

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
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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.

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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.

I 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: .i 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.

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Approved:

Lloyd Berg
Chairperson, Graduate Committee

Lloyd Berg
Head, Major Department

Henry L Parsons
Graduate Dean

MONTANA STATE UNIVERSITY
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TABLE OF CONTENTS

	Page
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

		Page
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

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

LIST OF TABLES

Table		Page
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
Appendix Tables		
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

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

LIST OF FIGURES

Figure		Page
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

Figure | Page

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

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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 upflow 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 combusion of the char. The process diagram is shown in Figure 1. Table I presents the physical and chemical properties of the feed [3].

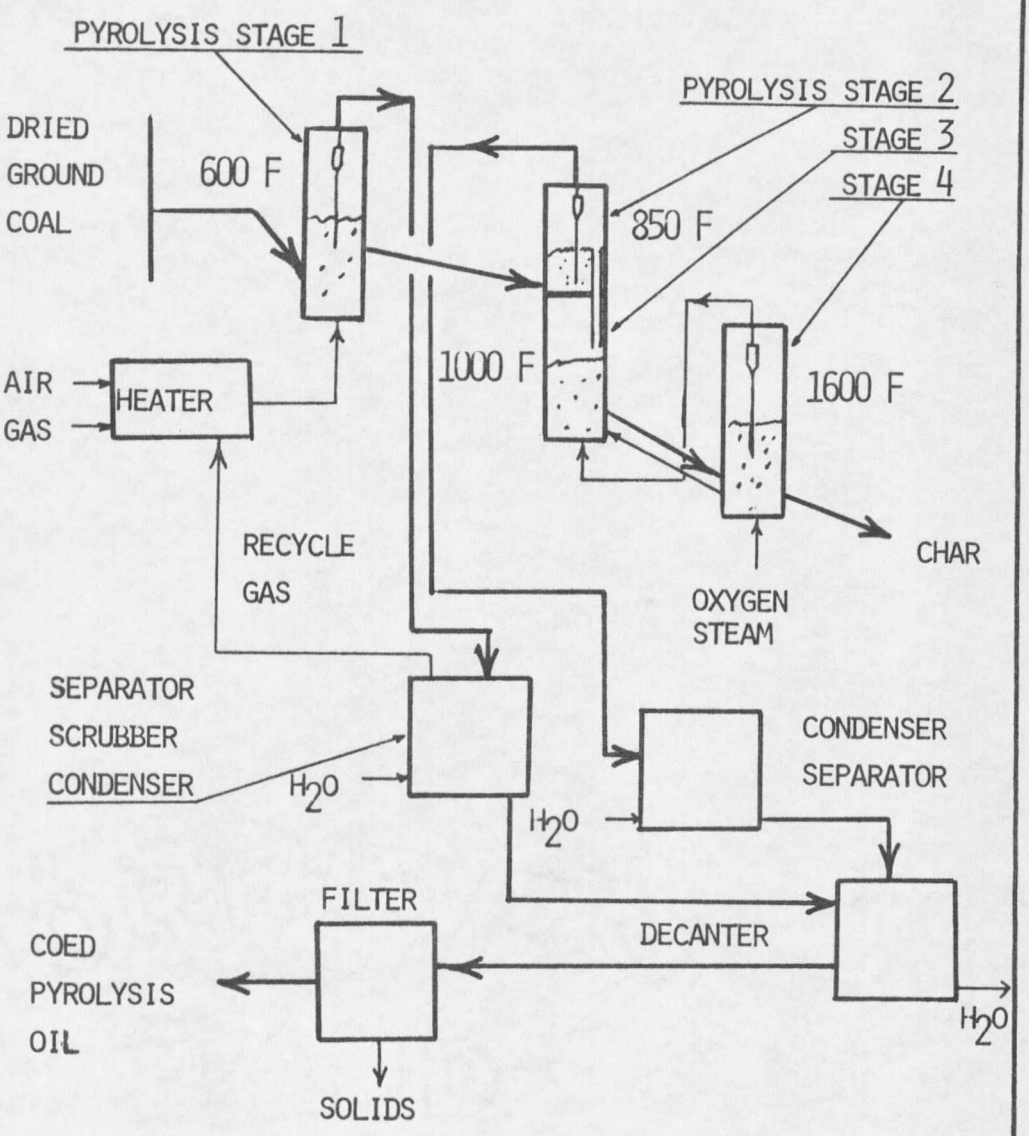
Table I

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.



PROJECT COED PYROLYSIS PROCESS

FIGURE 1. PROJECT COED PYROLYSIS PROCESS

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^2/gm), and the pore size will be small. Silica aluminas and aluminas will have surface areas of 100 to 250 m^2/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, $\bar{\ell}$. 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 ($a < 100$ Å) interconnected by macropores ($a > 100$ Å). 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_3 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:

CoMo/SiAl > CoMo/Al >> NiW/Si

This trend exactly follows acid strength.

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

NiW/Si > CoMo/SiAl > CoMo/Al

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 Cr_2O_3-Al_2O_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 hydrotreating 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^2/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_2/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_2/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.

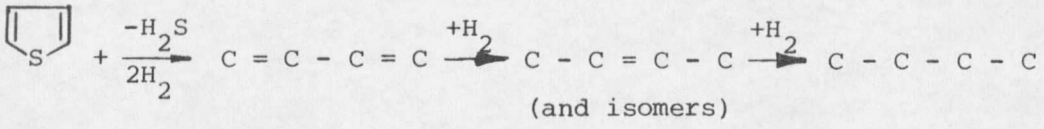
3.2. Desulfurization

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_2 pollution.

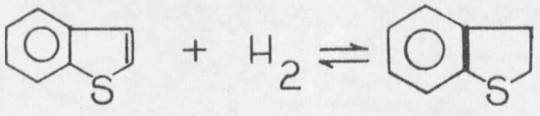
Also stated in the same article is that at the usual industrial conditions (600-800°F, up to 3000 psig) the hydrodesulfurization reactions are irreversible, exothermic, and have heats of reaction of about 50 to 100 BTU per standard cubic foot of hydrogen consumed.

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,



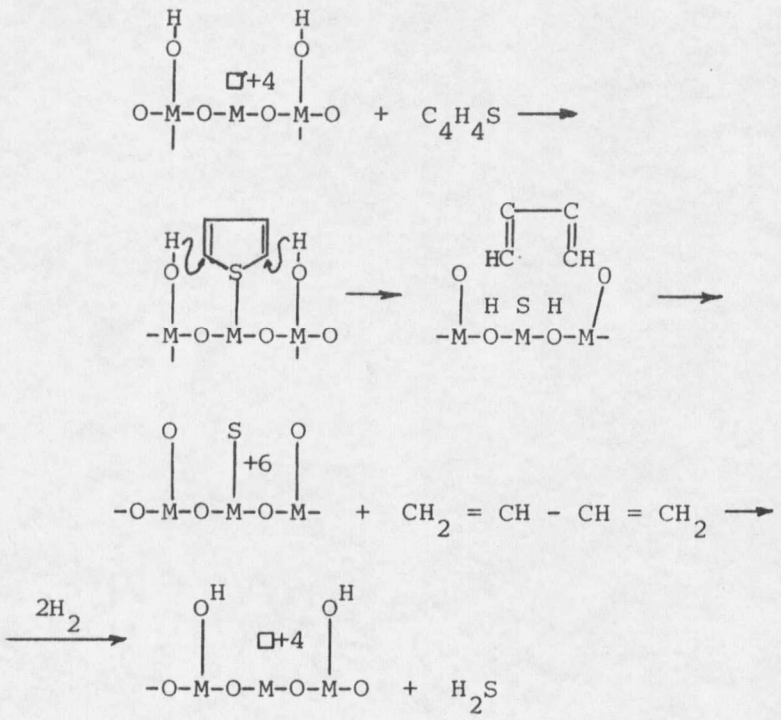
In the above reaction, the rate determining step is C - S bond cleavage to form 1-3 butadiene, and not saturation of the aromatic bonds in thiophene.

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 (□) 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]

$$R_{HDS} = \frac{\alpha_2 \; k_2 \; P_{H_2} \; C_S}{(1 + K_{H_2} P_{H_2} + K_{H_2S} P_{H_2S})}$$

α_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 H_2S inhibits the reaction and the rate of desulfurization decreases with increasing molecular weight of the sulfur containing compounds.

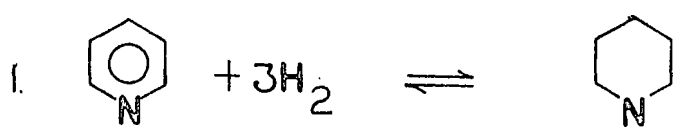
3.3. Hydrodenitrogenation

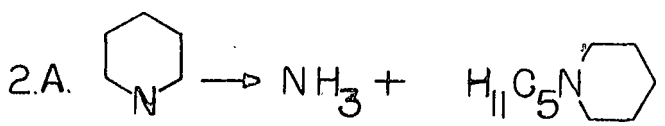
The three reasons to remove nitrogen from coal liquids are to protect acid sites on cracking and reforming catalysts in downstream

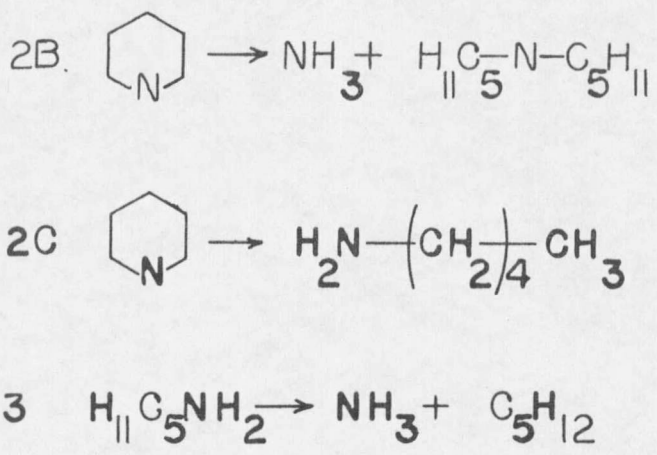
processing, to reduce nitrogen oxides pollution when the final products are used, and to remove nitrogen compounds which cause harsh performance and varnish in many fuel applications.

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.

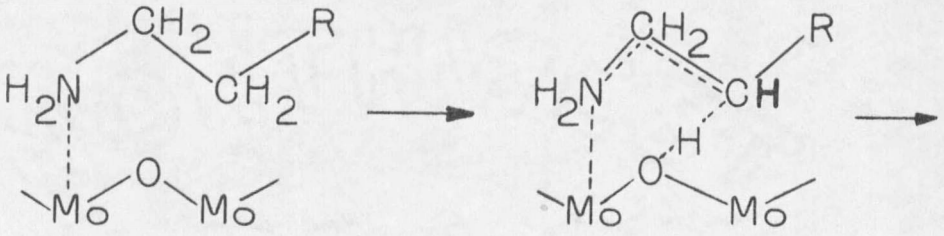
Model nitrogen compounds that are present in coal liquids are pyridines and substituted pyridines (quinoline); and pyrroles and substituted pyrroles (indole) as the basic nitrogen heterocyclics. The non-basic compounds are the saturated derivatives of the above [7, p. 124]. Pyridine will be used to illustrate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

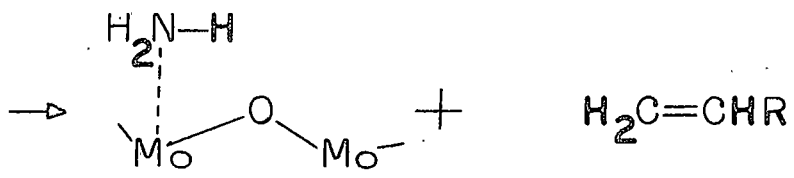






In the above, Step 1 is in equilibrium; Steps 2A and 2B further react to pentylamine. The rate determining steps are the hydrocracking of the bases. The surface mechanism on a cobalt-moly catalyst was suggested as, [7, p. 126]





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 hydrotreating 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:

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

E_A, k_o 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,

$$\log \frac{C_{in}}{C_{out}} \alpha (h^{-0.32} (LHSV)^{-.68} dp^{.18} \nu^{-.05} (\frac{\sigma c}{\sigma})^{.21} N)$$

C = concentration

h = catalyst bed depth

LHSV = liquid hourly spare velocity

dp = particle diameter

ν = kinematic viscosity

σ = 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.

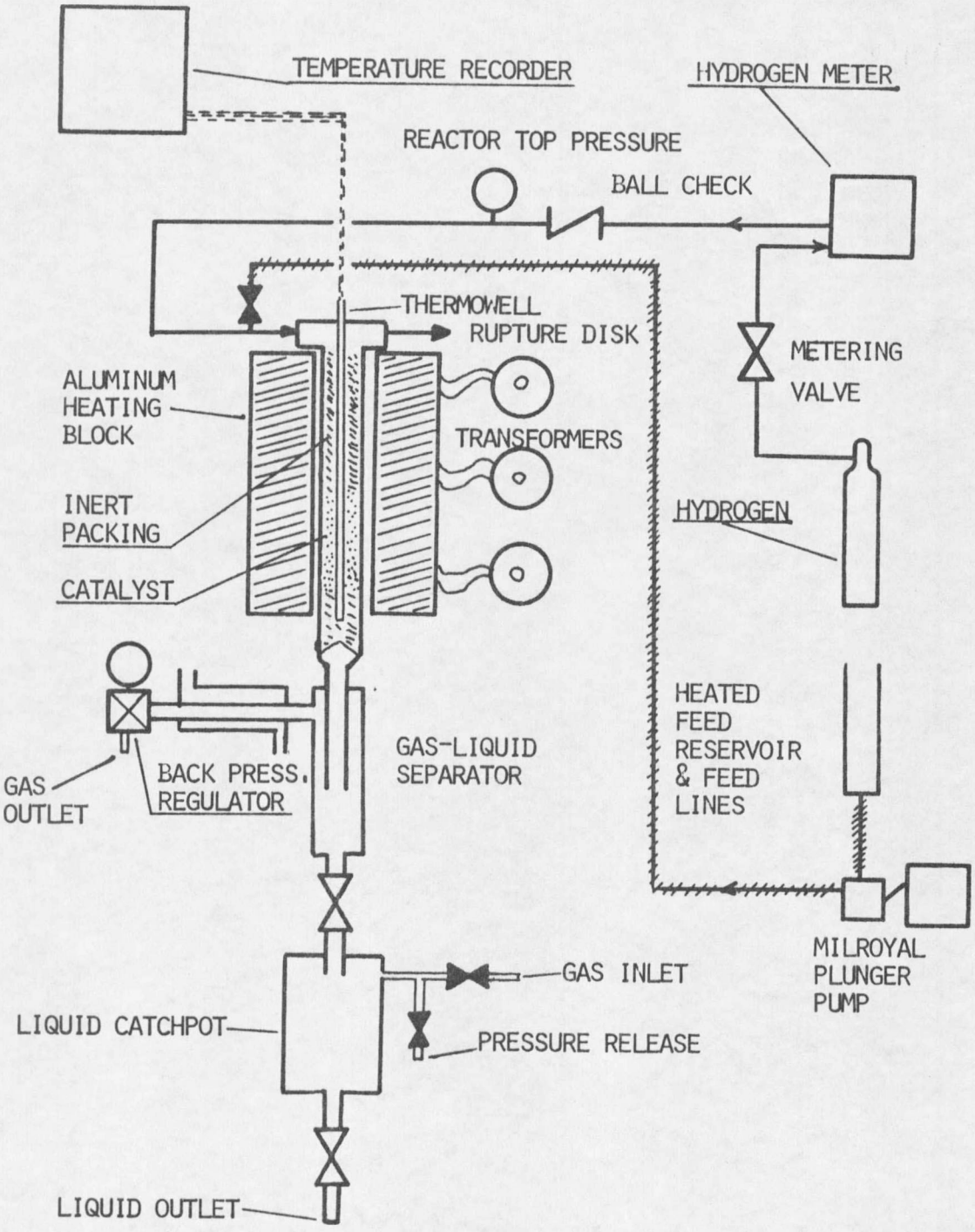


FIGURE 2 TRICKLE BED REACTOR

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 comletely 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 ^{R} 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_2 and SO_3 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 = $(NH_4)_6Mo_7O_{24}4H_2O$).
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 ($Ni(NO_3)_2 \cdot 6H_2O$), 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% H_2S in 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_2 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.

