MONTANA STATE UNIVERSITY

The role of the support in catalytic hydrodesulfurization of diesel fuel

by Carlton Dencker Grimm

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
© Copyright by Carlton Dencker Grimm (1971)

Abstract:
Promoted alumina silica catalyst supports were studied for their hydrodesulfurization properties. Two support classes were used in this investigation—molecular sieves with their uniform crystalline structure and low pore diameter of 10 Å and the noncrystalline silica alumina supports whose pore diameters ranged from 50 Å upward to 180 Å.

Cobalt and molybdenum were deposited on the molecular sieves near two target figures: 3% Co 15% Mo and 5% Co 10% Mo. An ammonium ion molecular sieve was used to ion exchange cobalt or nickel onto the support with the deposited cobalt and molybdenum. Nickel and tungsten promoted molecular sieves were near 3% Ni 15% W. The noncrystalline supports were promoted near 3% Co 15% Mo.

The influence of pore size, pore volume, alumina and silica content, surface area, and density were noted for each promoted base material.

Gas oils near 31 °API gravity with 1.5 to 2.0 weight percent sulfur were used for the hydrodesulfurization runs. Temperatures 650, 725, and 800 °F were checked and the liquid hourly space velocities 1.5, 4.0, and 7.0 were run at each temperature. The plug flow reactor was pressurized to 300 psig. Sulfur analyses were made on samples taken at each flow and temperature condition and a ASTM distillation was made of the product from the LHSV 1.5, 800 °F condition.

An increase in pore volume brought increased desulfurization in similarly promoted molecular sieves. The high surface area molecular sieves did not compete with the large pore diameter noncrystalline supports, but gave 20 to 30 percent less desulfurization.

Promoted noncrystalline bases that had pore volumes between 0.30 and 0.48 cc./gm. gave the same desulfurization as bases with pore volumes between 0.78 and 1.22 cc./gm. at LHSV 1.5, but the smaller pore volume supports' performance dropped behind the larger pore volume bases at LHSV 4.0 and 7.0.

The promotion amount and support surface areas did not affect desulfurization results as did pore size and pore volume.

THE ROLE OF THE SUPPORT IN CATALYTIC HYDRODESULFURIZATION OF DIESEL FUEL

by

Carlton Dencker Grimm

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Approved:

Lloyd Berg
Head, Major Department

Lloyd Berg
Chairman, Examining Committee

L. Loeving
Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

June 1971

ACKNOWLEDGMENT

The author wishes to acknowledge the support of Norton Company, Akron, Ohio for its financial contribution to this catalyst carrier investigation. The efforts and counseling of Dr. Lloyd Berg are appreciated and the resolving of equipment problems and fabrication by Mr. James Tillery and Mr. Silas Huso added to the project completion.

TABLE OF CONTENTS

Page

List of Tables..... vi

List of Figures..... vii

Abstract..... xi

I. Introduction..... 1

II. Research Objectives..... 13

III. Equipment and Experimental Procedure

A. Equipment..... 14

B. Experimental Procedure..... 16

IV. Catalyst Support Materials

A. Molecular Sieves..... 19

B. Noncrystalline Supports..... 20

V. Catalyst Preparation..... 22

VI. Discussion

A. Organization of Data and Interpretations..... 26

B. Molecular Sieve Catalysts
1. Nonpromoted Supports as Catalysts..... 27
2. Specific Samples and Their Promotions
a. Norton 0081..... 30
b. Norton 0255..... 31
c. Norton 0256..... 32
d. Norton 44001..... 33
e. Norton 20072..... 35
f. Linde 13-X..... 37

TABLE OF CONTENTS (Continued)

Page

3. Comparisons
   a. Samples Near 3% Co 15% Mo..... 38
   b. Samples Near 5% Co 10% Mo..... 39
   c. Best Sample Promotions..... 40
4. Product Distillations..... 40
5. Sulfur Removed vs. Distillation Temperature..... 42
6. °API Gravity of Products..... 43

C. Noncrystalline Supports
   1. Specific Samples and Their Promotions
      a. Nalcat 2910-A..... 44
      b. Nalcat 2910-B..... 46
      c. Harshaw 1802..... 46
      d. Harshaw 1602..... 47
      e. Alcoa H-151..... 48
      f. Norton 6473..... 49
      g. Houdry C and Harshaw 4401-E..... 50
   2. Comparisons
      a. Promotions Near 3% Co 15% Mo..... 51
      b. Promotions Near 5% Co 10% Mo..... 52
      c. Best Sample Promotions..... 53
      d. Equal Pore Volume Supports..... 54
   3. Distillation of Products..... 55
   4. Sulfur Removed vs. Distillation Temperature..... 57
   5. °API Gravity of Products..... 58

VII. Conclusions..... 60

VIII. Recommendations..... 62

IX. Appendix..... 63

X. Literature Cited..... 171

LIST OF TABLES

Table	Title	Page
I	Fuel Properties	66
II	Synopsis of Hydrodesulfurization Runs	67
III	Molecular Sieve Support Properties	69
IV	Noncrystalline Base Support Properties	70
V	Molecular Sieve Supports, Promotions, Best Results	71
VI	Noncrystalline Supports, Promotions, Best Results	73
VII	°API Gravity from Molecular Sieve Catalyst Treatment	123
VIII	°API Gravity from Noncrystalline Catalyst Treatment	170

