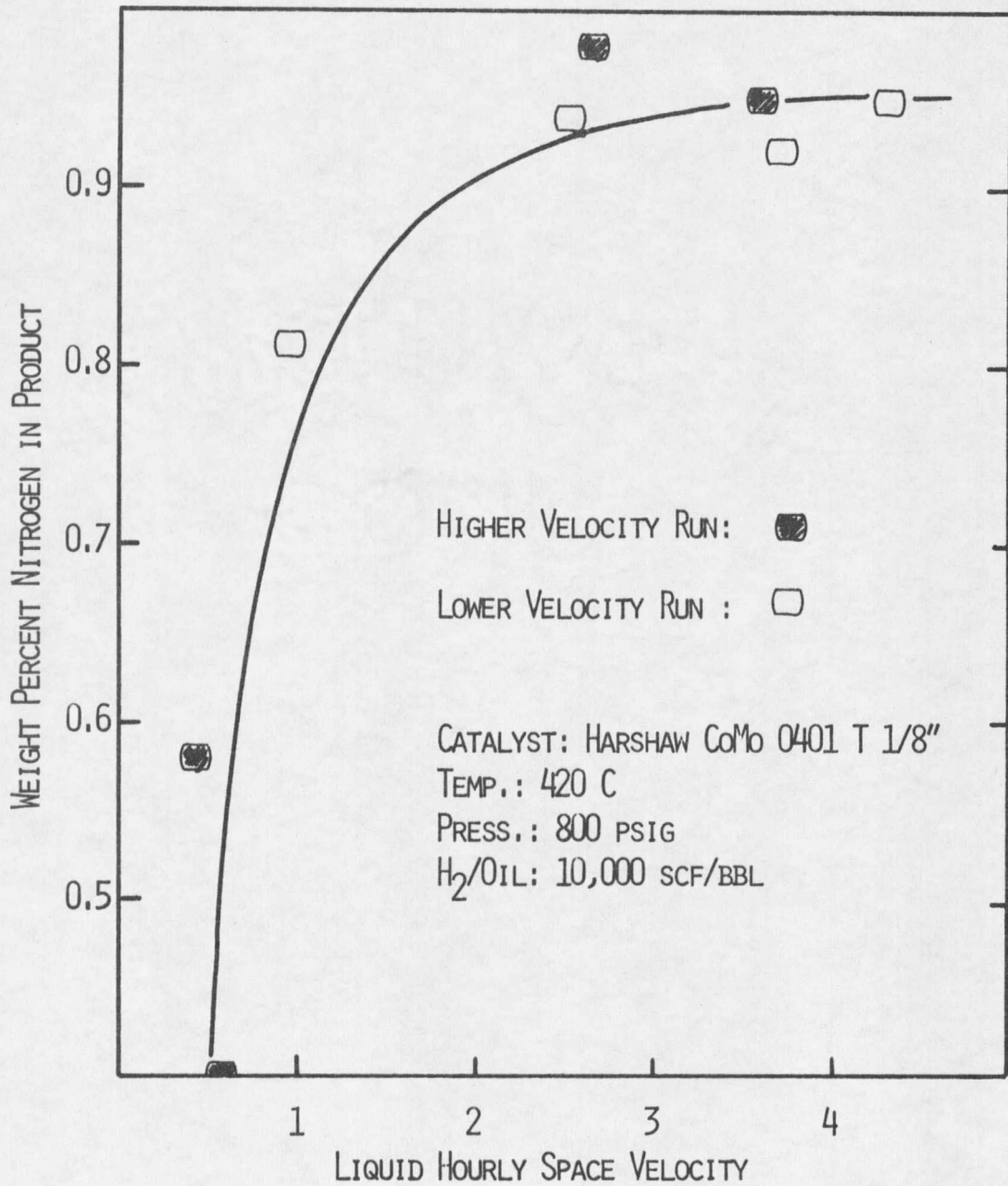


FIGURE 6. WEIGHT PERCENT NITROGEN VS LHSV, DIFFUSION TESTS

the products than in the feed at the higher space velocities--possible if sulfur is removed and gas made with no nitrogen conversion), it is reasonable that either surface reaction or pore diffusion limited hydrodenitrogenation reaction.

A co-worker on this project, Gary Hass [31], using a different feedstock which behaved similarly to COED pyrolysis oil, ran tests with different catalyst particle sizes, and concluded that pore diffusion was significant for nitrogen removal [31]. So it is possible that the nitrogen containing molecules have no problem getting to the catalyst exterior surface from the bulk stream, and thus the tests for film diffusion would show negative.

The film diffusion tests were run at a reactor inlet temperature of 420°C. It was decided to lower the inlet temperature to 410°C with the hope of ensuring that nitrogen removal would not be controlled by film diffusion. This would ensure that screening tests would give results based on the catalyst chemical and pore properties and not on first order molecular diffusion.

For the screening tests, from the above results, it was decided to use the following standardized test conditions:

- Catalyst: 80 ml diluted with 80 ml inert support.
- Temperature: Reactor inlet at 410°C with an average of top, middle, and bottom bed thermocouples no more than 420°C.