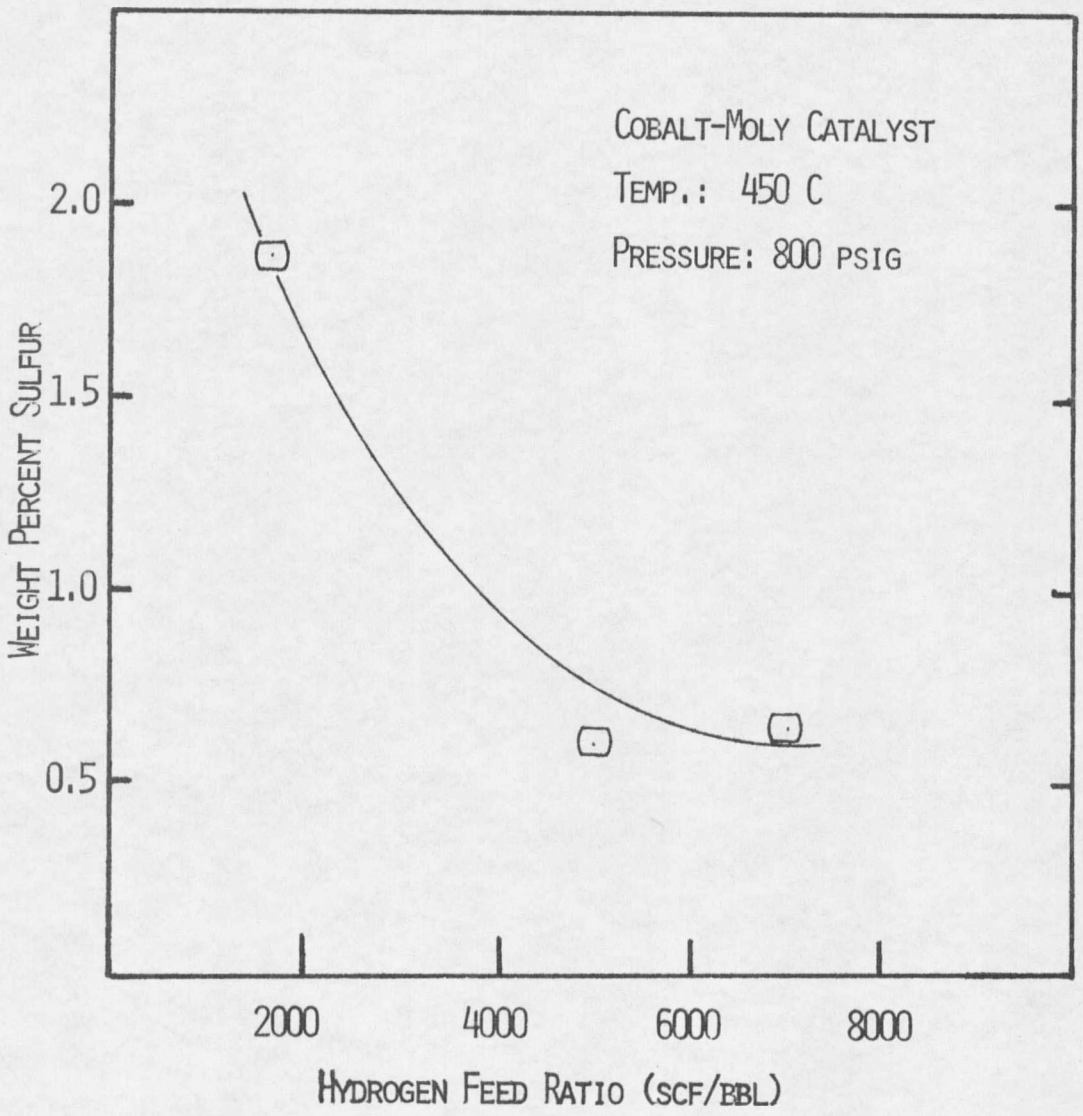


FIGURE 3. WEIGHT PERCENT SULFUR VS HYDROGEN FEED RATIO

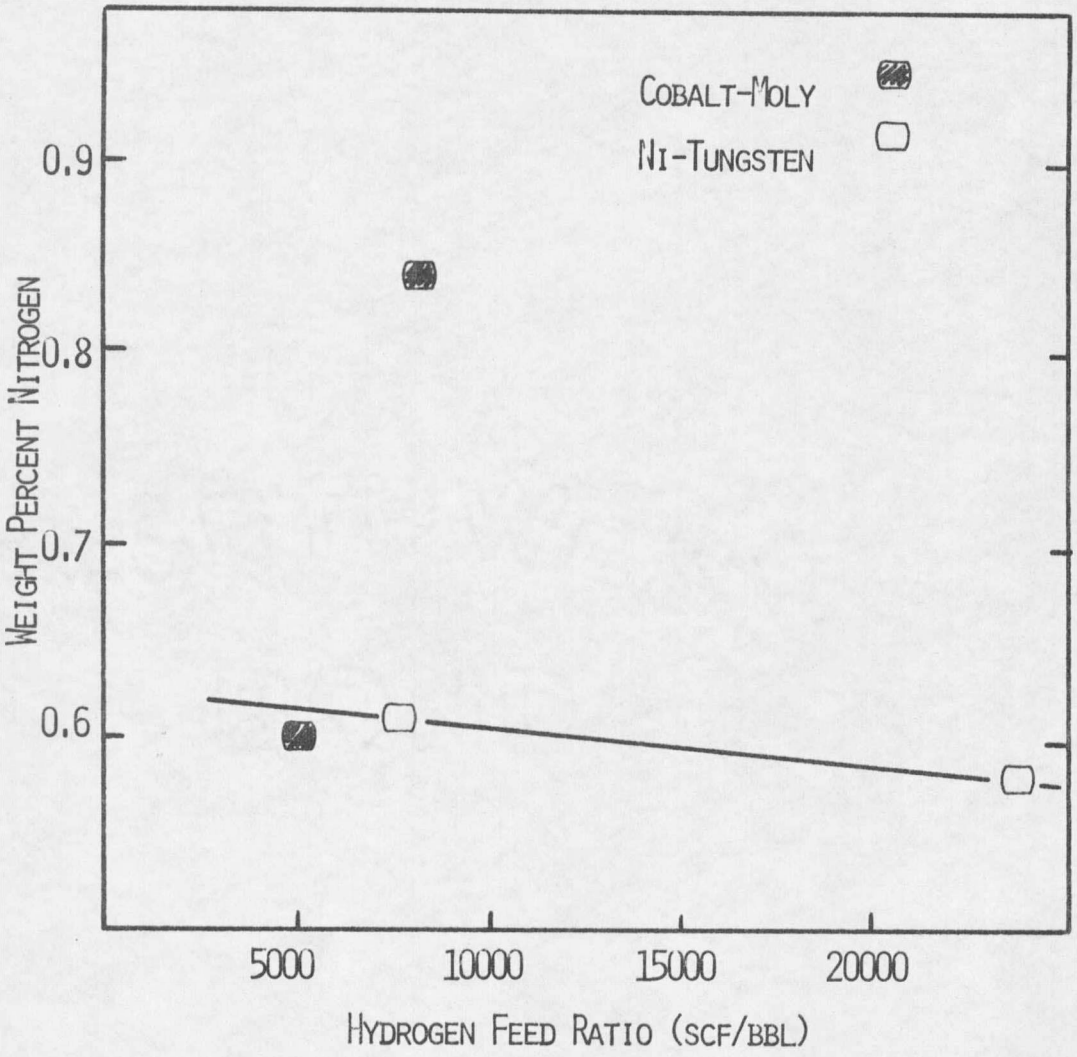


FIGURE 4. WEIGHT PERCENT NITROGEN VS HYDROGEN FEED RATIO

(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

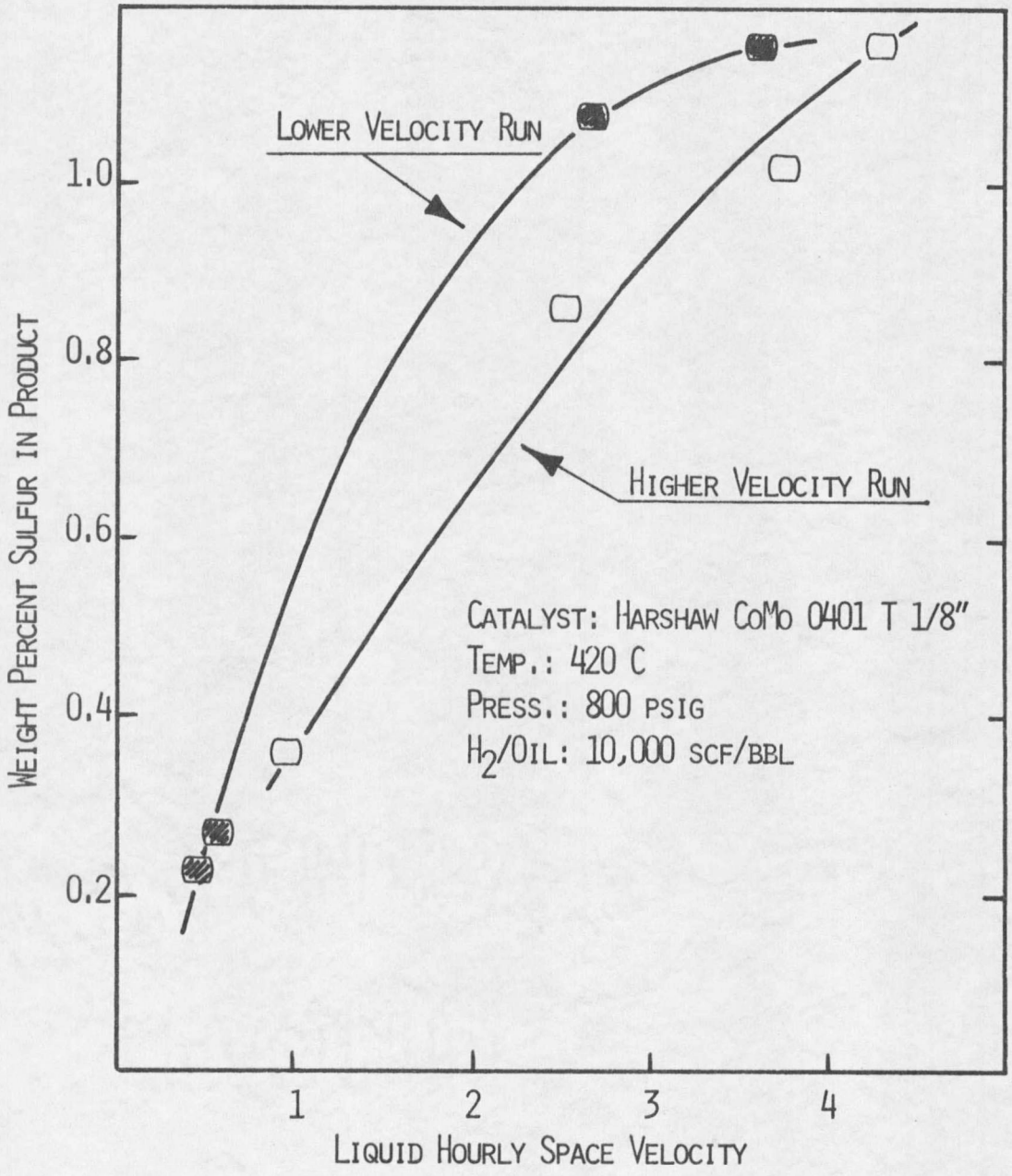


FIGURE 5. WEIGHT PERCENT SULFUR VS LHSV, DIFFUSION TESTS

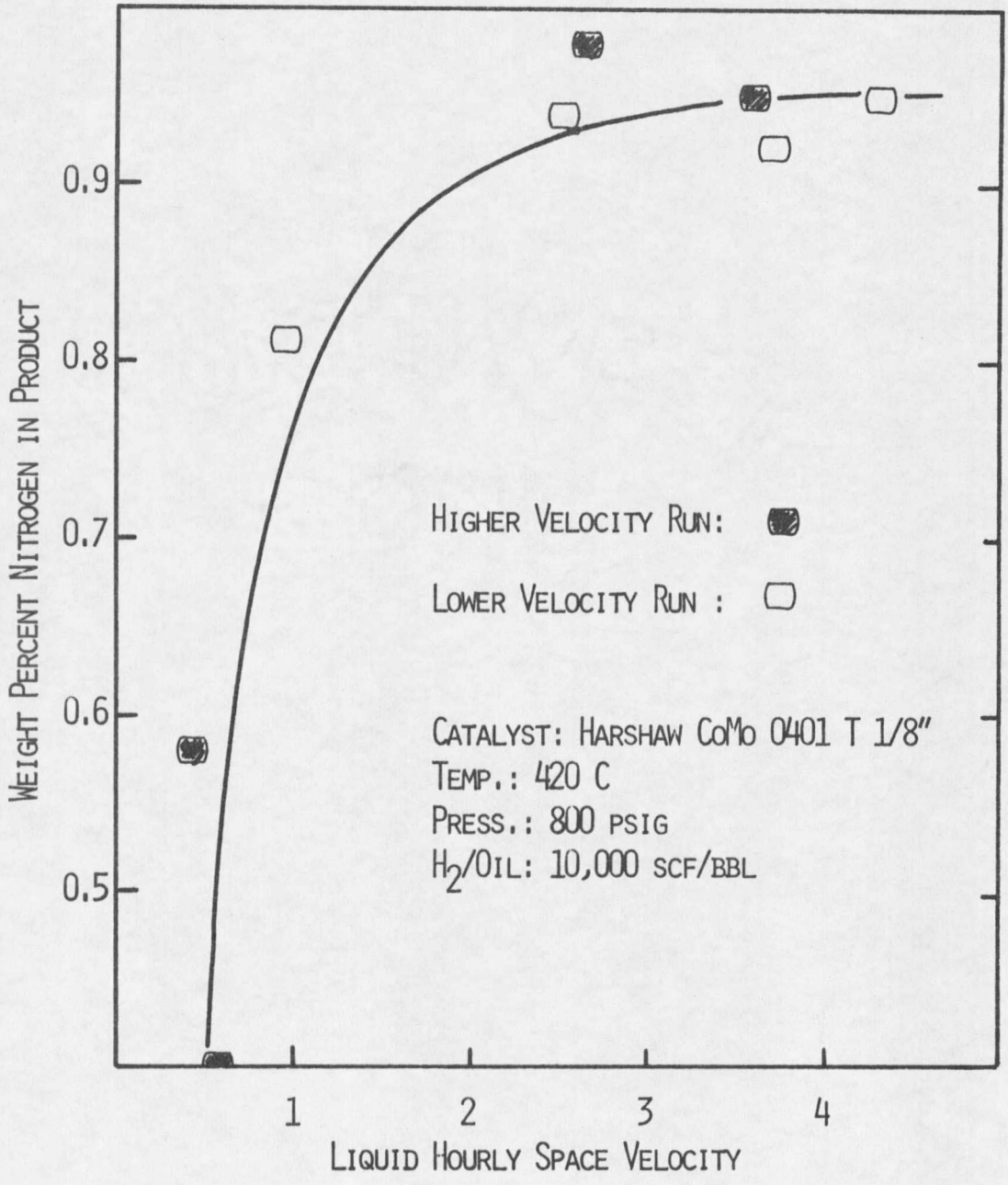


FIGURE 6. WEIGHT PERCENT NITROGEN VS LHSV, DIFFUSION TESTS

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_2 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