LIST OF FIGURES

Figure		Page
1	Equipment Schematic.....	64
2	Schematic of Reactor and Heating Unit.....	65
3	Cobalt and Molybdenum Content on Molecular Sieves.....	74
4	Cobalt and Molybdenum Content on Noncrystalline Bases.	75
5,6,7	Percent Desulfurization vs. 1/LHSV for Base Materials Used as Desulfurization Catalysts.....	76
8,9,10	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 0081.....	79
11,12,13	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 0255.....	82
14,15,16	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 0256.....	85
17,18,19	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 44001.....	88
20,21,22	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 20072.....	91
23,24,25	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 20072 with Nickel Ion Exchanged.....	94
26,27,28	Percent Desulfurization vs. 1/LHSV for Promoted Norton Sample 20072 with Cobalt Ion Exchanged.....	97
29,30,31	Percent Desulfurization vs. 1/LHSV for Promoted Linde 13-X.....	100
32,33,34	Percent Desulfurization vs. 1/LHSV for Crystalline Supports Promoted Near 3% Co 15% Mo.....	103
35,36,37	Percent Desulfurization vs. 1/LHSV for Crystalline Supports Promoted Near 5% Co 10% Mo.....	106

LIST OF FIGURES (Continued)

Figure		Page
38,39,40	Percent Desulfurization vs. 1/LHSV for Best Molecular Sieve Promotions.....	109
41	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton 0081.....	112
42	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton 0255.....	113
43	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton 0256.....	114
44	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton 44001.....	115
45	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton 20072.....	116
46	Distillation Temperature vs. Percent Recovered for Products of Promoted Linde 13-X.....	117
47	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Norton 44001.....	118
48	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Norton 20072.....	119
49	Percent Sulfur Removed vs. Distillation Temperature for Products of Nickel Ion Exchanged Norton 20072.....	120
50	Percent Sulfur Removed vs. Distillation Temperature for Products of Nickel Tungsten Promoted Norton 20072.	121
51	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Linde 13-X.....	122
52,53,54	Percent Desulfurization vs. 1/LHSV for Promoted Nalcat 2910-A.....	124
55,56,57	Percent Desulfurization vs. 1/LHSV for Promoted Nalcat 2910-B.....	127

LIST OF FIGURES (Continued)

Figure		Page
58,59,60	Percent Desulfurization vs. 1/LHSV for Promoted Harshaw 1802	130
61,62,63	Percent Desulfurization vs. 1/LHSV for Promoted Harshaw 1602	133
64,65,66	Percent Desulfurization vs. 1/LHSV for Promoted Alcoa H-151	136
67,68,69	Percent Desulfurization vs. 1/LHSV for Promoted Norton 6473	139
70,71,72	Percent Desulfurization vs. 1/LHSV for Promoted Houdry C and Harshaw 4401-E	142
73,74,75	Percent Desulfurization vs. 1/LHSV for Promoted Noncrystalline Supports Near 3% Co 15% Mo	145
76,77,78	Percent Desulfurization vs. 1/LHSV for Promoted Noncrystalline Supports Near 5% Co 10% Mo	148
79,80,81	Percent Desulfurization vs. 1/LHSV Noncrystalline Supports Best Results	151
82,83,84	Percent Desulfurization vs. 1/LHSV Noncrystalline Supports with Pore Volumes Near 0.45 cc./gm	154
85	Distillation Temperature vs. Percent Recovered for Products of Nalcat 2910-A	157
86	Distillation Temperature vs. Percent Recovered for Products of Nalcat 2910-B	158
87	Distillation Temperature vs. Percent Recovered for Products of Promoted Harshaw 1802	159
88	Distillation Temperature vs. Percent Recovered for Products of Promoted Harshaw 1602	160
89	Distillation Temperature vs. Percent Recovered for Products of Houdry C	161

LIST OF FIGURES (Continued)

Figures		Page
90	Distillation Temperature vs. Percent Recovered for Products of Promoted Alcoa H-151.....	162
91	Distillation Temperature vs. Percent Recovered for Products of Promoted Norton LA 6473.....	163
92	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Nalcat 2910-A.....	164
93	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Nalcat 2910-B.....	165
94	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Harshaw 1802.....	166
95	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Harshaw 1602.....	167
96	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Alcoa H-151.....	168
97	Percent Sulfur Removed vs. Distillation Temperature for Products of Promoted Norton LA 6473.....	169

ABSTRACT

Promoted alumina silica catalyst supports were studied for their hydrodesulfurization properties. Two support classes were used in this investigation--molecular sieves with their uniform crystalline structure and low pore diameter of 10 Å, and the noncrystalline silica alumina supports whose pore diameters ranged from 50 Å upward to 180 Å.