- Pressure: 800 psig, this was arbitrarily chosen.
- Space Velocities: In the range of 1 to 4 per hour.
- H<sub>2</sub> Flow Rate: 10,000 scf/bbl (1780 NL/L)

## 6.2. Catalyst Screening Tests

In this section, the results of continuous screening tests are presented for the following catalysts:

Nickel tungstates: Harshaw 4401, 4301, and 4303; Ketjen HC-5 and Ketjenfine 330-3E

Nickel molybdates: Shell 324, Harshaw HT 100 and HT 500, Houdry HR-811, and Cyanamid HDS9A.

Cobalt molybdates: Harshaw 0401 and HT 400; Shell 344, Cyanamid HDS-20A; Houdry HR801, and CCI C20-6.

The data produced in these runs are presented in Tables AI, AII, and AIII in the Appendix. Figures 7 through 12, following, present the performance of these catalyst for sulfur and nitrogen removal.

6.2.1 Cobalt molybdate catalysts. The experimental results using Cobalt molybdate catalysts are presented in Figures 7 and 8 and Table III. Harshaw HT 400 and Shell 344 gave the best sulfur removal, followed closely by Cyanamid HDS 20A.

Nitrogen removal for these catalysts is presented in Figure 8. At lower space velocities, nitrogen removal is as good for these as for the nickel-moly catalysts shown later. The calculated average



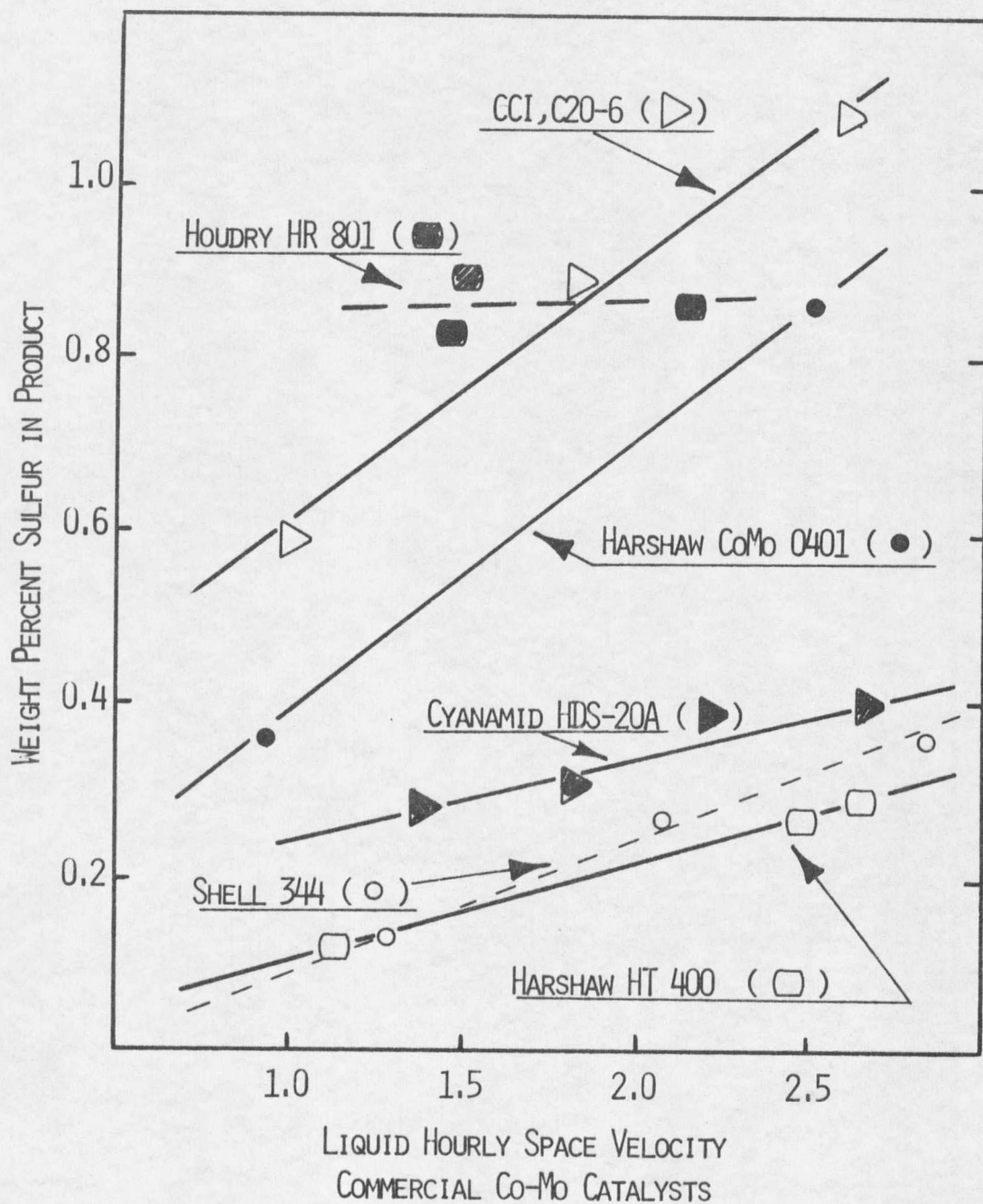


FIGURE 7. WEIGHT PERCENT SULFUR VS LHSV, CO-MOLY CATALYSTS























































































































