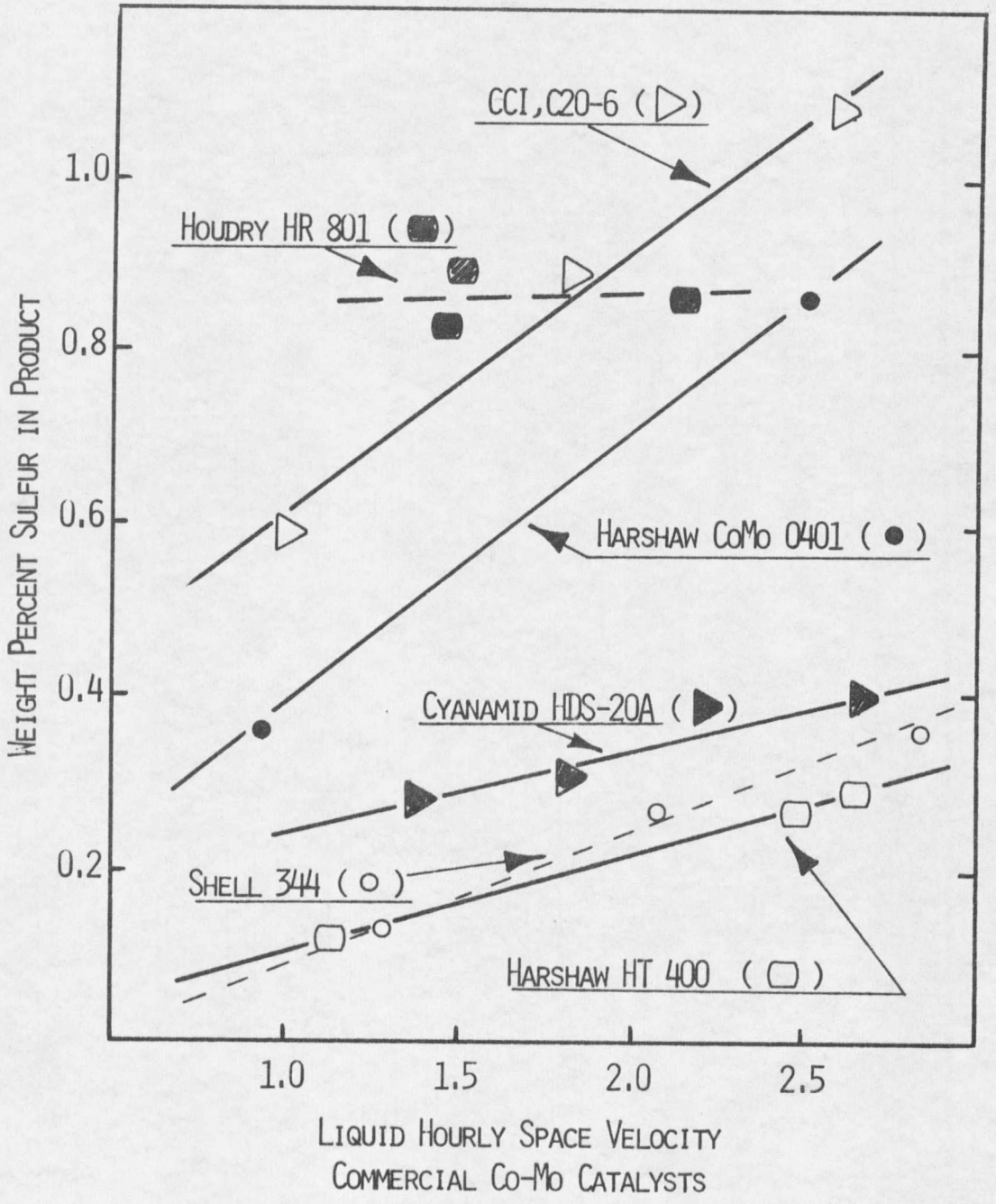


FIGURE 7. WEIGHT PERCENT SULFUR VS LHSV, Co-MOLY CATALYSTS

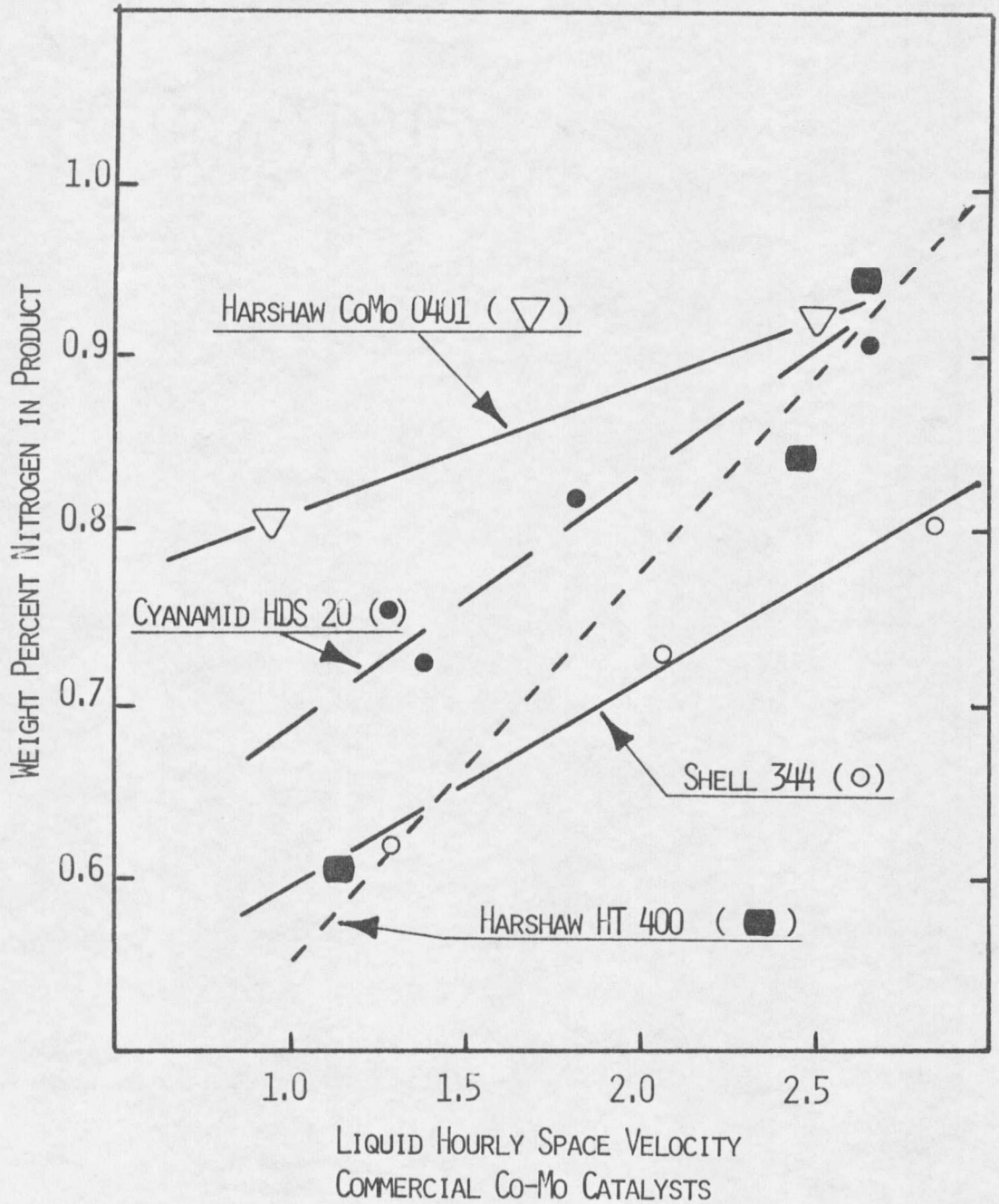


FIGURE 8. WEIGHT PERCENT NITROGEN VS LHSV, Co-MOLY CATALYSTS

Table III

Liquid Product Distribution from ASTM Distillation

Cobalt Moly Catalysts

Catalyst	LHSV	IBP-425	425-600	600-700	Rec.
Harshaw 0401	.93	19	32	20	74
	2.5	16	23	31	74
	3.72	14	27	28	72
Harshaw HT400	1.13	--			--
	2.46	12	32	30	76
	2.64	--			--
Shell 344	1.27	--	--	--	--
	2.06	19	28	29	78
	2.84	16	27	25	70
Houdry HR801	1.46	24	23	20	73
	1.49	18	22	25	71
	2.13	18	24	18	72
CCI-C20-6	1.01	20	24	24	73
	1.82	17	21	22	66
	2.58	16	21	29	70
Cyanamid HDS20A	1.38	18	27	21	69
	1.81	16	27	20	67
	2.66	17	25	22	69

pore diameter (as explained in the Introduction) for the Shell, Harshaw, and Cyanamid catalysts are, respectively, 123 Å, 91 Å, and 90 Å. The figure suggests that the catalyst with larger pores removes the most nitrogen. This suggests that the rate of hydrodenitrogenation is severely limited by pore diffusion.

Table III gives a liquid product distribution from the ASTM D86 distillation. Shell 344 and Harshaw HT 400 appear to give the highest amount of low boiling products, however, the boiling curves did not vary much in any of the products from the six catalysts tested.

6.2.2 Nickel tungsten catalysts. All of the nickel tungsten catalysts had 6% nickel and 19% tungsten oxides on them. Harshaw 4401, 4301 and Ketjenfine 330-3E were made on silica-alumina support, which was intended to increase hydrocracking activity. The silicated supports were characterized by a much smaller average pore size than the non-silicated catalysts.

Sulfur removal for these catalysts was lower than the cobalt-molybdate catalysts. Also, nitrogen removal was less; in many cases there being more nitrogen in the product than in the feed (0.9%). Again, heteroatom removal followed average pore size, the large pore non-silicated catalysts, Ketjen HC-5 and Harshaw 4303 doing the best job. The catalyst performance curves are presented in Figures 9 and

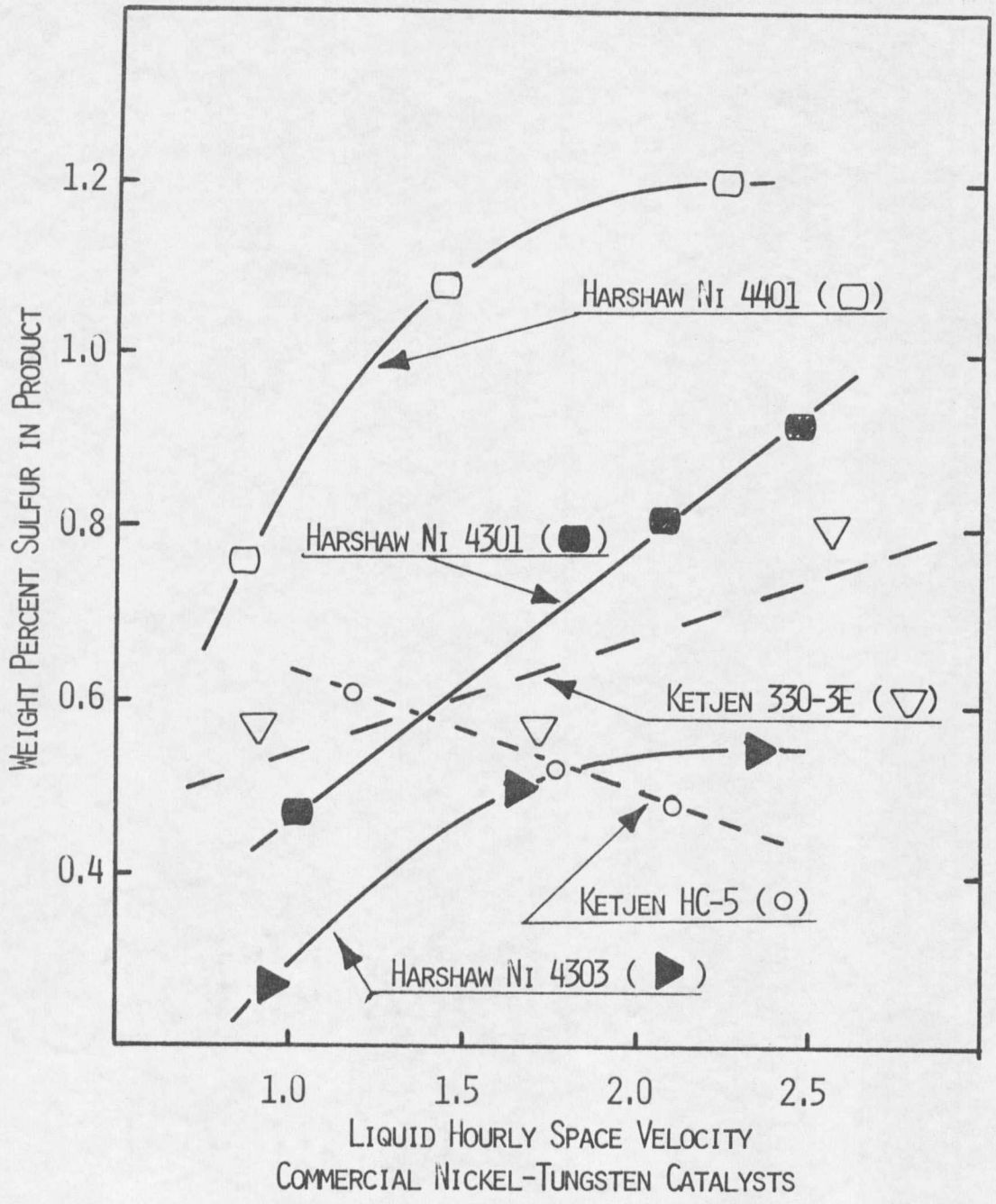


FIGURE 9. WEIGHT PERCENT SULFUR VS LHSV, NICKEL TUNGSTEN CATALYSTS

10, and the run data and catalyst pore sizes are presented in Appendix Table A-11.

From the distillation data of Table IV, it appears that the silicated supports yielded a higher percent of lighter products in certain boiling ranges. Harshaw 4401 appeared to give a higher volume in the 600-700°F range, and Ketjenfine 330-3E gave a greater volume of IBP to 425°F products.

6.2.3 Nickel molybdate catalysts. Tables V and A-III present the data from the nickel-moly catalyst runs. Figures 11 and 12 present the performance for the best catalysts of the group. Sulfur removal and liquid products yield was poorer than the cobalt-moly catalysts. Nitrogen removal was the best so far in a continuous run. Cyanamid HDS9A took out the most nitrogen, closely paralleled by Harshaw HT 500 and Houdry HR 811; however, the Houdry catalyst appeared to be poisoned quickly during the course of the run. Interestingly, Shell 324 removed the most sulfur of the nickel-moly catalysts while being the second worst nitrogen remover. No reason for this is apparent though. The Shell 324 catalyst did give the best liquid product yields, but the Cyanamid HDS9A catalyst gave a higher percent in the desirable 425-600°F boiling range than any other catalyst.

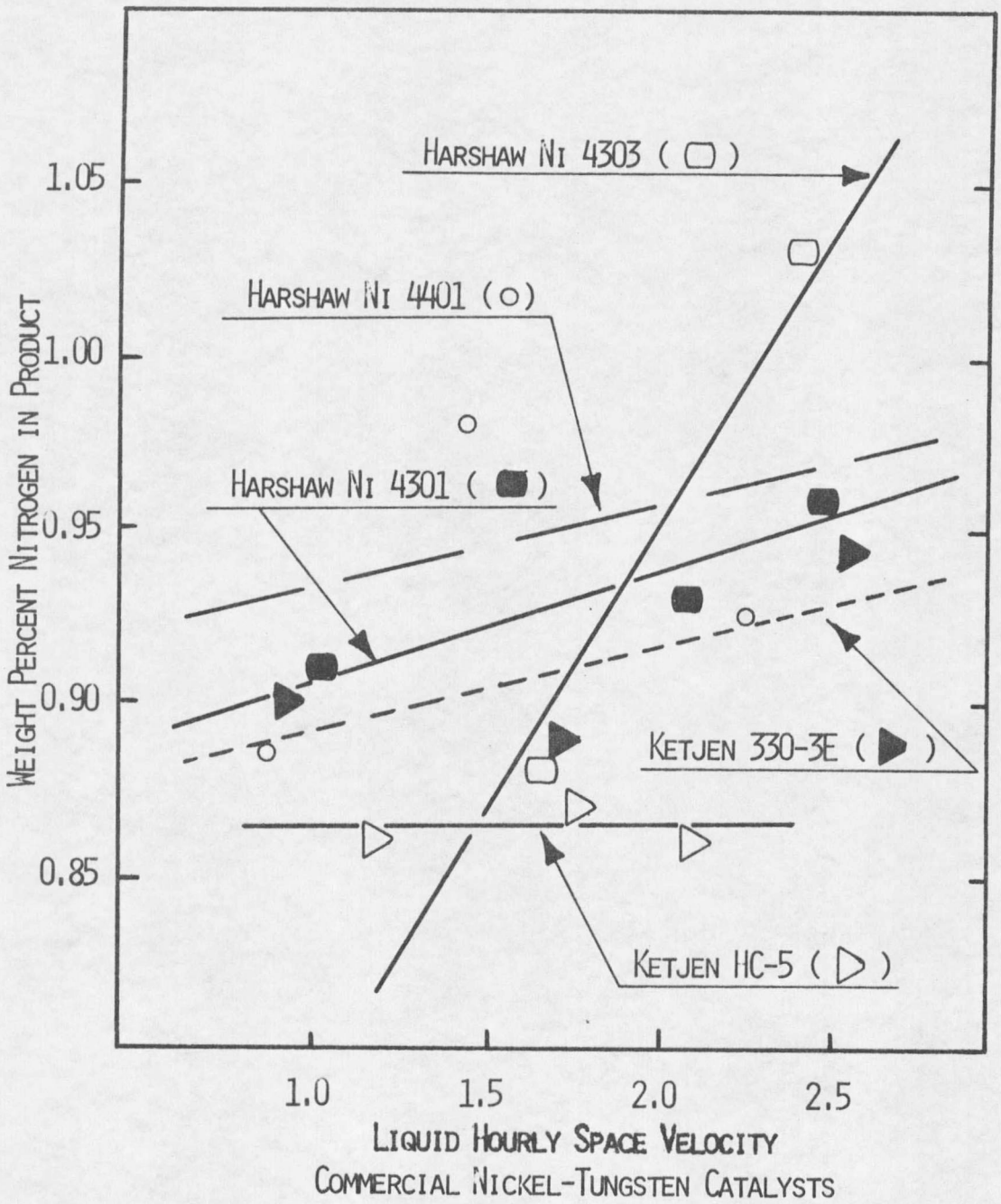


FIGURE 10. WEIGHT PERCENT NITROGEN VS LHSV, NICKEL TUNGSTEN CATALYSTS

Table IV

Liquid Product Distribution from ASTM Distillation

Nickel Tungsten Catalysts

Catalyst	LHSV	IBP-425	425-600	600-700	Rec.
Harshaw 4401	.86	19	26	24	74
	1.43	8	22	30	63
	2.23	10	21	29	66
Harshaw 4301	1.02	12	26	16	61
	2.06	9	24	21	60
	2.46	5	29	24	64
Harshaw 4303	.95	17	29	17	68
	1.65	16	25	17	64
	2.35	13	27	16	62
Ketjenfine 330-3E	.91	24	22	16	68
	1.71	22	23	22	72
	2.56	8	25	24	63
Ketjen HC-5	1.17	20	22	23	70
	1.75	22	20	19	66
	2.09	10	33	19	66

Table V

Liquid Product Distribution from ASTM Distillation

Nickel Molybdate Catalysts

Catalysts	LHSV	IBP-425	425-600	600-700	Rec.
Shell 324	1.63	22	28	19	73
	1.77	19	25	21	68
	1.1	20	29	17	69
	2.24	13	28	19	64
	2.26	14	28	20	66
Harshaw HT100	1.41	13	28	17	63
	1.71	10	27	20	62
Harshaw HT500	1.12	11	27	23	68
	1.66	11	21	28	64
	2.31	7	28	17	60
Cyanamid HDS9A	.89	11	35	28	80
	2.08	11	30	18	65
	2.63	7	29	16	60
Houdry HR811	1.54	14	24	17	63
	1.56	15	23	20	68
	2.17	11	28	17	64