Cobalt and molybdenum were deposited on the molecular sieves near two target figures: 3% Co 15% Mo and 5% Co 10% Mo. An ammonium ion molecular sieve was used to ion exchange cobalt or nickel onto the support with the deposited cobalt and molybdenum. Nickel and tungsten promoted molecular sieves were near 3% Ni 15% W. The noncrystalline supports were promoted near 3% Co 15% Mo.

The influence of pore size, pore volume, alumina and silica content, surface area, and density were noted for each promoted base material.

Gas oils near 31 °API gravity with 1.5 to 2.0 weight percent sulfur were used for the hydrodesulfurization runs. Temperatures 650, 725, and 800 °F were checked and the liquid hourly space velocities 1.5, 4.0, and 7.0 were run at each temperature. The plug flow reactor was pressurized to 300 psig. Sulfur analyses were made on samples taken at each flow and temperature condition and a ASTM distillation was made of the product from the LHSV 1.5, 800 °F condition.

An increase in pore volume brought increased desulfurization in similarly promoted molecular sieves. The high surface area molecular sieves did not compete with the large pore diameter noncrystalline supports, but gave 20 to 30 percent less desulfurization.

Promoted noncrystalline bases that had pore volumes between 0.30 and 0.48 cc./gm. gave the same desulfurization as bases with pore volumes between 0.78 and 1.22 cc./gm. at LHSV 1.5, but the smaller pore volume supports' performance dropped behind the larger pore volume bases at LHSV 4.0 and 7.0.

The promotion amount and support surface areas did not affect desulfurization results as did pore size and pore volume.

I. INTRODUCTION

Environmental control and ecology are terms used today to arouse the American public's interest in conserving resources, protecting his habitat, and providing a guarantee for the specie's survival. Attention is focused on all types of industry and what it does or should do to limit the fouling of man's world by the manufacturing processes or the use of industry's end production. Resources must be used and processed efficiently and possible pollution sources must be eliminated. These two goals do not follow each other, so there is a difficult optimization problem to find the best solution which is sometimes the more costly alternative. Moral, political, economic, and technological forces all play a part and these forces cannot be separated for analysis one by one.

Hydrodesulfurization is a term used by industry to indicate the sulfur removal from petroleum fractions by hydrogen treatment of the fraction. The resulting desulfurized hydrocarbon and hydrogen sulfide can be easily separated with the hydrocarbon sent on to some end product use while the hydrogen sulfide is additionally treated to obtain elemental sulfur which can be safely stored with little pollution danger to the environment until its subsequent use as a building block by industry is required.

Pollution laws enacted during the latter 1960's provide the stimulus to lower the sulfur content in heating and diesel fuels.

State and federal legislation set the upper sulfur limits and these limits are being reduced as time passes. New York City has a target of 0.5 weight percent sulfur in heating oils for May 1, 1971 after meeting the one percent sulfur target May 1970. The ultimate sulfur content goal is 0.3 weight percent[1]. Most crude oils found throughout the world contain sulfur in considerable amounts. The existence of low or no sulfur content in crudes is the exception and a premium price is paid for these crudes. Venezuela, Kuwait and the Middle East, and most U.S. crude oils contain sulfur with figures ranging between three and five percent. Oil is available from other sources too, but contaminants are present in them also. Tar sands contain sulfur and sulfur compounds, while oil shales contain oxygen, nitrogen, and sulfur compounds. These elements must be removed to provide an acceptable fuel for our society.

Some form of hydrotreating is needed to bring the sulfur down to the legal limits and if possible reduce the sulfur content to trace amounts. Extraction, chemical processing, and non-catalytic methods have been and are being used to remove some sulfur compounds, but the only way to reduce all sulfur compounds in a crude oil or partially refined fraction is to catalytically hydrodesulfurize the sulfur containing hydrocarbons[2]. Hydrogenation is effective in simultaneously removing oxygen, sulfur, and nitrogen.

Hydrogenation which forms the basis for hydrodesulfurization is not new, rather than being a product of the 50's or the 60's, its history goes back 50 or 60 years to Bergius who recognized the possibilities of non-catalytic high pressure hydrogenation[3]. Commercial development was slow; the first patents issued were in the late 1920's. The demand for lower sulfur content in hydrocarbons was spurred by the realization that corrosion damage occurred to equipment in which the fuel was burned. Not until a cheap hydrogen source became available with hydroreforming just prior and during World War II did the commercial hydrodesulfurization processes develop.

Catalytic hydrodesulfurization involves passing a hydrocarbon and hydrogen stream over a catalyst bed at elevated temperatures and pressures. The catalyst as described in some patents may be composed of oxides or sulfides of Group II to VII in the chemical periodic table and in conjunction with Group VIII or Groups I and II[2]. This covers a very wide range of chemical possibilities. Usually a catalyst carrier such as silica gel or alumina gel is employed for the base upon which the Group metal is deposited or admixed. The broad promotion classification can be narrowed down to several metal compounds. The cobalt and molybdenum oxides and sulfides and the nickel and tungsten oxides and sulfides are the catalyst promoters most employed. The role of the metal is thought to keep acidic sites

active during hydrogenation while the metal crystallite size controls the support area that can be kept free from coke and made available for cracking[4]. In cobalt molybdate catalyst, the cobalt is thought to provide hydrogenation and isomerization of the olefinic products from the desulfurization that the molybdenum sites provide[5,6].

Elemental sulfur, mercaptans, hydrogen sulfide, open chain sulfides, disulfides, saturated cyclic sulfides, and thiophenes are all sulfur compounds found in crude oil. The following reactions taken from McKinley[2] are indicative of typical desulfurization reactions:

"1. Hydrogenation of various type compounds to yield saturated hydrocarbons and hydrogen sulfide.

2. Decomposition of various type compounds to yield unsaturated hydrocarbons and hydrogen sulfide.

3. Splitting of alkane sulfides to yield thiols and alkanes.

4. Condensation of thiols to yield alkane sulfides and hydrogen sulfide.

5. Hydrogenation of disulfides to yield thiols."

Thermodynamics predicts these reactions will go essentially to completion at temperatures less than 900°F. Usually the maximum desulfurization temperature condition used is 800°F. The presence of a catalyst of course does not change the possible equilibrium conversion calculated by thermodynamics unless the catalyst is part of the reaction, but the catalyst can change the time required for

equilibrium to be reached.

Some references[3] state a 2:1 molybdenum to cobalt ratio is preferred for hydrodesulfurization catalyst promotion while others give lower figures for the cobalt content such as 5:1[7]. Andrews[3] also says cobalt and molybdenum content on a carrier may be built up to an amount where a maximum desulfurization is obtained, then additional cobalt and molybdenum amounts will give little additional increase in performance and possibly even a slight decrease. Nickel tungsten catalysts have a 3:1 WO_3 to NiO weight ratio.

The catalyst may be formed several different ways. The cobalt and molybdenum (as possible promoting metals for hydrodesulfurization catalysts) may be mixed with a slurry of the base material, then the slurry compressed by extrusion and dried; the metals may be coprecipitated on the catalyst carrier; the metals may be added separately to support pellets or a fine support powder; or the metals may be added to a alumina slurry, then hot digested and the slurry spray dried. The individual metal deposition is most satisfactory as with other methods the support strength is sacrificed in comparison to the preformed pellets which are promoted by separate metal addition and have excellent mechanical properties. Research projects at MSU have tended to favor the separate metal promotions on the preformed pellets[8,9,10].

The catalyst support is vital to catalytic hydrodesulfurization

as it holds the active transition series metals in place. Ashley and Mitchell[5,6] published their findings on the possible coordination structure of the metals in fresh, unused catalyst and proposed the metals actually entered the support lattice when promoted. The cobalt and molybdenum are closely associated on the alumina surface of the Co-Mo-Al_2O_3 samples. The cobalt II ion will enter octahedral cation vacancies in gamma alumina which contains random octahedral and tetrahedral vacancies.

Support materials contain alumina, silica, and some disodium oxide. Each of these three chemical compounds influences the catalyst behavior. Cracking catalyst contains 13 to 25 weight percent alumina, with the major component being silica[11,12]. Hydrodesulfurization catalysts usually contain activated alumina as their major component. Silica in hydrodesulfurization catalyst improves the stability and the disodium oxide is responsible for a negative effect--catalyst sintering during the catalyst life. It is an impurity present during the silica alumina support preparation. The disodium oxide content is kept below 0.2 weight percent because of the sintering effect. Also it does not affect catalyst activity early in the catalyst use, but over a long time may cause deactivation because of sintering. The most active alumina is the gamma variety and this is used in the support materials rather than bauxite.

Many commercial supports contain the silica and alumina in a

random, noncrystalline structure. The silica and alumina particles are arranged so there are spaces between them, but these spaces, openings, or tunnels do not fit any orderly layout. They are formed by the uneven joining of the alumina and silica molecules. A pore size distribution which tells the most probable pore size or spacing between the particles can be obtained and the pore volume measured by mercury or kerosene porosimetry methods. The available surface area for the supports which counts the surface of the passages and cavities within the support may be measured by the Brunauer-Emmett-Teller method.

Crystalline materials that have definite crystalline lattices are found in nature and may be made synthetically. These materials, often called zeolites, are composed of "building blocks". The zeolite crystal is formed from four oxygen ions that surround the smaller size silicon or aluminum ion. Since the ionic charge is not balanced, each of these fundamental blocks combines with other silica or aluminum ions and extends the crystal lattice in all directions. Charge deficits for oxygen in combination with the alumina lend the structure the ability to accept positively charged ions to stabilize it. Thus exchangeable ions as sodium and potassium can make up the charge deficit and are loosely connected to the oxygen tetrahedra that surround the aluminum ion. The sodium or potassium ion may be exchanged for hydrogen or ammonium ion and then in turn exchanged for

other ions[13]. If natural mordanite, a molecular sieve material, is used for catalysts the sodium ion appears to block the pore entrances. The molecular sieve pore size is determined by the silicon-oxygen and aluminum-oxygen tetrahedra. Cavities are present behind the building blocks and their size depends on the zeolite variety.