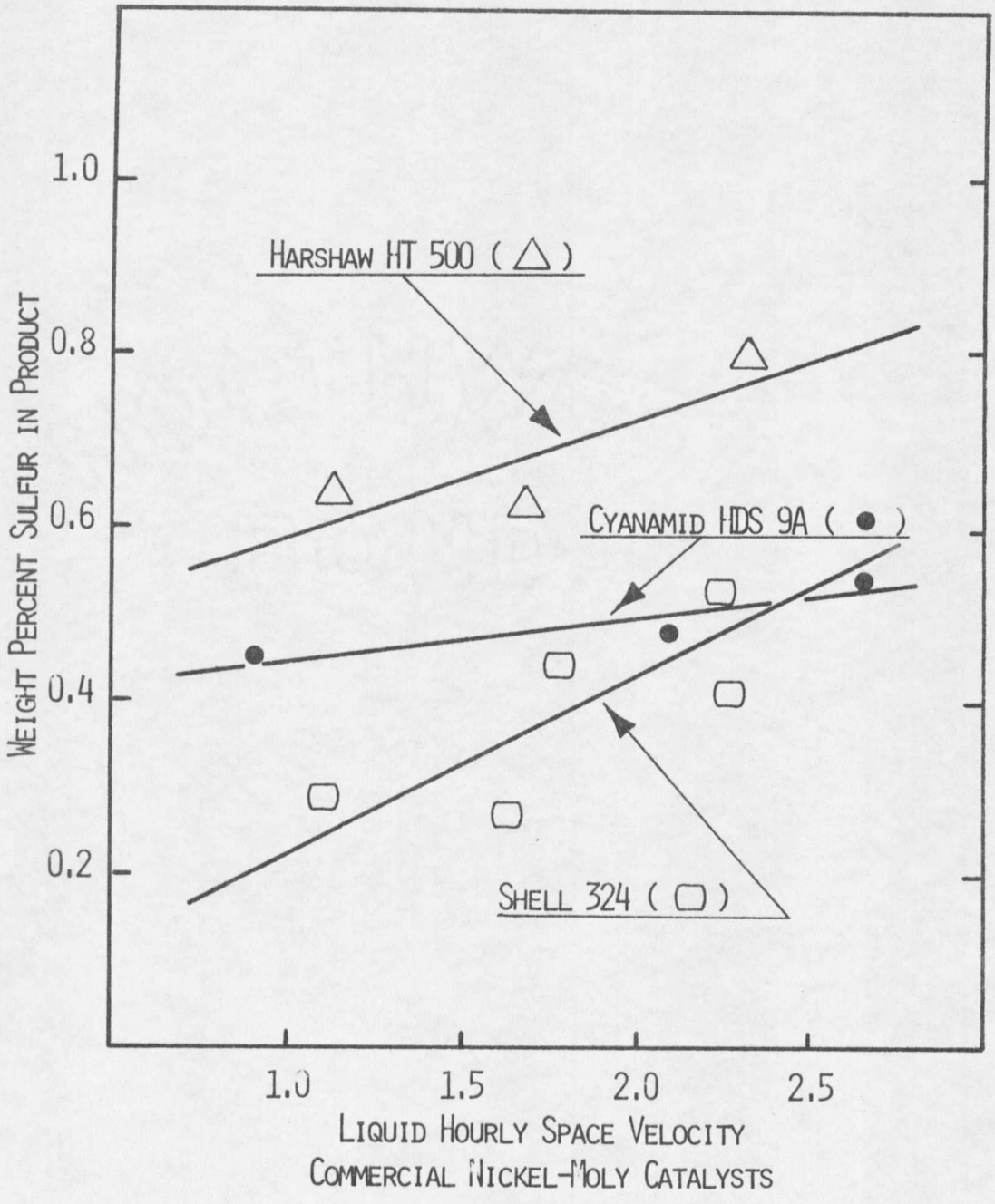


FIGURE 11. WEIGHT PERCENT SULFUR VS LHSV, NICKEL-MOLYBDATE CATALYSTS

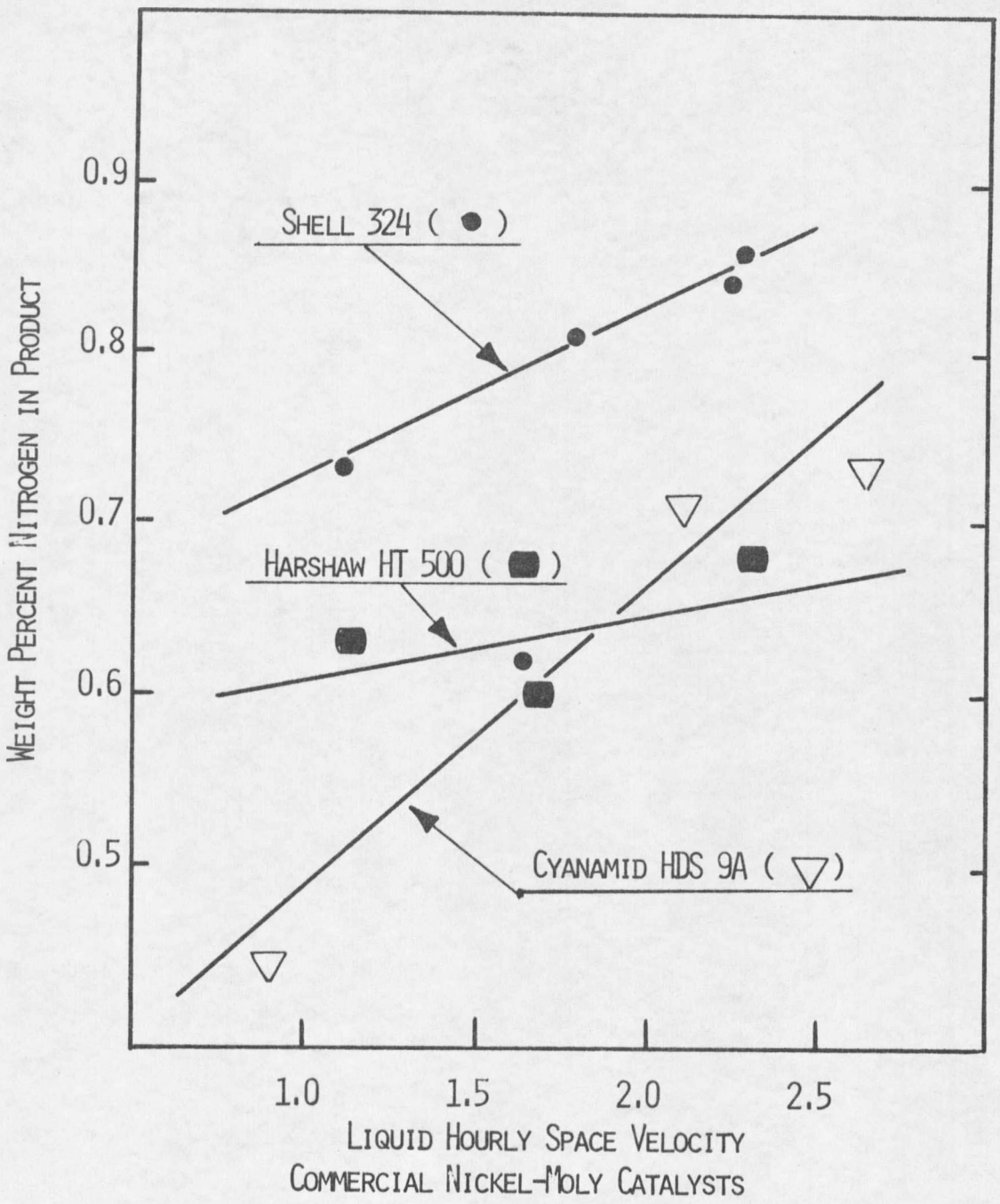


FIGURE 12. WEIGHT PERCENT NITROGEN VS LHSV, NICKEL-MOLYBDATE CATALYSTS

6.2.4 Overall screening test results. From the experimental evidence, it appears that the best nickel-moly and cobalt-moly catalysts show similar activity for hydrotreating COED pyrolysis oil, the cobalt molybdate catalyst remove more sulfur, while the nickel molybdate catalysts show more activity for nitrogen removal. The nickel tungsten catalysts show lower activity than the cobalt and nickel moly catalysts for hydrotreating.

From the limited average pore size data available for the catalysts tested, it appears that nitrogen removal and, to a lesser extent, sulfur removal is severely limited by pore diffusion. This conclusion, however, would be more definite if pore size distribution of the catalysts was available.

6.3. Batch Tests on Commercial Catalysts

Fourteen commercial catalysts were tested in a Parr Rocking Bomb Autoclave in the manner described in the Equipment and Procedures section. The purpose of the tests was twofold:

1. Establish the relationship between catalyst performance in the bomb as compared with the continuous runs.
2. Use the batch tests to group commercial catalysts in a coarse activity series.

It was believed that of the catalysts that performed well in the bomb, further continuous testing would have to be done to establish the

order of activities. The continuous tests on the high activity catalysts have been presented in the preceding section. The catalysts that did not perform well in the bomb were usually not tested continuously because if the catalyst did not work at the severity of the condition in the bomb, then it was felt that they would not perform in the less severe environment of the continuous reactor.

The batch tests on the commercial catalysts were used to set a precedent for batch tests on catalysts made at Montana State University. It was felt that if the MSU catalyst did not perform as well in the batch tests as the better commercial catalysts, there was little point in further development work being done on that particular catalyst. This decision was made in the light of what was stated in the Introduction about batch reactors being used to screen catalysts. If the good catalysts were driving the reactions to equilibrium in the bomb, then the catalysts we made should be at least able to accelerate the reaction to equilibrium. Table VI describes the tests of the batch commercial tests. Figures 13 through 17 illustrate the product distillation and sulfur and nitrogen removal obtained with five of the commercial catalysts. The catalysts are described in Table A-IV in the Appendix.

As seen in Table VI, the cobalt and nickel molybdate catalysts and the nickel tungsten catalysts all removed over eighty percent of the sulfur. The nitrogen removed for the above was somewhere between

Table VI

Batch Run Data Summary[3] - COED Feed

Run No.	Catalyst	% Desulfurization	% Denitrogenation[2]	ASTM Distillation IBP-425F	425-600F	600-700F	D-86 (Vol %) Yield
Cobalt-Moly Catalysts[4]							
15	Harshaw CoMo 0401	80	28	16	29	22	67
37	Shell 344	86	29	19	26	24	69
Nickel-Moly Catalysts							
19	Harshaw HT-100	83	31	15	28.5	21.5	65
26	Harshaw HT-500	78	14	15	19	31	65
36	Shell 324	86	24	17	26	24	67
Nickel-Tungsten Catalysts							
7	Harshaw Ni4401	91	64	18	24	23	65
13	Harshaw Ni4301	80	24	16	28.5	21.5	66
18	Harshaw Ni4303	84	7	17.5	28.5	23	69
27	Ketjen HC-5	81	22	18	24	24	66
28	Ketjenfine 330-3E	85	22	17	25	25	67
Others							
11	Harshaw Ni1601	44	33	9.5	24	24	57
14	Harshaw Ni3250	84	7	17.5	28	22	67
20	Harshaw Mo-1201	63	9	13	30	20	63
21	Harshaw W-0801	40	0	14	24	20	58

Notes: 1 yield:volume percent collected after drain of condenser as per ASTM D-86 at 700F, 640 mmHg. For COED Feed, ASTM D86 Data: IBP-425 - 3; 425-600 - 22; 600-700 - 31; yield - 53.

2. COED feed contains 2.3 wt% sulfur and 0.9 wt % nitrogen
3. Batch run conditions: 2200 psig initial H_2, 450°C run temperature; 1/2 hr at run temperature.
4. See Table A-IV for cat. descr.

20 and 30%. The only interesting thing about the results are that some of the better performing catalysts in the batch tests did not perform that well in the continuous runs. An example is Harshaw Ni-4401. In the batch tests this catalyst removed the highest amount of sulfur and nitrogen. In the continuous tests, this was the worst performing nickel tungsten catalyst. Likewise, Harshaw HT100 and HT500 reversed activities in the two reactors. The most probable explanation for the behavior is that the initial activities of the older generation catalysts (HT100, Ni-4401) were higher as shown by the batch tests, but the resistance to poisoning of the newer catalysts allowed them to keep their activity longer in the continuous tests.

Five of the catalysts were chosen to further illustrate the results of the batch tests. The first was the 10% WO_3 on alumina Harshaw W0801 catalyst. Tungsten disulfide was a traditional cracking catalyst, so this run, the results of which are shown in Figure 13, should give an idea of how well the tungsten catalyst works. The ASTM Distillation curve here comparing the feed with the product shows a substantial decrease in the boiling point range of the product. No nitrogen was removed, but 40% of the sulfur was taken out.

Figure 14 shows the results for a 10% MoO_3 on alumina catalyst (Harshaw Mo1201). The distillation curve is similar to that of the tungsten catalyst, with slightly more product over at the 700°F point. It was mentioned that molybdenum was specific for nitrogen removal, and

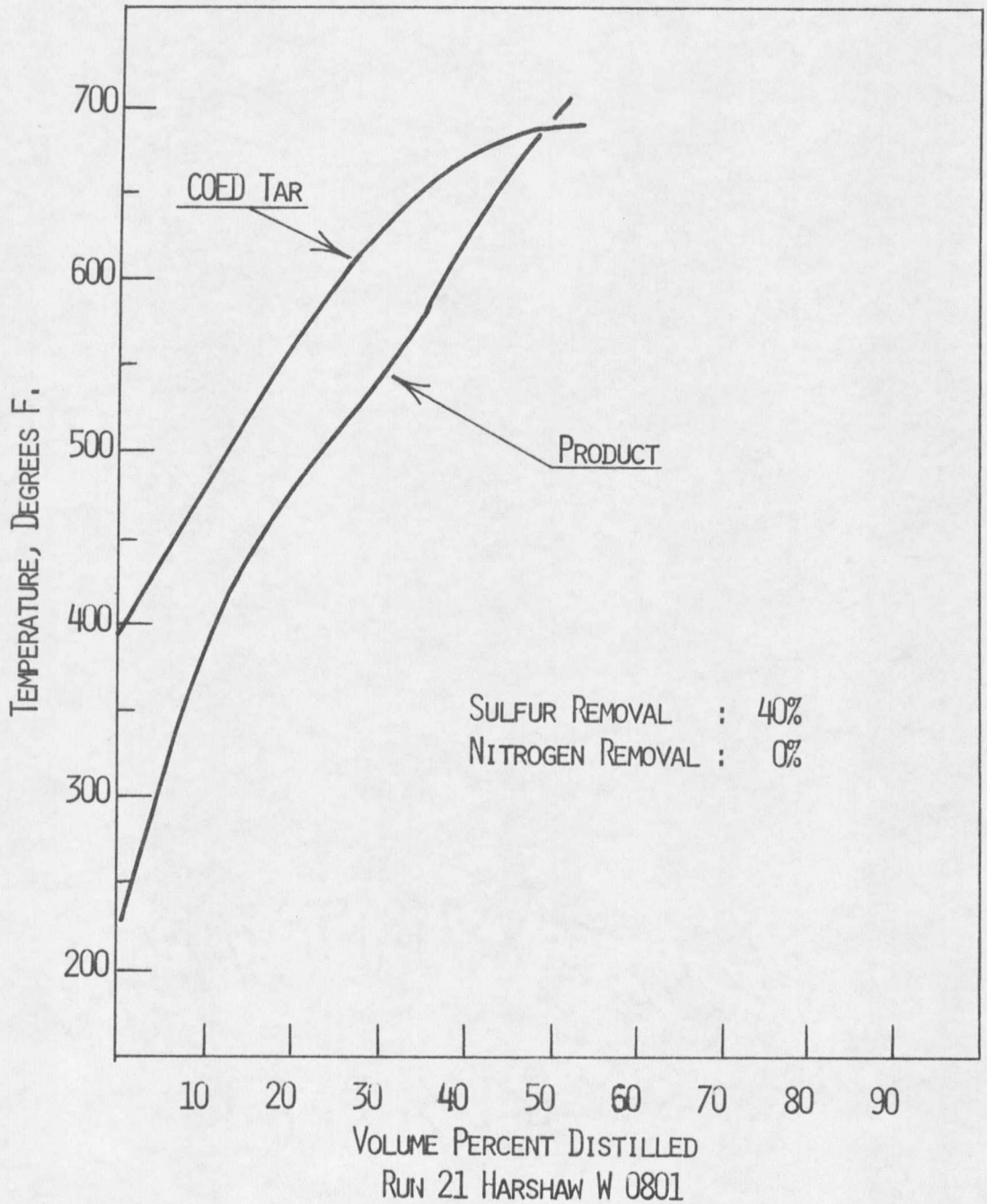


FIGURE 13. ASTM D-86 DISTILLATION, HARSHAW W0301

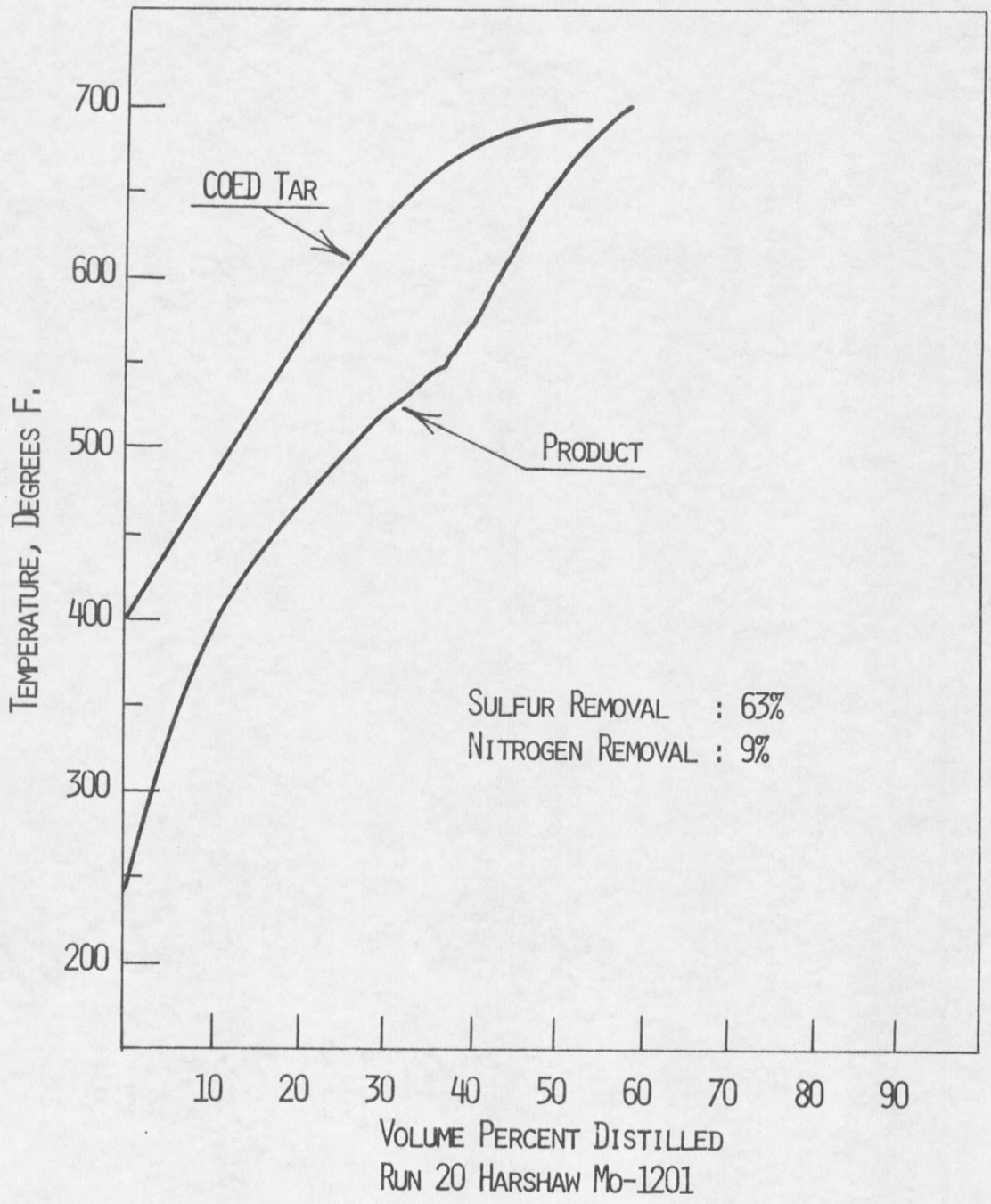


FIGURE 14. ASTM D-86 DISTILLATION, HARSHAW MO-1201

that seems to be shown here as 9% of the nitrogen was taken out along with 63% of the sulfur.

The results from a nickel tungsten catalyst are shown next in Figure 15. This shows quite a bit of boiling point reduction, a much greater sulfur removal, but a low nitrogen removal again. Other nickel tungsten catalysts batch tested did, however, remove quite a bit more nitrogen.

Shell 324 Ni-moly and Shell 344 Co-moly catalyst test results are shown in Figures 16 and 17. The boiling curves are very close to the nickel tungsten curves; this could probably be a case of equilibrium being approached. Again, the sulfur removal is above 80%, and the nitrogen removal is in the range found in batch and continuous tests of the best catalysts and also could probably be a case of equilibrium conditions being approached in the reactor.

In conclusion, it can probably be said that the batch tests will show a tendency for a catalyst to be a good performer, but, catalysts cannot be finely ranked without continuous runs.

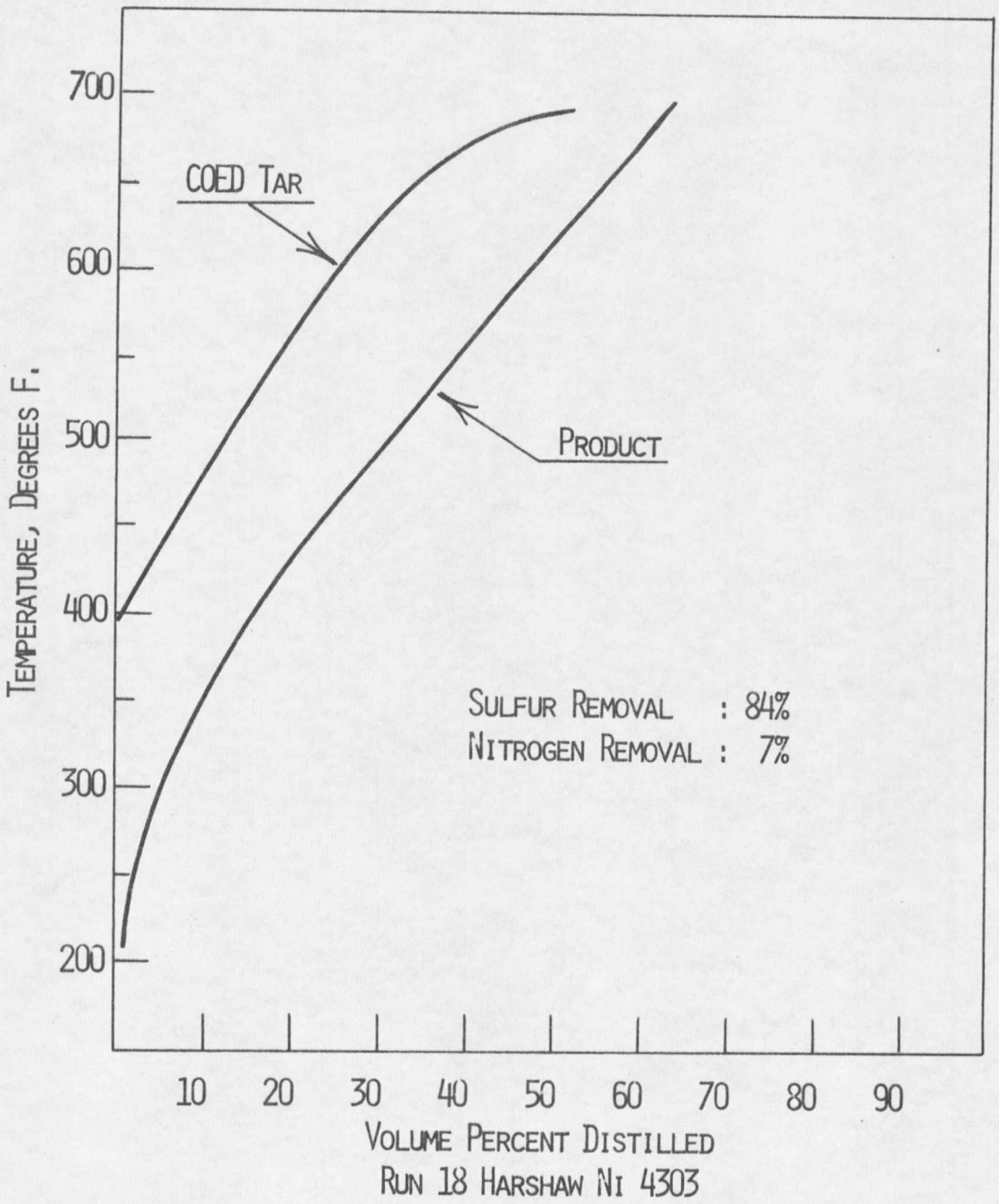


FIGURE 15. ASTM D-86 DISTILLATION, HARSHAW NI-4303

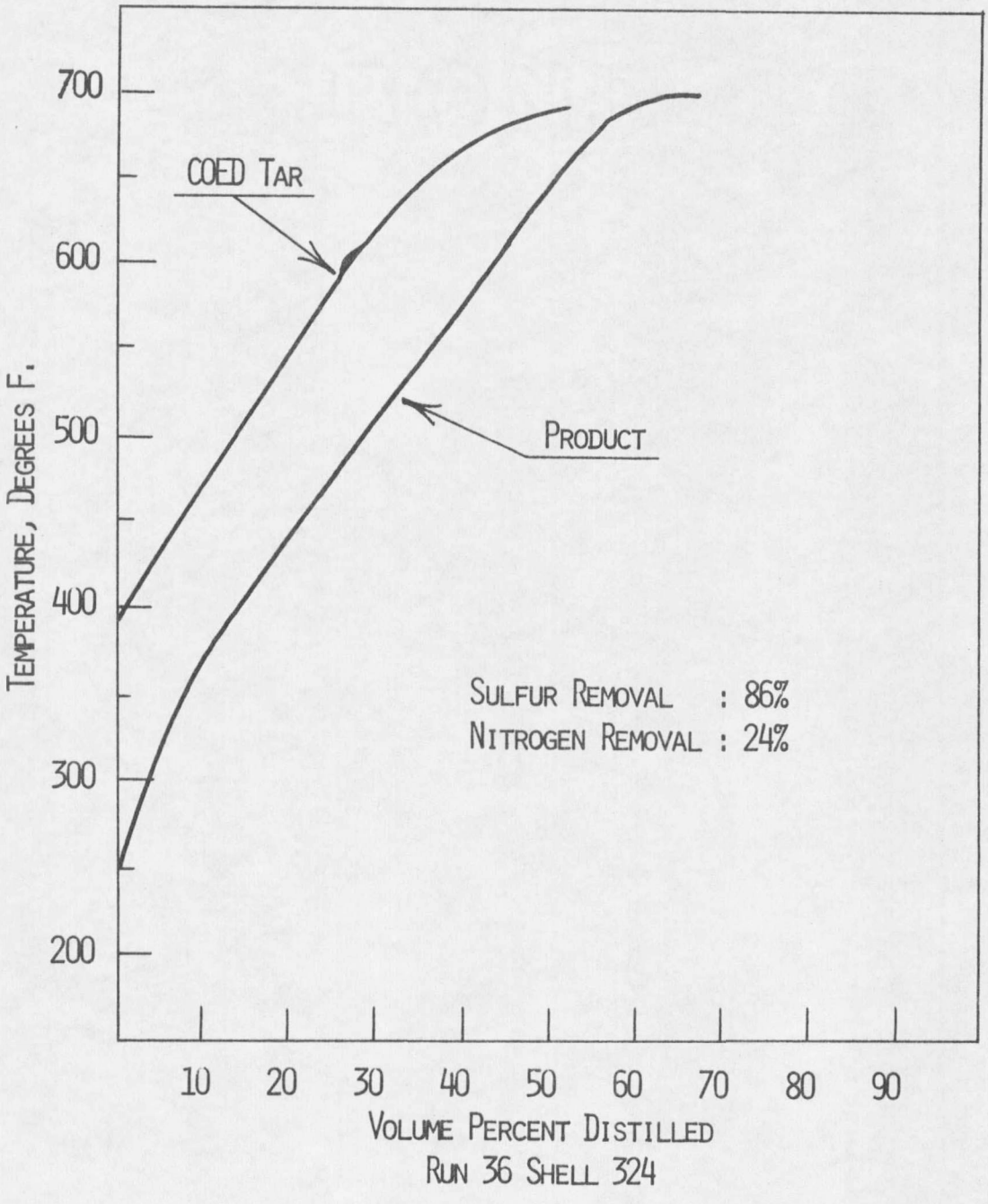


FIGURE 16. ASTM D-86 DISTILLATION, SHELL 324

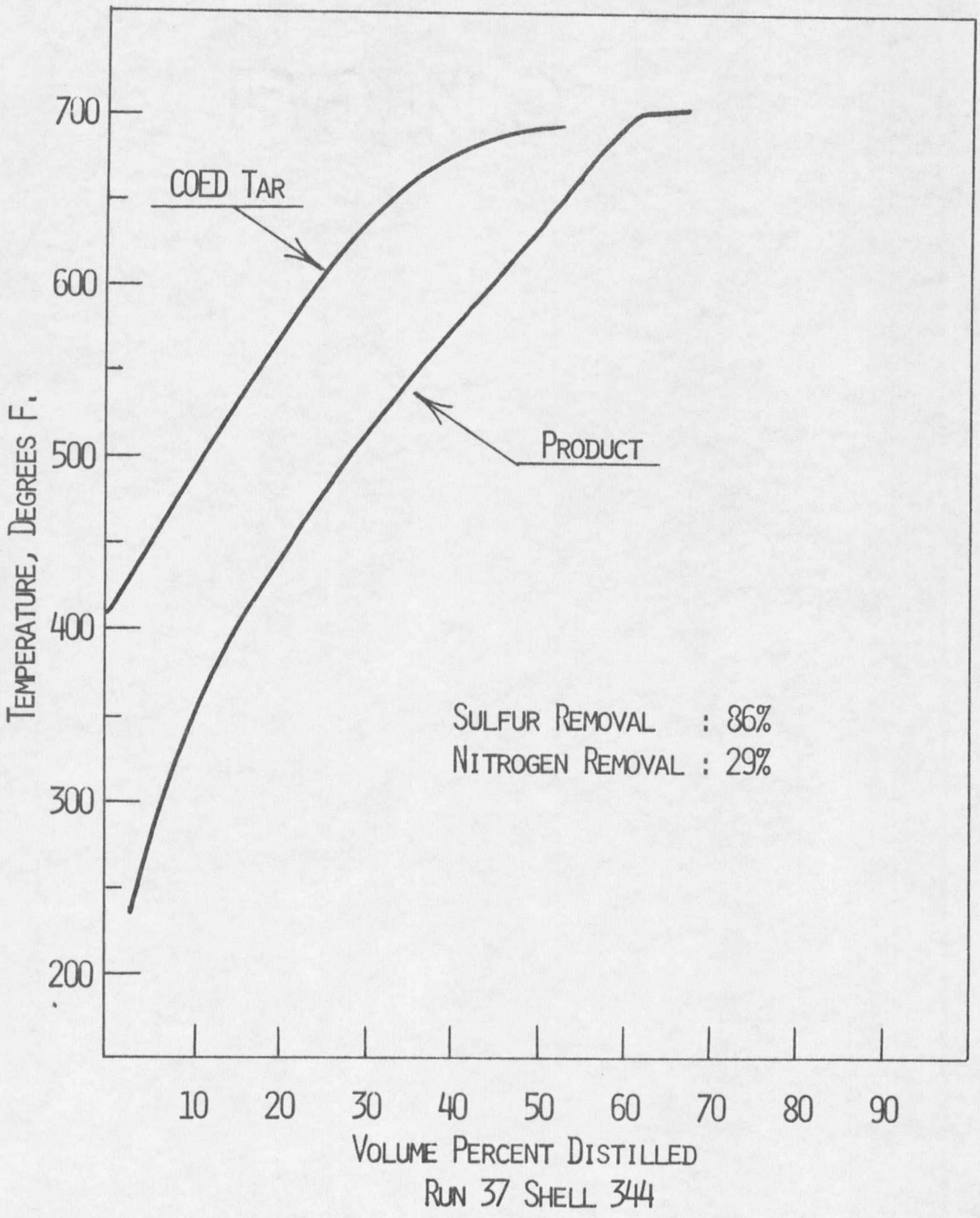


FIGURE 17. ASTM D-86 DISTILLATION, SHELL 344

7. RESULTS - MSU CATALYSTS

7.1. Batch Tests

From the data presented above, it appears that nickel-moly catalysts give the best overall performance for hydrotreating COED pyrolysis oil, especially since nitrogen removal is the most important heteroatom to be removed. Catalysts were prepared based on an alumina support (Norton 6176) that was impregnated with first molybdenum, then nickel, and then are additionally promoted by the methods previously described. It was felt that the additional promoter might increase the selectivity of the catalyst for nitrogen removal. Tables VII and VIII present the results of the batch tests.

Overall, the only combinations that compared in performance to the commercial catalysts were the two that incorporated cobalt and nickel oxides on the alumina support. On the average, these removed 86% of the sulfur, 21% of the nitrogen, and gave an ASTM D86 yield of 70% at 700°F. This was as good a heteroatom removal as the commercial catalysts, while being a slightly better overall distillate yield. Because this catalyst seemed to show improved performance, it was decided to try to develop it further. The results of this will be discussed in the next section.

Although the other combinations did not perform as well as the cobalt-nickel-moly catalysts there are several interesting things about them that should be stated. For example, STK 10 (18.9% Mo, 2.6%

Table VII

Batch[2] Run Data Summary

Run No.	Catalyst Description				H_2[3] Consumption p.s.i.	Sulfur[4] In Prod %	Sulfur[4] % Removal	Nitrogen In Prod %	Nitrogen % Removal
		Mo	Ni	Promoter					
33	ST-5	18.2	0.4	1.2% Co	1840	.33	86	.64	29
34	STK-6	18	1.2	1.6% Co	1850	.32	86	.66	27
40	STK-10	18.9	2.6	1.7% Co 0.9% Fe	1710	.37	84	.76	16
41	STK-8-2	9.5	1.4	11.2%W	1740	.51	78	.77	14
42	STK-11	11.0	1.2	3.7% Cr	1650	.41	82	.82	9
43	STK-14	17.4	2.3	1.8% Cu	1790	.34	85	.77	15
45	STK-9	21.0	0	2.0% Zn	1690	.71	69	.83	8
46	STK-12	17.8	2.0	1.7% Zn	1640	.31	87	.76	16
47	STK-13	11.0	3.0	0.5% Fe	1850	.37	84	.75	17
48	STK-8-1	8.6	1.4	11.0% W	1710	.54	77	.79	12

1. All Supports Norton 6176, 1/8" Alumina Pellets. Metal oxide weight percents shown.
2. Batch runs: 2200 psi H_2 initial, 450°C run temperature, 1/2 hour at 450°C.
3. H_2 consumption is the difference between the cold charge and cold final pressure in p.s.i.
4. Containing 2.3% sulfur and 0.9% nitrogen in feed.

Table VIII

MSU Catalyst Batch Tests ASTM Distillations

Run	Catalyst	IBP-425	425-600	600-700	Yield
33	STK-5	18.5	24.5	28	71
34	STK-6	18	26	25	69
40	STK-10	19	33	18	73
41	STK-8-2	18	26	19	69
42	STK-11	18	27	19	65
43	STK-14	19	27	23	73
45	STK-9	19	27	26	76
46	STK-12	18	26	23	71
47	STK-13	19	28	25	75
48	STK-8-1	17	26	23	67

Ni, 1.7% Co, 0.9% Fe) had almost exactly the same heteroatom removal as STK-13 (11.0% Mo, 3% Ni, .5% Fe). The less promoted catalyst (STK 13), however, produced more distillate and more product in the 600-700°F range. STK 10 produced more lighter product in the 425° to 600°F range.

STK 9 had 2% Zn with 21% Mo while STK-12 had 1.7% Zn, 2% Ni, and 17.8% Mo. The Zn-moly catalyst produced more distillate, but adding the nickel doubled the nitrogen removal while increasing the sulfur removal.

STK 8-2-1 and STK 8-2-2 replaced about half of the molybdenum with tungsten. The catalysts did a comparably good job, but since they showed no improvement over the Co-Ni-moly catalyst, and because of the higher cost of tungsten, it was felt that it would not be worth further development of this catalyst.

Finally, STK-11 was made to determine if chromium as an added promoter might give more distillate. As can be seen, it didn't improve anything. STK-14 was an attempt to use copper. This catalyst had high nitrogen removal and high hydrogen consumption, but it still did not equal the commercial catalysts as the Co-Ni-moly catalysts did.

As stated, it was decided to further develop the cobalt-nickel-moly catalysts. The support effects had to be determined first, so,

as will be described in the next section, catalysts were made up on six supports to be tested in the continuous reactor.

7.2. Continuous Tests

7.2.1 Catalyst support studies. Six supports were impregnated with molybdenum, nickel, and cobalt solutions in the manner previously described. The amounts of metals on each support was different; this was due to the differing properties of the support causing more or less of the solution to be taken up. The properties of the supports are described in Table IX, and the catalyst metal loadings are shown in Table X.

The six supports vary mainly in silica content and average pore size. Since the metal oxide loadings of the final catalysts are not equal, the data from the runs cannot be interpreted as being due solely to support properties.

Of the six catalysts, one, STK-6-2-4 on Ketjen LA-3P support, can be eliminated because of the inability to impregnate the particles with ammonium hepta-molybdate.

The catalysts STK-5-2-3 and STK-5-2-5 have a particle diameter greater than 1/16", so there is a possibility that the data from the runs using these might be affected by diffusion more than the catalysts with smaller, particle diameter, namely, STK-5-2-1, STK-5-2-2, and STK-5-2-6.

Table IX

Support Properties

Norton 6176:

Al_2O_3 (>99.85%)
Na_2O (<.014%)
SiO_2 (<.12%)
S.A. = 250 ± 20 m^2/g
P.V. = .8 - 1.1 cc/g
Avg. Pore Dia ∿152 Å [1]

Ketjen Supports

Support No.	Weight Percent Al_2O_3	SiO_2	Na_2O	S.A.	P.V.	P.D.[1]
003-1.5E	bal.	1.33%	.01%	240	.7	117
006-1.5E	bal.	.37	.10	200	.73	146
005-2E	bal.	.55	.06	150	.64	171
000-3E	bal.	1.5	.13	230	.64	111
LA-3P	13.8	bal.	.13	410	.56	55

1. Avg. Pore Dia. = 40,000 x P.V. ÷ S.A. in Å

Table X

Catalyst Description

Catalyst No.	Support No.	Weight Percent(1)		
		Mo	Ni	Co
STK-5-2-1	Norton 6176	23.9	0.48	0.75
STK-5-2-2	Ketjen 003-1.5E	13.1	0.26	1.15
STK-5-2-3	Ketjen 000-3E	16.4	0.50	1.10
STK-5-2-4	Ketjen LA-3P	5.0	1.00	0.90
STK-5-2-5	Ketjen 005-2E	14.00	0.50	0.80
STK-5-2-6	Ketjen 006-1.5E	15.5	0.20	1.10

(1) Metal oxide weight percent

The catalysts were tested in the continuous reactor in the same manner as the commercial catalysts. The results are plotted in Figures 18 and 19, and the overall performance is given in Table A-V.

7.2.1.a Nitrogen removal. Figure 18 plots the weight percent nitrogen in the product against space velocity for the three best MSU catalysts and one of the best commercial catalysts. None of the MSU catalysts performed as well as the Harshaw catalyst, however, the slightly better nitrogen removal by STK-5-2-6 seems to indicate that either a catalyst with larger average pore size or less silica improves nitrogen removal. (This assumes that the impregnated pore size stays larger when comparing STK-5-2-6 with STK-5-2-2.) The catalyst STK-5-2-1 which was on 1/16" Norton 6176 in contrast with the 1/8" Norton 6176 used in the Ni-Co-moly catalyst precursors, STK-5 and STK-6, contained much more molybdenum than the 5-2-2 and 5-2-6 catalysts, and so could not be directly compared with them. The poorer performance of STK-5-2-1 could therefore be due to pore plugging.