A British patent[14] states that molecular sieves may be used for catalysts. These crystalline materials with their inherent uniform pore diameters and with the proper choice of the particular sieve size and type may be selective to the molecules they admit to their inner cavities. This selective characteristic plus the large surface area they possess lends them to catalyst applications. The series with the largest pores allows benzene to enter it and this type should first be considered for the hydrotreating of the complex molecules found in petroleum fractions.

Surface area is another important consideration in support selection. Most silica alumina supports of the noncrystalline variety have surface areas greater than 200 m^2./gm. Molecular sieves that have relatively small pore diameters when compared to non-crystalline materials (3 to 15 Å vs. 50 Å and greater for the respective molecular sieve and noncrystalline supports) have surface areas exceeding 400 m^2./gm. The surface area must be made available for efficient catalyst use so the active sites provide the place for the reaction to occur. Problems with film and pore diffusion can

result from the wrong choice of reactor flow rate and catalyst size. A 1/16 inch diameter catalyst pellet has 95 percent of its available surface area on its exposed outside surface, while a 1/8 inch pellet exposes 55 to 60 percent. Thus if different size pellets and pellet shapes are available for a base with a given surface area per unit weight, pore diameter, and pore volume the changes in desulfurization can be attributed to pore diffusion. Film diffusion effects can be analyzed by taking different size samples and exposing them to feed flow conditions that vary proportionally with catalyst charge, i.e. maintain the same liquid fuel-solid catalyst ratio as the catalyst weight is increased for successive runs[15]. Also up to a point, the smaller the catalyst pellet size, the greater the activity will be without serious disadvantages arising from increased resistance to fluid flow in the reactor[3].

The void volume is important in catalyst supports and the accessibility of that void volume is the governing factor. As a catalyst support porosity increases, as measured by pore volume, the optimum metal amount for maximum catalyst activity increases[7]. The increase in pore volume will increase the activity to a certain point, but coupled with the increase a large amount of promoting material is required to maintain the activity.

Van Zoonen in Journal of the Institute of Petroleum[16] states there are three methods the internal catalyst surface areas may be

best utilized. First the distance between pellet center and surface is reduced. Second, the increasing of the diffusion coefficient of the sulfur bearing compounds in the oil is another method. Finally pellets should have wide pore diameter structure. The molecules then have fewer collisions with the walls, but also possible less chance for reaction as the reactions occur at active sites on the walls.

Desulfurization reactions with most heterogeneous catalysts are thought to be diffusion rate limited[4,16]. The reaction rate is so swift that the sulfur containing molecules do not reach the pelleted catalyst center before the sulfur is removed. Thus reaction products reach the inner volume of the support and possible additional reaction takes place other than the completed desulfurization reactions. This contention then opposes the need for a monomolecular film of metal promotion throughout the entire catalyst support space[3].

The diffusion can be either molecular diffusion where the molecules influence their nearest neighbors and happens if the mean free path of the molecules is less than the pellet pore size. A second diffusion type is Knudsen diffusion which postulates the molecular mean free path is larger than the pore diameter and the molecule collides only with the pore walls. This occurs at low pressures and in the vapor phase. Hydrodesulfurization catalyst pores may be filled with liquid even at high hydrogen to oil ratios[16]. Also in preparing a promoted catalyst the problem of depositing most

of the promotion on the outside surface arises. For small sized pellets, 1/16 inch diameter, this is where most of the active desulfurization sites are, as this is the greatest area available. In larger pellets, 1/4 inch diameter, more of the surface area is contained within the pellet itself rather than the outside surface. A buildup of promoted metal can obstruct diffusion from the surface to the catalyst inner spaces.

Catalyst poisoning occurs from trace metals and nitrogen compounds found in crude oil fractions. Nitrogen deactivation has more effect on the catalyst such as cobalt molybdate when low ^{o}API gravity feeds containing nitrogen are used[17]. Another poisoning source appears when the high molecular weight hydrocarbon compounds adsorb and coat catalytic surfaces[18]. Then high temperatures crack the high molecular weight compounds and coke laydown and polymer formation occur. The coke laydown on the active sites reduces the catalyst activity. Catalysts may be regenerated by burning the coke off the surface. Temperature must be monitored to prevent catalyst sintering during the "decoking" step or else sintering occurs and catalyst area and subsequent catalyst activity will be reduced.

Hydrodesulfurization operating conditions depend on the feed used. Temperatures from 300 to 400^{o}C, pressures from 50 to 2000 psig, liquid hourly space velocities 0.5 to 20, and hydrogen flow rates

50 to 10,000 scf./bbl. are listed in one U.S. patent for a cobalt molybdate catalyst[19]. Other references list optimum temperatures between 700 and 800°F, pressures 200 to 1000 psig, and hydrogen flow rates below 10,000 scf./bbl.[6,20,21,22] Research at MSU has settled on hydrogen flow rate of 5000 scf./bbl. and pressure of 300 psig for the 30 to 32 °API gravity gas oils[8].