7.2.1.b Sulfur removal. Figure 19 shows the sulfur removal effected by four of the MSU catalysts and one of the best commercial catalysts. Again, the commercial catalysts performed best. In this figure, STK-5-2-2 and STK-5-2-6 performed equally well, the data for 5-2-6 having more scatter, however. The two best MSU catalysts performed much

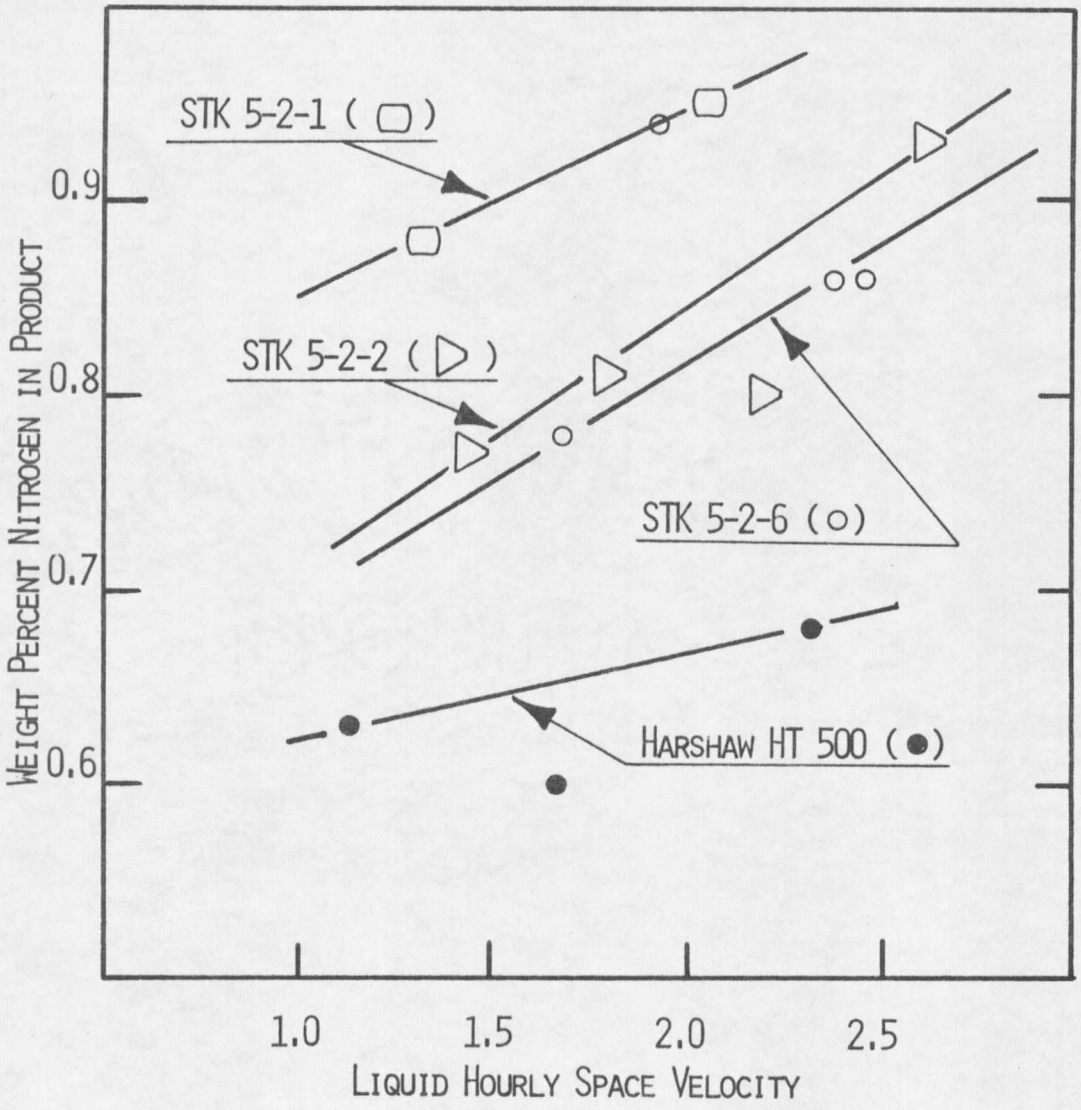


FIGURE 18. WEIGHT PERCENT NITROGEN VS LHSV, STK 5-2 CATALYSTS

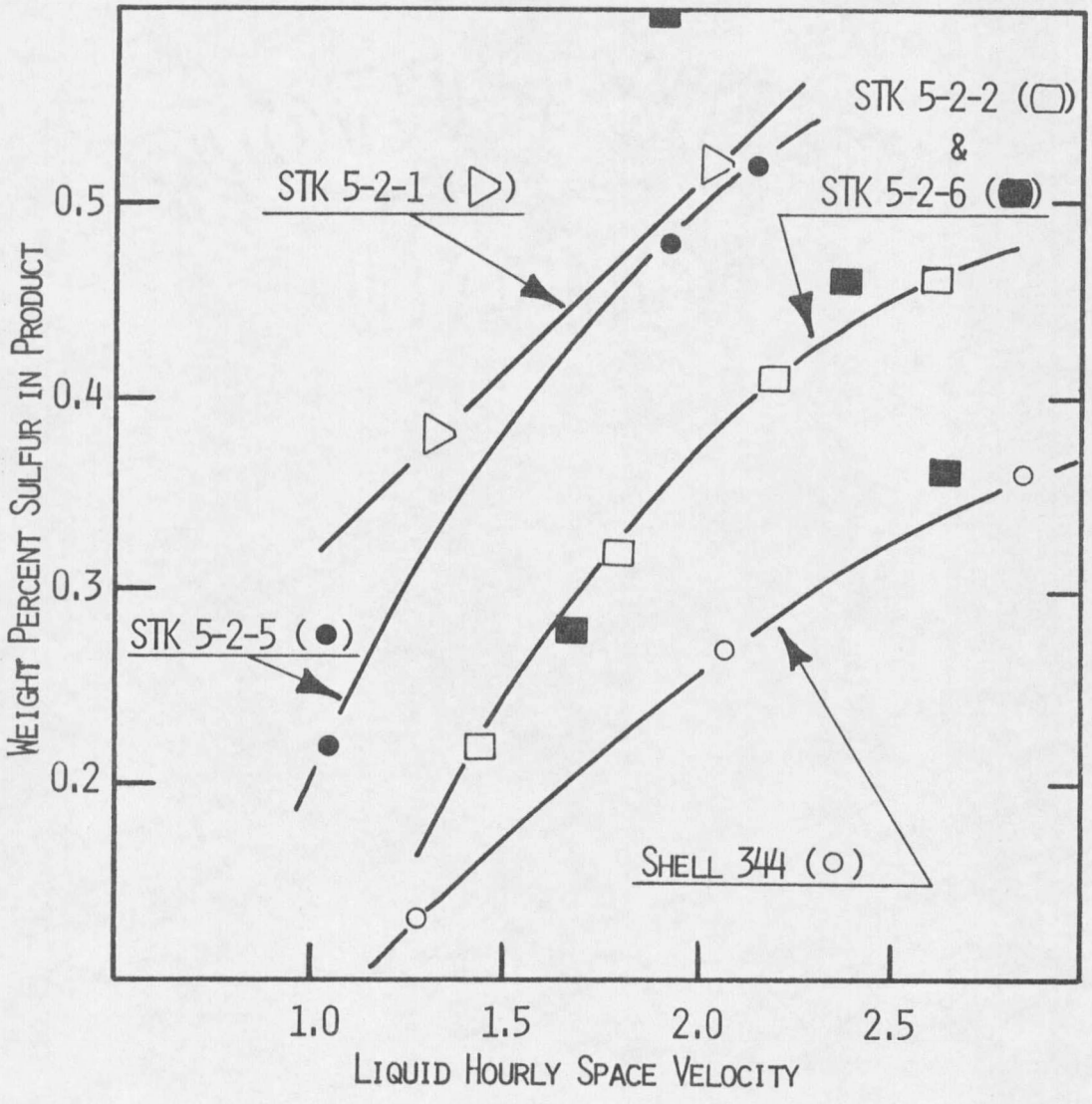


FIGURE 19. WEIGHT PERCENT SULFUR VS LHSV, STK 5-2 CATALYSTS

closer to the commercial catalyst in sulfur removal than in nitrogen removal.

STK-5-2-1, it is assumed, again probably had pores plugged by high molybdenum content. The performance of STK-5-2-5 could possibly be explained by its larger diameter since it is believed that film diffusion is present to a great extent in this system. The conversion could therefore be less even though 5-2-5 had the same metal loading as 5-2-2 and 5-2-6 and probably a larger average pore size.

In general, it appears from the data presented in Figures 18 and 19 that pore size does have an influence on nitrogen removal but not on sulfur removal. However, if this is true, then the Norton support should have performed better than the two Ketjen supports. Since the Ketjen supports contained silica, this could also have been a factor in nitrogen removal. Since the Norton support contained much more molybdenum, it is unknown whether this caused poorer performance.

In the light of the above, it was decided to take one of the Ketjen supports (Ketjen 003-1.5E) and study whether the molybdenum and the promoters had an effect on nitrogen removal. This study will be discussed in the next section.

7.2.2 Metal loading studies. In the above catalyst support studies, it was shown that the two Ketjen supports, 003-1.5E (STK-5-2-2) and 006-1.5E (STK-5-2-6) were the best for heteroatom removal. Ketjen

003-1.5E was chosen as the support to make catalysts with varying amounts of the hydrogenation components and promoters in order to determine their effects upon heteroatom removal.

The physical and chemical properties of this Ketjen support are:

Ketjen 003-1.5E	
Surface Area :	240 m^3/g
Pore Volume :	0.7 cc/g
Particle Size:	1/16" extrudates
Composition :	1.33% SiO_2, 0.01% Na_2O, bal. Al_2O_3
Avg. Pore Diam.	117 Å (unimpregnated)

Eight catalysts were made up on the support. The target metal loadings on these were to be: nickel oxides, 0.5 and 1.5 weight percent; cobalt oxides, 1.5 and 3 weight percent; molybdenum oxides, 12 and 18 weight percent. Eight continuous test runs were made at the conditions of 800 psig. 415°C; 10,000 scf/bbl; and an 80 ml diluted catalyst bed. The catalyst descriptions and results of the runs are shown in Table XI.

The data from the runs were analyzed as a 2^4 factorial experiment. The four factors and their levels were LHSV (1.25, 2), Co (1.5%, 3%), Ni (0.5%, 1.5%) and Mo (12%, 18%). The assumptions necessary to analyze the data, along with the pertinent statistical tables,

Table XI

Cobalt-Nickel-Moly Catalyst Performance

Catalyst	% Co	% Ni	% Mo	LHSV	% N	% S
1003	3.0	1.4	18.0	2.12	.87	.52
				1.20	.75	.30
				2.69	.72	.45
2003	1.42	1.37	19.2	1.98	.78	.31
				1.25	.72	.27
				2.32	.93	.44
3003	3.6	0.5	17.7	1.66	.83	.32
				1.71	.88	.40
				1.07	.79	.29
4003	1.6	0.5	17.4	2.09	.83	.32
				1.27	.74	.30
				.96	.70	.20
5003	3.15	1.8	10.3	1.91	.86	.34
				1.19	.84	.38
				2.35	.94	.51
6003	1.41	1.72	13.2	1.82	.86	.38
				1.28	.82	.26
				2.44	.96	.57
7003	3.0	0.5	11.6	1.33	.81	.26
				1.08	.74	.26
				1.93	.85	.32
8003	1.84	0.5	11.7	1.96	.84	.48
				1.89	.86	.50
				1.61	.80	.35
				1.63	.86	.42

are presented in the Appendix. Only the significant results will be presented here.

For nitrogen removal, the main effects of the amounts of cobalt oxides and molybdenum oxides were found significant (space velocity was also found significant, obviously). Figure 20 presents the results as the average amount of nitrogen in the product versus the metal loadings. For molybdenum, the higher loading improved denitrogenation. For cobalt, the lower values gave better nitrogen removal. At the levels present, nickel did not significantly affect nitrogen removal, a result seemingly contrary to industrial practice which states that nickel-moly catalysts are more active for denitrogenation.

For sulfur removal, only the main effect of space velocity and the first order interaction of cobalt and molybdenum were found significant. Figure 21 presents the results. Since the cobalt-moly interaction was found significant, this means that the effect of both of them on the catalyst is greater or lesser than would be expected for just one of the components alone. This is illustrated by the lines in Figure 21 not being parallel or crossing. At the higher space velocity, the interaction becomes greater as can be seen in the lower part of the figure. For sulfur removal, it seems that a low cobalt, high molybdenum catalyst is best.

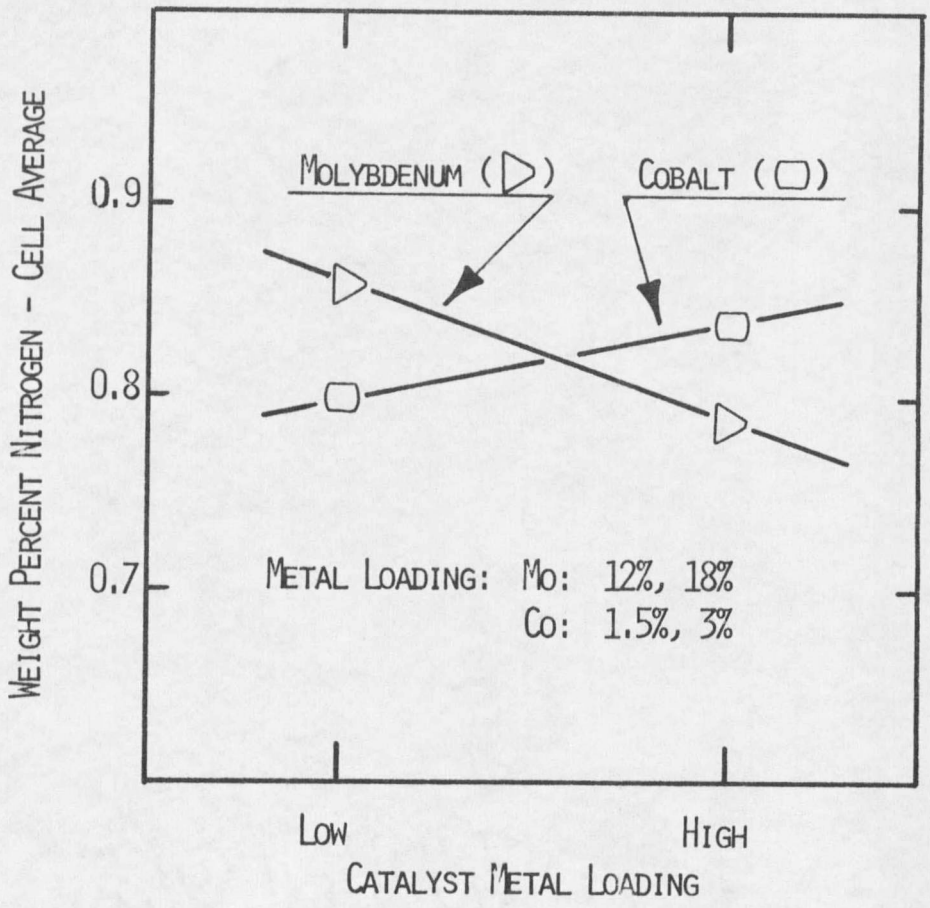


Figure 20. Weight Percent Nitrogen vs Catalyst metal Loading, MSU Catalysts

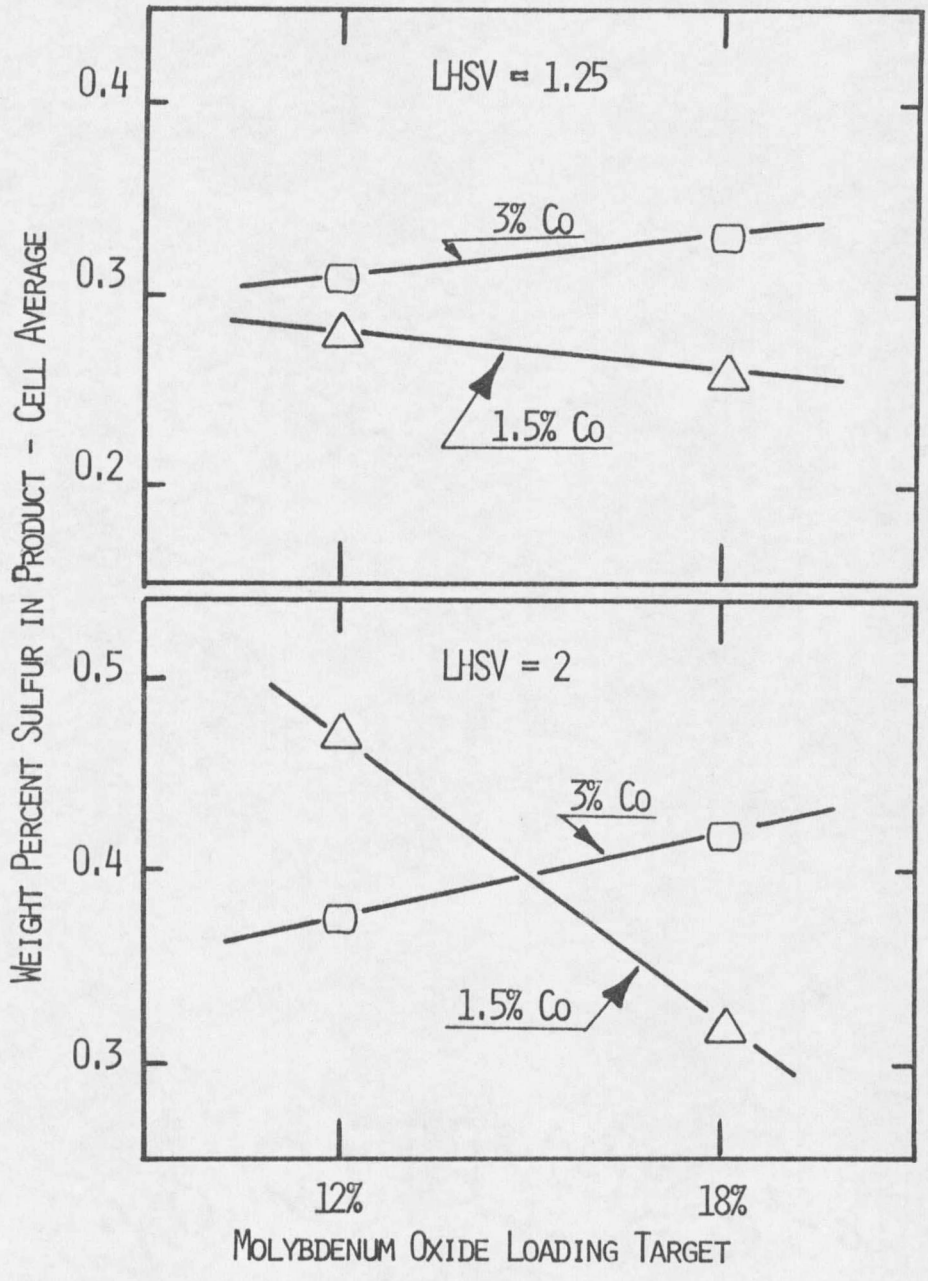


FIGURE 21. WEIGHT PERCENT SULFUR VS CATALYST METAL LOADING, MSU CATALYSTS

In summary, the metals loading experimental results seem to indicate that, at the levels used, only a cobalt molybdate catalyst is necessary to hydrotreat COED pyrolysis oil.

8. SUMMARY AND CONCLUSIONS

As stated in the Introduction, the purpose of this research was twofold:

- Determine the best among the commercial hydrotreating catalysts available.
- Develop improved catalysts.