The catalysts are most active when the promoting metals are in the sulfided form. Presulfided catalysts are available, but with a H_2S--H_2 source, the catalyst may be sulfided in place. McKinley reports that with just a fraction of one percent hydrogen sulfide in a hydrogen stream the catalyst may be adequately sulfided[2]. The sulfided promotion metals are in the Co_9S_8 and MoS_2 or Ni_3S_2 and WS_2 forms. Sulfiding may be successfully accomplished at temperatures greater than 600°F and the only requirement is that adsorbed water be removed from the catalyst pores prior to sulfiding[20]. If the catalyst is to maintain its activity a hydrogen sulfide partial pressure must be maintained. This requirement is met during hydrodesulfurization by the formation of hydrogen sulfide from the reactions.

II. PROJECT OBJECTIVES

Hydrodesulfurization of a No. 2 diesel fuel (30 °API gravity) that contains between 1.5 and 2.0 weight percent sulfur is to be attempted with transition metal promoted molecular sieves and with promoted noncrystalline alumina silica supports. The effectiveness of the two support types is to be compared.

The pore volume, pore size, surface area, and silica to alumina ratios of the molecular sieves and noncrystalline supports are to be investigated for their desulfurization effects.

The catalyst support physical and chemical compositions are to be used to predict successful hydrodesulfurization results on gas oils. The cracking ability of each catalyst preparation is to be noted.

III. EQUIPMENT AND EXPERIMENTAL PROCEDURE

A. Equipment

Desulfurization is accomplished in a plug flow, heated reactor fed by a pulse feed pump. FIGURE 1 shows the equipment schematic for all the apparatus used for the hydrodesulfurization on this project, while FIGURE 2 is a cutaway drawing of the reactor and its associated heating equipment.

The reactor was made from type 304 stainless steel and was from one inch schedule 80 pipe with a total length of three feet. This reactor fitted into a hole drilled in a solid aluminum block. Nichrome resistance wire in three series of coils was wrapped around the aluminum block and served as the heating source. Power supply was regulated by three variacs on 120 volts AC and currents of 4.5 to 5.5 amperes were drawn for each of the heating elements over the temperature range studied. The fuel oil was metered from a large glass reservoir and a smaller burette. The burette was used to obtain accurate liquid flow rates throughout equipment operation. A Lapp pump which had a variable stroke provided the desired liquid flow rate.

A manifold for hydrogen, nitrogen, and hydrogen sulfide--hydrogen compressed gas let a a rotameter. A precision valve allowed gas velocities to be varied through the rotameter and then through the reactor. The rotameter was calibrated with a wet test

meter and the flow rates were checked periodically during the runs.

A condenser was built into the line just after the reactor tube left the heating block. Water was used for cooling. Next downstream from the condenser was a back pressure valve used to maintain the required operating pressure.

Sample collection was done following the back pressure valve. A series of solenoid operated valves could be used to take samples at desired intervals if needed; however during actual operation these solenoid valves were susceptible to plugging and thus rarely used.

The gas streams containing the unused hydrogen and the resulting hydrogen sulfide from the hydrodesulfurization reactions were passed through scrubbing solutions and then vented to the atmosphere. There was no recycle of the gas stream.

A thermowell ran two-thirds the reactor length and contained three chromel alumel thermocouples connected to a Leeds and Northrup temperature recorder; one iron constantan thermocouple was also present in the thermowell and its temperature indication was read directly with a potentiometer.

The reactor was packed with inert alundum pellets one quarter inch in diameter for 18 inches of the reactor length. Then three to four inches of one eighth inch alundum pellets followed. The actual catalyst bed contained 30 cc. of experimental catalyst plus 30 cc. of the one eighth inch alundum pellets. This 60 cc. total charge was

well mixed so the alundum pellets would eliminate or reduce hot spots during the exothermic hydrodesulfurization reaction. After the catalyst bed, three more inches of one eighth inch alundum pellets were packed and the remaining reactor volume was filled with one quarter inch pellets. A stainless steel screen was placed prior to the reactor exit.

B. Experimental Procedure

The reactor operating pressure was 300 psig; hydrogen flow rate was 5000 scf./bbl.; the temperatures checked were 650, 725, and 800 degrees Fahrenheit; liquid hourly space velocities (LHSV) of 1.5, 4.0, and 7.0 were run. The gas oil obtained from the Husky Oil Company, Cody, Wyoming was from the Oregon basin. The 31.1 ^{o}API gravity feed contained 1.62 weight percent sulfur. This feed was used for the early runs of the test series (1 through 16) and then a feedstock of the same origin, but having 30.4 ^{o}API gravity and 1.82 weight percent sulfur was used on the remaining runs (17 through 57). Fuel properties including distillation data and sulfur content of six distillation fractions of the feed are contained in TABLE I. A run recapitulation is given in TABLE II.

A typical catalyst evaluation run took four to five days with each of the three flow rates checked at each of the three temperatures. One day was required for equipment startup and sulfiding,

then on successive days one temperature was checked per day.

A run started with the equipment being brought up to the operating temperature with the hydrogen flow rate at 0.5 scf./hr. After 650°F had been reached the system was purged with dry nitrogen for several hours at 0.5 scf./hr. This step was necessary to remove water from the catalyst and alundum pellets prior to sulfiding and fuel injection. Operating pressure was set by the back pressure valve and 50 psi pressure drop was allowed through the catalyst bed.