Along with the above, the corollary purpose was to determine why the catalysts performed as such.

From the tests on commercial catalysts the following conclusions are evident.

1. For the removal of sulfur, the following cobalt molybdate catalysts performed best: Shell 344, Harshaw HT400 and Cyanamid HDS-20A.
2. For denitrogenation, the following nickel molybdate catalysts performed best: Shell 324, Harshaw HT500, and Cyanamid HDS-9A.
3. However, the nitrogen removal for the best cobalt-molybdate and the best nickel-molybdate catalysts were very close together at certain conditions of space velocities, therefore, there might be a set of processing conditions (not tested in this research) where cobalt-molybdate catalysts could be used to remove both sulfur and nitrogen. Since

nickel molybdates are more expensive than cobalt molybdates, this could be very economically advantageous.

4. In both hydrodesulfurization and hydrodenitrogenation, the larger pore catalysts performed better, therefore implying that pore diffusion was a major resistance to the reaction.

Batch tests showed that:

1. Only good versus very bad catalysts can be screened in the autoclave.
2. Molybdenum, in combination with cobalt or nickel, is most specific for hydrotreating COED pyrolysis oil.
3. The MSU developed cobalt-nickel-molybdate catalyst showed promise of being better than the commercial catalysts.

The final continuous tests on the MSU catalysts mainly showed that:

1. Large pore supports do help denitrogenation.
2. Sulfur removal possibly was film diffusion limited in the tests.
3. Cobalt and molybdenum, in a low-high combination, are most specific for nitrogen removal in the test catalysts. Nickel probably does not affect the results at the low level that it was present.

In summary, it appears that a cobalt-moly catalyst with an optimum pore size distribution would best hydrotreat COED pyrolysis oil. The commercial catalysts probably have not yet optimized the pore

structure and the cobalt present is possibly too high for optimum denitrogenation and desulfurization activity.

9. RECOMMENDATIONS FOR FURTHER STUDY

To increase the scope of this research, several modifications of the reactor should be made. First of all, the system should be rebuilt to withstand pressure of up to 3000 psig. This would allow study of the possibility of an equilibrium denitrogenation reaction being offset by the pressure effect. Secondly, the heaters should be modified for more uniform heating of the reactor. Third, the feed reservoirs and pumps should be steam heated to keep the feed at constant temperature and thus keep the liquid flow rate even.

The analytical support of the project must be increased. Gas analysis must be used to determine the material balance and to detect the presence of ammonia and hydrogen sulfide in the off gas. Liquid chromatography should be used to see what the catalysts are doing to the polynuclear aromatic compounds; whether they are being cracked and the extent they are being saturated. Finally, the pore volume distribution of the catalysts needs to be known to be able to optimize the physical properties of the catalyst.

After the above are obtained, research should concentrate on determining what aspects of the catalyst affect the hydrotreating process. Contacts should be made with commercial catalyst companies to provide catalysts, made with their art, of varied pore size distribution and metal loadings. Designed, repeated runs should then be made using these catalysts, while varying process conditions to

determine the optimum hydrotreating catalysts and conditions for COED pyrolysis oil.

In the final analysis, the reactions that occur in the hydrotreating process depend on the pore sized distribution and acid-base properties of the support, and the metal surface areas of the hydrogenation components. If heterogenerous catalysts are to be feasible in the process, the above properties must be studied, varied, and optimized to develop a catalyst that will provide high activity over a long period of time.

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LITERATURE CITED

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APPENDIX I

DATA TABLES

Table A-1

Cobalt Molybdate Catalyst Performance

Catalyst Avg. Bed Temp. (°C) H_2 Feed Rate (NL/L)	Liquid Hourly Space Velocity	% S in Product	% Removal of sulfur	% N in Product	% Removal of Nitrogen	ASTMD-86 Distillation of Liquid Product Vol. % Boiling Below 425F	600F	700F	Recovery
Harshaw 0401-T-1/8"	.93	.36	84	.81	10	19	51	71	74
420	2.5	.86	63	.94	0	16	39	70	74
1761	3.72	1.02	56	.92	0	14	41	69	72
Harshaw HT-400-E-1/16"	1.13	.12	95	.61	32	--	--	--	--
414	2.46	.27	88	.88	2	12	44	74	76
1700	2.64	.29	87	.89	1	--	--	--	--
Shell 344-E-1/16"	1.27	.13	94	.64	29	--	--	--	--
408	2.06	.27	88	.76	16	19	47	76	78
1616	2.84	.36	84	.81	10	16	43	68	70
Houdry HR-801-E-1/16"	1.46	.83	64	.91	0	24	47	67	73
396	1.49	.89	61	.94	0	18	40	65	71
1722	2.13	.86	63	.93	0	18	42	60	72
CCI-C20-6-E-1/16"	1.01	.59	74	.93	0	20	44	68	73
404	1.82	.89	61	.96	0	17	38	60	66
1769	2.58	1.08	53	.94	0	16	37	66	70
Cyanamid-HDS20A	1.38	.28	88	.75	18	18	45	66	69
413	1.81	.31	86	.84	9	16	43	63	67
1840	2.66	.40	82	.92	0	17	42	64	69

Catalyst Descriptions	% Co	% Mo	Support	S.A.	P.V.	Ave. Pore Size
Harshaw 0401	3	9	Silica Alumina	160	.4	100 Å
Harshaw HT400	3	15	Alumina	220	.5	91 Å
Shell 344	2.4	9.9	Alumina	195	.6	123
Houdry HR-801	3	15	Alumina	300	--	--
CCI C20-6	3	15	Alumina	--	--	--
Cyanamid HDS20A	5	16.2	Alumina	230	.52	90A

Table A-II

Nickel Tungsten Catalyst Performance

Catalyst Ave. Bed Temp. (°C) H_2 Feed Rate (NL/L)	Liquid Hourly Space Velocity	% S in Product	% Removal of Sulfur	% N in Product	% Removal of Nitrogen	ASTMD-86 Distillation of Liquid Product Vol. % Boiling Below 425F	600F	700F	Recovery
Harshaw 4401	.86	.76	67	.885	2	19	45	69	74
415	1.43	1.08	53	.98	0	8	30	60	63
1844	2.23	1.2	48	.925	0	10	31	60	66
Harshaw 4301	1.02	.47	80	.91	2	12	38	54	61
413	2.06	.81	64	.93	0	9	33	54	60
1757	2.46	.92	60	.96	0	5	34	58	64
Harshaw 4303	.95	.26	89	.77	16	17	46	63	68
414	1.65	.5	78	.88	4	16	41	58	64
1779	2.35	.54	76	1.03	0	13	40	56	62
Ketjen 330-3-E	.91	.57	75	.90	2	25	47	63	68
412	1.71	.57	75	.89	3	22	45	67	72
1746	2.56	.80	65	.95	0	8	33	57	63
Ketjen HC-5	1.17	.61	73	.86	7	20	42	65	70
414	1.75	.52	77	.87	5	22	42	61	66
1798	2.09	.48	79	.86	7	10	43	62	66

Catalyst Descriptions	% N.	% W.	Support	S.A.	P.V.	Avg. Pore Size
Harshaw 4401	6	19	50% SiO_2, 25% Al_2O_3	--	--	--Å
Harshaw 4301	6	19	Silica Alumina	228	.37	65 Å
Harshaw 4303	6	19	Alumina	152	.54	142 Å
Ketjen 330-3E	6.6	19.8	Silica Alumina	193	.43	89 Å
Ketjen HC-5	6.5	21	Alumina	200	.62	124 Å

Table A-III

Nickel Molybdate Catalyst Performance

Catalyst Avg. Bed Temp. (°C) H_2 Feed Rate (NL/L)	Liquid Hourly Space Velocity	% S in Product	% Removal of Sulfur	% N in Product	% Removal of Nitrogen	ASTMD-86 Distillation of Liquid Product Vol. % Boiling Below 425F	600F	700F	Recovery
Shell 324-E-1/16"	1.63	.27	88	.62	33	22	50	69	73
414 (80 CC bed)	1.77	.44	81	.81	12	19	44	65	68
1704									
Shell 324-E-1/16"	1.1	.29	87	.73	21	20	49	66	69
412 (68 CC bed)	2.24	.53	77	.84	9	13	41	60	64
1765	2.26	.41	82	.86	7	14	42	62	66
Harshaw HT-100-E-1/12"	1.41	.46	80	.88	4	13	41	58	63
414	1.71	.56	75	.90	2	10	37	57	62
1831									
Harshaw HT-500-E-1/8"	1.12	.64	72	.63	32	11	38	61	68
412	1.66	.63	72	.6	35	11	32	60	64
1768	2.31	.80	65	.68	26	7	35	52	60
Cyanamid HDS-9A	.89	.45	80	.44	52	11	46	74	80
414	2.08	.48	79	.71	23	11	41	59	65
1812	2.63	.54	76	.73	21	7	36	52	60
Houdry HR811-E-1/8"	1.54	.70	69	.69	25	14	38	55	63
414	1.56	.58	75	.67	27	15	38	58	68
1856	2.17	.71	69	.64	30	11	39	56	64

Catalyst Descriptions	% Ni	% Mo	Support	S.A.	P.V.	Ave. Pore Size
Shell 324	2.7	13.2	Alumina	160	.5	125 Å
Harshaw HT-100	3.8	16.8	1.5% SiO_2, Alumina	175	.54	123 Å
Harshaw HT-500	3.17	15.5	Alumina	210	.49	93 Å
Cyanamid HDS9A	3-4	17.5-18.5	Alumina	--	--	--
Houdry HR811	3	15	Alumina	300	--	--

Table A-IV

Commercial Catalyst Description

Harshaw CoMo 0401 T 1/8	3% CoO, 9% MoO_3 on silica alumina
Harshaw HT 100	3.8% NiO, 16.8% MoO_3 on silica alumina
Harshaw HT 500	3.2% NiO, 16% MoO_3 on alumina
Harshaw Ni 4401	6% NiO, 19% WO_3, 50% SiO_2, 25% Al_2O_3
Harshaw 4301	6% NiO, 19% WO_3 on silica alumina
Harshaw Ni 4303	6% NiO, 19% WO_3 on alumina
Harshaw Ni 1601	3% NiO, 3% CoO, 3% Fe_2O_3 on alumina
Harshaw Ni 3250	50% Nickel on basic alumina
Harshaw Mo-1201	10% MoO_3 on alumina
Harshaw W 0801	10% WO_3 on alumina
Harshaw Ni 1600	3% CoO, 3% NiO, 3% Fe_2O_3 on silica alumina
Shell 324	3% NiO, 13% MoO_3
Shell 344	2.4% CoO, 9.9% MoO_3
Ketjen HC-5	6.5% NiO, 21% WO_3 on alumina
Ketjen Ketjenfine 330-3E	6.6% NiO, 19.8% WO_3, 1.2% SiO_2 on alumina
CCI-C20-6	4% CoO, 15% WO_3 on alumina
Harshaw HT 400	3% CoO, 15% MoO_3 on Al_2O_3
Houdry HR 801	3% CoO, 15% MoO_3 on Al_2O_3 S.A. = 300 m^2/g
Houdry HR 811	3% NiO, 15% MoO_3 on Al_2O_3 S.A. = 300 m^2/g
Cyanamid HDS20A	5% CoO, 16.2% MoO_3 on Al_2O_3 S.A. = 230 m^2/g, P.V. = .52 CC/g
Cyanamid HDS9A	3.5% NiO, 18.0% MoO_3 on Al_2O_3 S.A. = 300 m^2/g

Table A-V

Cobalt - Nickel - Molybdate Catalyst Performance

Catalyst Avg. Bed Temp. (°C) H_2 Feed Rate (NL/L)	Liquid Hourly Space Velocity	% S in Product	% Removal of Sulfur	% N in Product	% Removal of Nitrogen	ASTM D86 Distillation of Liquid Product Vol. % Boiling Below 425F	600F	700F	Recovery
STK 5-2-1	1.32	.38	83	.88	4.3	14	41	60	67
416	2.05	.52	77	.95	0	14	38	58	68
1811									
STK 5-2-2	1.44	.22	90	.77	17				
413	1.78	.32	86	.81	12	15	41	61	68
1831	2.19	.41	82	.80	13	15	42	61	70
	2.61	.46	80	.93	0				
STK 5-2-3	1.66	.57	75	.92	0				
415	1.81	.52	77	.90	2	14	40	57	64
1755	1.97	.57	75	1.04	0				
	2.36	.65	71	.93	0				
STK-5-2-4	1.23	1.19	48	.97	0	11	35	51	60
412	1.71	1.22	46	.94	0				
1792									
STK 5-2-5	1.05	.22	90	.97	0	15	43	60	66
413	1.93	.48	79	.91	1				
1843	2.24	.52	77	.91	1	13	35	53	65
STK 5-2-6	1.67	.28	88	.78	20				
413	1.91	.6	74	.94	0				
1699	2.37	.46	80	.86	7	14	43	68	76
	2.45	.36	84	.86	7	15	42	64	74

Table A-VI

Preliminary Run Data

Run	Catalyst	LHSV	H_2:0.1	% S in Product	% N in Product
3	CCI C20-6	5.44	1629 scf/bbl	1.86	--
4	CCI C20-6	2.25	5000	.60	.602
		2.25	7000	.64	.84
6	Harshaw Ni 4401	0.8	6000	.56	.57
		1.7	11,000	.70	.61
		3.1	9,000	.78	.61
10	Harshaw Ni 1600	.28	34,000	1.2	.55
		.40	46,000	1.39	.58
		.83	28,000	1.51	--

Note: H_2O:1 in SCF of H_2/bbl feed

Run Conditions Temp = 450 C
Press = 800 psig

APPENDIX II

STATISTICAL ANALYSIS OF METALS LOADING RUNS

One run was made on each of the eight catalysts, and three samples were taken during each run. The sampling procedure consisted of running 500 ml of feed through the reactor, sampling a 150-200 ml amount of product at that space velocity, changing space velocity and allowing the reactor to line out over 200 ml of feed. Another sample was then taken, and then the procedure was repeated for a third sample. The order of space velocities was kept at high to low to medium LHSV during the course of the run. The data generated is presented in Table A-VII.

Table A-VII

Continuous Metal Loading Tests

Sample	Catalyst[1]	LHSV[2]	H_2:Oil[3]	T avg. (°C)[4]	% N	% S
71-1	4003	2.09	1606	415	0.83	0.32
-2		1.27	1920	413	0.74	0.30
-3		.96	1891	415	0.70	0.20
72-1	7003	1.33	1175	413	0.81	0.26
-2		1.08	1751	414	0.74	0.26
-3		1.93	1840	409	0.95	0.32
73-1	3003	1.66	1571	410	0.83	0.32
-2		1.71	1604	411	0.88	0.40
-3		1.07	1812	409	0.79	0.29
74-1	8003	1.96	1758	415	0.84	0.48
-2		1.89	1900	417	0.86	0.50
-3		1.61	1673	411	0.80	0.35
-4		1.63	1646	412	0.86	0.42

Table A-VII (continued)

Sample	Catalyst[1]	LHSV[2]	H_2:O.1[3]	T avg.(°C)[4]	% N	% S
75-1	6003	1.82	1862	418	0.86	0.38
-2		1.28	1925	417	0.82	0.26
-3		2.44	1824	412	0.96	0.52
76-1	2003	1.98	1703	415	0.78	0.31
-2		1.25	1783	415	0.72	0.27
-3		2.32	1920	416	0.93	0.44
77-1	1003	2.12	1678	414	0.87	0.52
-2		1.20	1860	421	0.75	0.30
-3		2.69	1795	420	0.72	0.45
78-1	5003	1.91	1752	416	0.86	0.34
-2		1.19	1792	413	0.84	0.38
-3		2.35	1870	414	0.94	0.51

[1] Catalyst descriptions: see Table XI.
[2] LHSV: Liquid Hourly Space Velocity.
[3] H_2:Oil feed ratio: 1780 NL/L = 10,000 SCF/bbl
[4] T avg.: Centrigrade average of top, middle and bottom bed temperatures.

The data from Table A-VII was taken and plotted on the curves in Figures A-1, A-2, A-3, and A-4. A smooth curve was drawn through the points where possible; if the data was scattered, linear regression was used to draw a straight line through the points. Nitrogen and sulfur data was taken from the graph at the points LHSV = 1.25 and LHSV = 2.00. This data was then used as the response variables for a 2^4 factorial experiment of one replicate.