The system was checked for leaks while on the nitrogen purge, then sulfiding with a 20 percent hydrogen sulfide--80 percent hydrogen mixture took place at 650°F, gas flow rate 0.5 scf./hr. The catalyst for most runs was sulfided at 650°F and 300 psig; however some catalysts were sulfided between 650 and 725°F and from 100 to 300 psig with no change in effectiveness. Sulfiding lasted from five to seven hours.

The gas oil and hydrogen feed were introduced to the reactor after the catalyst had been sulfided. The lowest temperature 650°F was checked first at the lowest flow rate of 1.5. The 4.0 and 7.0 LHSVs were checked next in sequence. As stated before, one temperature was checked per day, with the reactor being heated to the next highest temperature the following night. At 800°F the sequence of flow rates was changed during the catalyst evaluation. The highest LHSV--7.0 was checked first, then followed by 4.0 and finally LHSV

1.5, the lowest liquid hourly flow rate.

Liquid samples were of course taken at each flow rate for each temperature. Actually three samples spread over a three hour period were taken for each flow and temperature condition. Also the reactor was allowed to stabilize from one to three hours prior to sample collection. With three samples taken at each condition, a comparison between the three easily showed if the reactor had stabilized and steady state flow and reaction conditions had been achieved.

Sulfur analysis was done by the lamp method (ASTM D-1266-647)[24]. A known fuel sample weight was burned, the combustion gases passed through a hydrogen peroxide solution, then sodium hydroxide titration provided data from which the percent sulfur was calculated.

A distillation of the sample taken at the most severe operating conditions (800°F LHSV 1.5) was done according to ASTM D 86-IP 123[25]. A second distillation was made on the same sample with six separate volume fractions collected at specified temperatures. Sulfur analyses of these fractions were compared with similar fractions in the feed. The specific gravity in terms of °API was determined for the sample taken at 800°F and LHSV 1.5.

TABLE II lists those deviations from the operating procedures specified here. It also contains some reasons for making various runs.

IV. CATALYST SUPPORT MATERIALS

A. Molecular Sieves

Six different molecular sieve base materials, six commercially available noncrystalline catalyst supports, and two commercially promoted catalysts were tested. Five molecular sieve supports were supplied by Norton Company and these were mordanite crystal structure types. The mordanite has the chemical formula:

$$Na_2O \cdot Al_2O_3 \cdot 10\ SiO_2 \cdot 6\ H_2O$$

Linde's 13-X faujasite molecular sieve has the general formula:

$$Na_{86}\left[(AlO_2)_{86}(SiO_2)_{106}\right] \cdot 260\ H_2O$$

and contained 20 percent natural clay as binder.

Norton's molecular sieves ranged from pure mordanite in sample 0081, 93.8 percent in 20072, 90 percent in 0255, to 60 percent in sample 0256. Sample 44001 was a bonded high silica powder. Those bases containing less than pure mordanite had amorphous aluminum silicate as binder. A summary of the molecular sieves or crystalline structure catalyst supports is found in TABLE III. The sieve pore diameters were 10 Å and smaller, while the pore volumes went from 0.67 cc./gm. for Linde 13-X to 0.33 cc./gm. for the five Norton samples. Surface areas were high--above 450 m^2./gm. Norton's personnel said the molecular sieve surface areas were difficult to measure, so the data comes from the mercury porosimetry readings rather than the BET methods used for the noncrystalline materials.

One of Norton's base materials was in the ammonium ion form and this led to ion exchange with promoting metals plus the deposition of the hydrodesulfurization catalyst promoters. All the crystalline bases contained SiO_2 as the major chemical component. One of Norton's materials had a silica to alumina ratio of 44 to 1. Norton's other materials contained silica to alumina ratios of 10 to 1.

B. Noncrystalline Supports

TABLE IV lists the noncrystalline support material compositions and physical data. The six base materials went from the high silica Nalcat 2910-A with the large pore diameter 180 Å, pore volume 1.22 cc./gm. to the high alumina Alcoa H-151 which possessed a pore diameter of 50 Å, pore volume 0.30 cc./gm. The pore volumes were known for all the supports presented, but the minimum pore diameters were unobtainable for the two samples Harshaw 1602 and 1802. In some cases the SiO_2 or the Al_2O_3 contents were known, but not both figures, then the known amount was reported and the difference could be assumed to be the missing figure. Disodium oxide content was low for all the base materials studied.

Two commercially made catalysts were evaluated. These (Houdry C and Harshaw 4401-E) were relatively low minimum pore diameter, non-crystalline supports. Alumina content of Houdry C exceeded 90 percent before promotion while 4401-E contained 50 percent silica. The Houdry

C contained 3.2 weight percent CoO and 14.6 weight percent MoO_3. All catalysts made by this author were reported in weight percent cobalt and weight percent molybdenum. Harshaw 4401-E was a presulfided 6.0 percent nickel 19.0 percent tungsten catalyst. These two catalysts were used to test operating procedures and to give data from which to compare the performance of the catalysts made by the author.