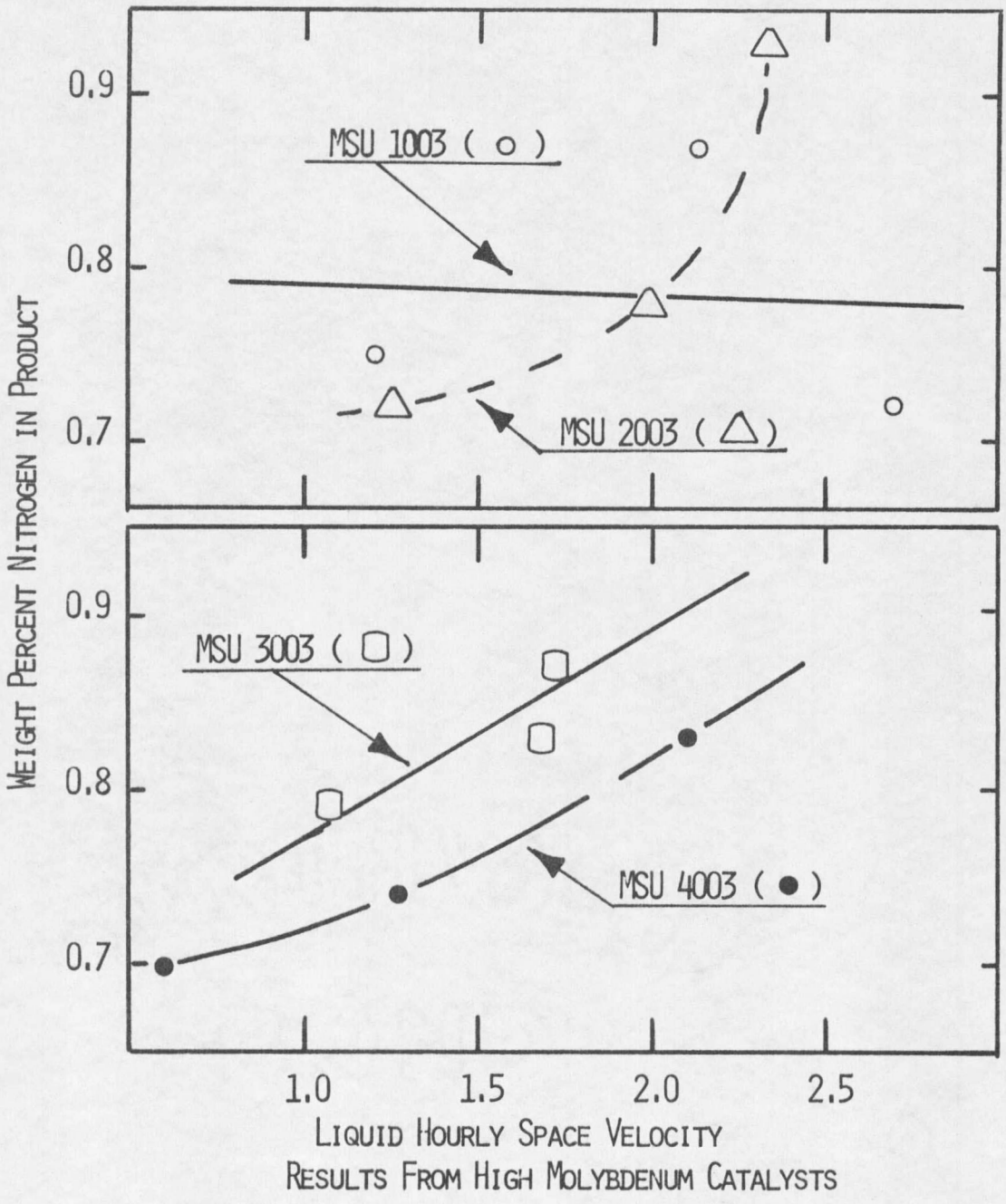


Figure A-1. Weight Percent Nitrogen vs LHSV, MSU High Moly Catalysts

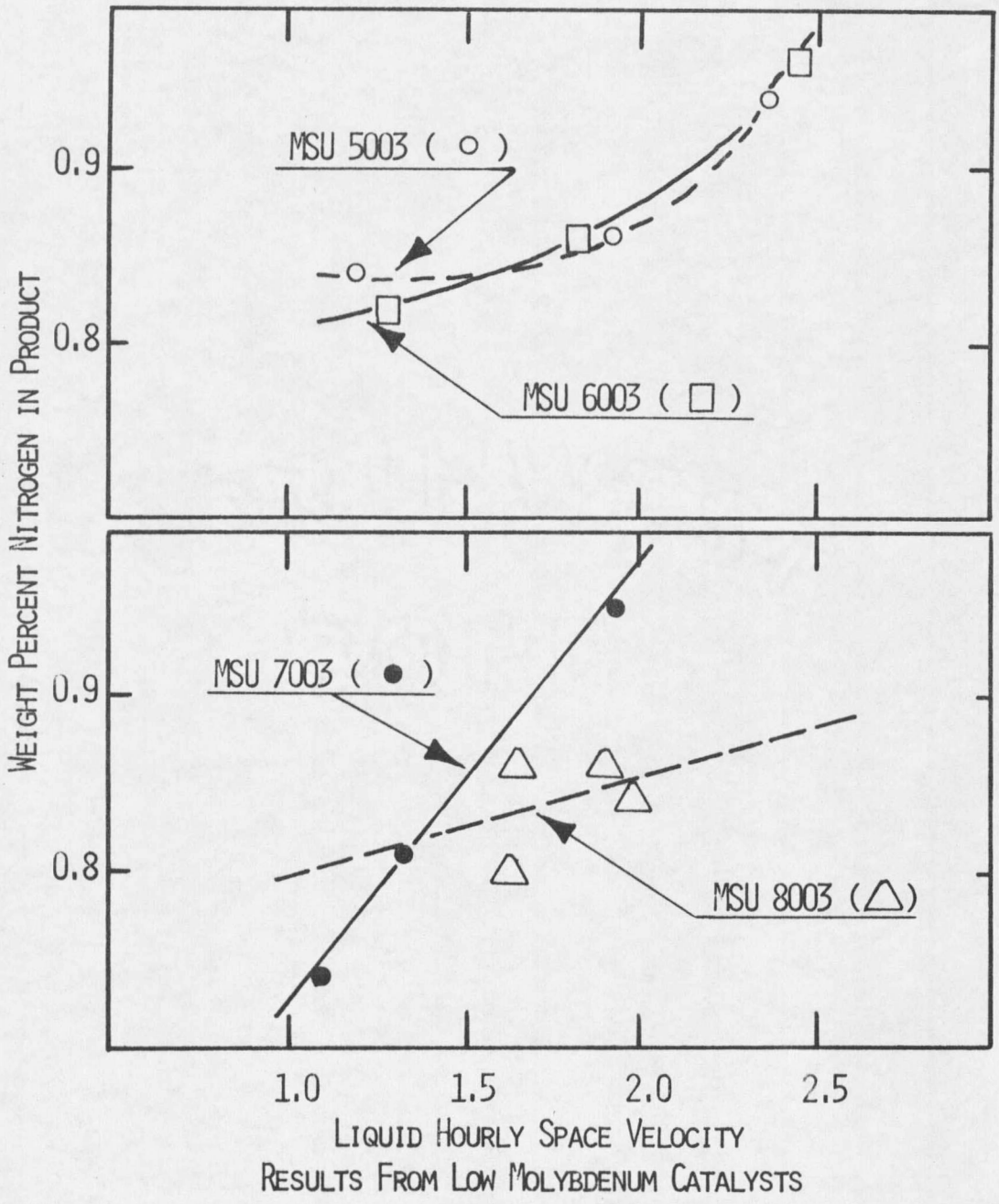


FIGURE A-2. WEIGHT PERCENT NITROGEN VS LHSV, MSU LOW MOLY CATALYSTS

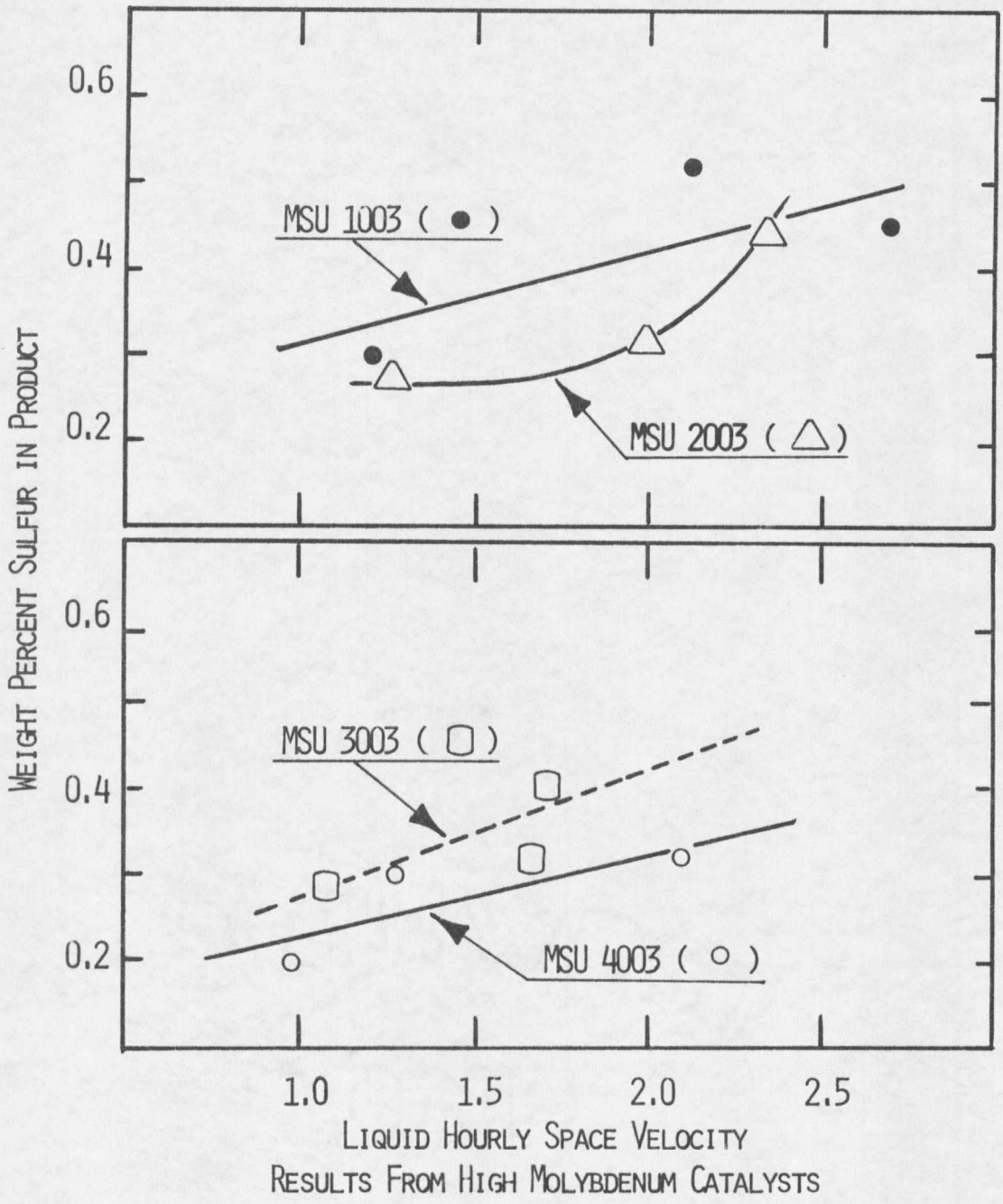


Figure A-3. Weight Percent Sulfur vs LHSV, MSU High Moly Catalysts

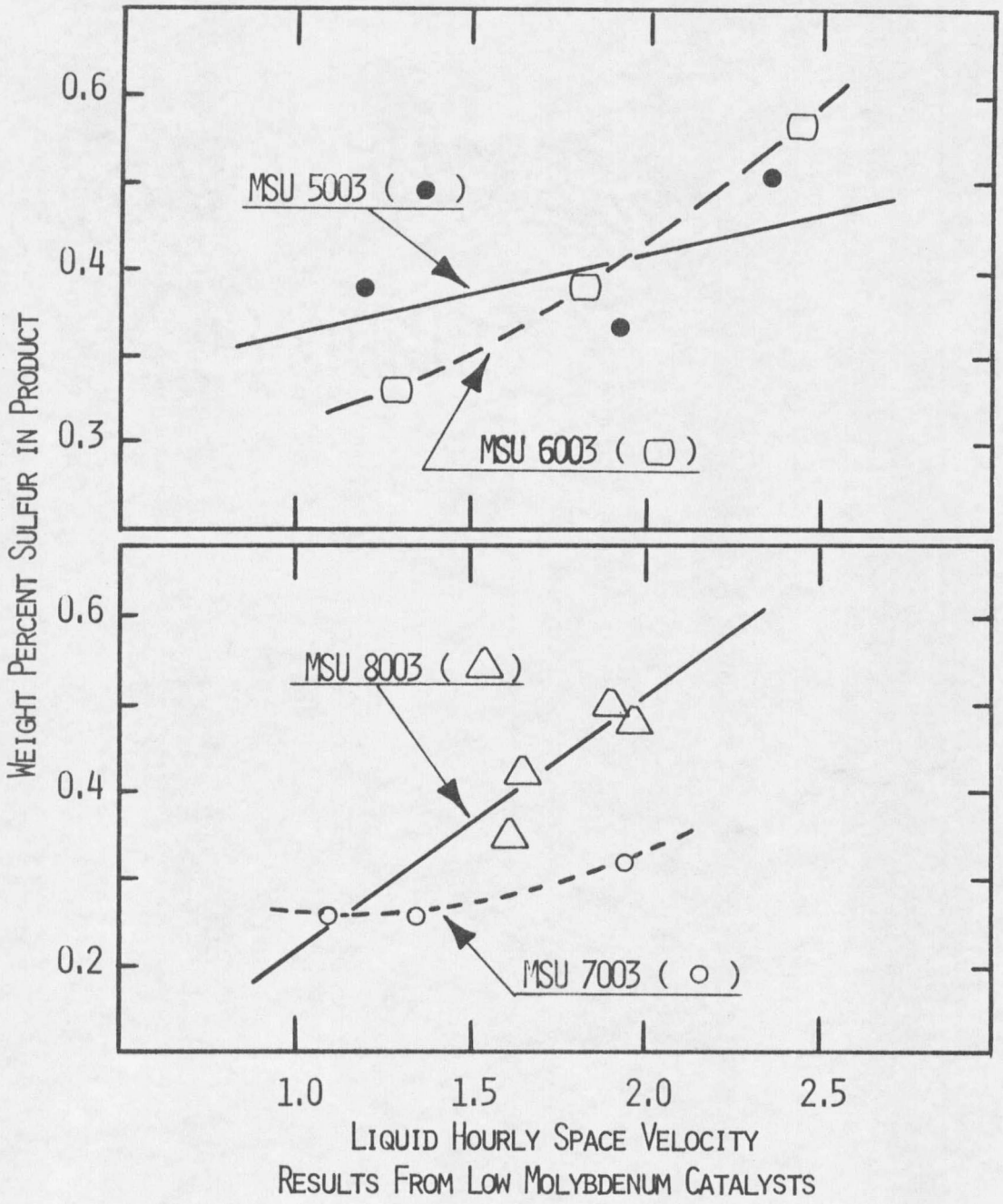


FIGURE A-4. WEIGHT PERCENT SULFUR VS LSHV, MSU LOW MOLY CATALYSTS

The four independent variables were, LHSV (1.25 and 2); cobalt loading (1.5% and 3%); nickel loading (0.5 and 1.5%); and molybdenum loading (12% and 18%). The data was then set up for analysis as in Table A-VIII for nitrogen and A-IX for sulfur.

Table A-VIII

Weight Fraction Nitrogen in Product for 2^4 Analysis

		Mo 12%			Mo 18%		
LHSV	Co	0.5%	Ni	1.5%	0.5%	Ni	1.5%
1.25	1.5%	.81		.82	.74		.72
	3%	.79		.84	.80		.79
2	1.5%	.85		.88	.82		.78
	3%	.98		.87	.89		.78

Table A-IX

Weight Fraction Sulfur in Product for 2^4 Analysis

		12%			18%		
LHSV	Co	0.5%	Ni	1.5%	0.5%	Ni	1.5%
1.25	1.5%	.29		.26	.25		.27
	3.0%	.26		.35	.31		.34
2	1.5%	.51		.43	.32		.32
	3.0%	.33		.42	.42		.42

An analysis of variance (ANOVA) was made on the data in Tables A-VIII and A-IX after it was coded by multiplying by a factor of ten. The results of the ANOVA are presented in Table A-X

Table A-X

ANOVA Table for Coded Data

Source	df	SS(Nitrogen)	SS(Sulfur)	EMS
L	1	1.82	4.41	$6\phi_L + \sigma^2_E$
M	1	1.69	0.25	$6\phi_M + \sigma^2_E$
C	1	0.64	0.25	$6\phi_C + \sigma^2_E$
N	1	0.25	0.09	$6\phi_N + \sigma^2_E$
NC	1	0.16	0.57	$4\phi_{NC} + \sigma^2_E$
NM	1	0.16	0.005	$4\phi_{NM} + \sigma^2_E$
CM	1	0.04	1.33	$4\phi_{CM} + \sigma^2_E$
LN	1	0.43	0.07	$4\phi_{LN} + \sigma^2_E$
LC	1	0.03	0.21	$4\phi_{LC} + \sigma^2_E$
LM	1	0.07	0.31	$4\phi_{LM} + \sigma^2_E$
NCM	1	0.01	0.48	$2\phi_{NCM} + \sigma^2_E$
LNC	1	0.41	~ 0	$2\phi_{LNC} + \sigma^2_E$
LNM	1	~ 0	~ 0	$2\phi_{LNM} + \sigma^2_E$
LCM	1	0.19	0.62	$2\phi_{LCN} + \sigma^2_E$
LCMN	1	0.07	0.02	$\phi_{LNCM} + \sigma^2_E$
ERROR	0	UNRETRIEVABLE		

L = LHSV; M = wt% molybdenum; C = wt% cobalt; N = wt% nickel

Since only one replicate of the experiment was run, no degrees of freedom were left for error analysis. However, it was felt that the interaction terms could be used for error in the analysis. The interactions between metal loadings and space velocity should be non-existent, therefore these terms should be measuring error. A modified ANOVA Table was then set up using these terms for error.

Table A-XI

Modified ANOVA Table - Nitrogen

Source	df	SS	MS	F
L	1	1.82	1.82	10.71**
M	1	1.69	1.69	9.94**
C	1	0.64	0.64	3.76*
N	1	0.25	0.25	1.47
NC	1	0.16	0.16	0.94
NM	1	0.16	0.16	0.94
CM	1	0.04	0.04	0.20
NCM	1	0.01	0.01	0.06
ERROR	7	1.20	0.17	

* Significant at 90% confidence
** Significant at 95% confidence

Table A-XI (continued) - Sulfur

Source	df	SS	MS	F
L	1	4.41	4.41	25***
M	1	0.25	0.25	1.42
C	1	0.25	0.25	1.42
N	1	0.09	0.09	0.51
NC	1	0.57	0.57	3.24
NM	1	0.005	0.005	0.03
CM	1	1.33	1.33	7.57**
NCM	1	0.48	0.48	2.73
ERROR	7	1.23	0.18	

** Significant at 95% confidence
*** Significant at 99% confidence

Space velocity is shown to be very significant, as obviously is true, in the above modified tables. For nitrogen removal, the main effects of both the amount of molybdenum and cobalt are found to significantly affect nitrogen removal as is shown in Figure 20 in the Results. For sulfur removal, only the interaction between cobalt and molybdenum is found to be significant; a result which is illustrated in Figure 21.

There are several assumptions that were made when the data was analyzed as a 2^4 factorial experiment. They are,

1. The effect on the randomization process of using eight runs to generate sixteen data points is unknown. The data could be biased without knowing it.
2. It was assumed that each catalyst was at its same aging point for each sample. No tests of steady state activity were made.
3. It was assumed that variation in control of the process did not affect the results.

In the light of the above assumptions, it is felt that the results should be used more as a guide towards further experimentation and not as a definite statement of how the catalyst is interacting with the system. The fact that nickel does not show significance only means that at the levels tried, it did not have a very large effect. At other levels nickel might prove significant for hydrotreating.

APPENDIX III

NOMENCLATURE

Table A-XII

Nomenclature

Abbreviations

LHSV	Liquid Hourly Space Velocity - volume of feed per hour per volume of catalyst
Moly	Abbreviation for molybdenum as in cobalt-moly catalyst
NL/L	Normal liter per liter - liters of gas feed at STP per liter of liquid feed

Variables and Constants

$\bar{a}$	average pore radius in $\mathring{A}$
dp	catalyst particle diameter
EA	activation energy
h	catalyst bed depth
k	rate constant
k_o	pre-exponential factor in Arrhenius equation
α_2	fraction of unreactive sulfur molecules in feedstock
ν	kinematic viscosity
σ	surface tension

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