V. CATALYST PREPARATION

Twelve distinct catalyst support materials were promoted with various combinations of cobalt and molybdenum or nickel and tungsten. These transition metal catalyst promoters were deposited on the supports by soaking the support in solutions of the metal salts. Some catalyst samples were made with ion exchanged cobalt and molybdenum in addition to the standard deposition type catalysts.

Two promotion targets were set for the molecular sieve supports--3.0 % Co 15.0 % Mo and 5.0% Co 10.0% Mo. The noncrystalline material was targeted for the 3.0% Co 15.0% Mo promotion. At least three cobalt molybdenum promotion combinations were made on each base material with the exception of Norton 0255 and 0256 where only two promoted catalysts were run in the reactor. All of the molecular sieves and one noncrystalline support were tested as hydrodesulfurization catalysts without any promoting metal. Their performance and the promoted catalyst performance will be discussed in a later section.

All promotions of the crystalline and the noncrystalline base materials are given in TABLES V and VI. Their best performance and the conditions where this was achieved along with the specific run number are summarized there. FIGURES 3 and 4 give a graphical representation of the same data with FIGURE 3 showing the Co Mo promotions of molecular sieves and FIGURE 4 the Co Mo promotions of

noncrystalline supports.

The desired catalyst base material was calcined at 500 to 700°F prior to initial weighing. Usually a 70 to 80 gram sample was used for promotion. The cooled support was then immersed in a concentrated solution of molybdenum trioxide in ammonia hydroxide. The molybdenum trioxide concentration was kept around 0.2 gm./ml. NH_4OH. The heat of absorption was removed from the support and its surrounding solution by an ice or cold water bath. The support was allowed to soak for 24 hours in the MoO_3--NH_4OH solution. A pressure tight seal was maintained to prevent ammonia breakout and the possible surface deposition on the support. Then the remaining solution was drained off and the support was air dried. Subsequent drying was at 160°F in a tray drier, followed by calcination with the maximum temperature of 900°F reached after six hours, then temperature maintenance for twelve hours. The MoO_3 promoted base was weighed and the whole procedure could be repeated to bring the MoO_3 content to the required amount.

Cobalt promotion was done similarly to the molybdenum deposition. $CoCl_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6\ H_2O$ was used in a 0.2 gm./ml. H_2O concentration. After several hours of catalyst support material soaking in the cobalt solution, a vacuum was drawn on the enclosure and air was withdrawn from the catalyst support so the cobalt could penetrate the support easier. The maximum calcination temperature for the cobalt promoted base was 500°F. The temperature was maintained for six to

twelve hours after initial slow heating to the 500°F temperature.

Both molecular sieves and the noncrystalline materials were promoted in this manner. Norton's molecular sieve series tended to crumble after successive promotions so several attempts were made on each distinct cobalt molybdenum promotion target to obtain a useable catalyst. The Alcoa H-151 noncrystalline support was very difficult to promote as thermal fracture from the absorption heat resulted in "egg shells" breaking off the spherical support. The nickel and tungsten catalysts were prepared with the same method as the cobalt and molybdenum catalysts. Tungsten was promoted first from a tungstic acid solution, then the nickel from a nickel nitrate solution. After calcination the tungsten was taken to be in the WO_3 form and the nickel as NiO.

Both cobalt and nickel were ion exchanged onto Norton's base 20072. Support 20072 was in the NH_4^+ form and 8.7 percent of its weight could be ion exchanged. Either a cobalt or nickel salt solution was made up for the ion exchange. The weighed crystalline sample was added and allowed to soak in the solution. The ion exchanged sample was washed several times and dried. After washing the ion exchanged support was calcined at 1100°F to remove residual ammonia. Then cobalt and molybdenum were deposited on the samples as described in prior paragraphs.

While commercially prepared catalysts such as Houdry C reported their cobalt as percent CoO and molybdenum as percent MoO_3, this author gives all promotion amounts as percent cobalt (or nickel) percent molybdenum (or tungsten). Ion exchanged cobalt or nickel is reported just before the cobalt (nickel) and molybdenum (tungsten) deposition figures.

One molecular sieve sample is promoted with nickel as the sole promoter and is in the promoted molecular sieve catalyst class. A comprehensive listing of Co Mo, Ni W, and the ion exchanged catalysts for both the crystalline and the noncrystalline supports is given in TABLES V and VI and also FIGURES 3 and 4.

Physical examination of the catalysts between promotion steps and after the catalyst was finished showed the promotion appeared uniform throughout the support for the noncrystalline materials while for Norton's molecular sieves the very center of the support received little of the promoting metals. The promotion then decreased as the support center was approached in the crystalline materials. After the catalysts had been evaluated in the reactor, the promoted and sulfided support was examined, and for both the noncrystalline and molecular sieve supports a uniform black color pervaded the entire pellet cross section.

VI. DISCUSSION

A. Organization of Data and Interpretations

Two catalyst support types are studied in this project. The crystalline, molecular sieve supports and the noncrystalline materials are promoted with cobalt and molybdenum or nickel and tungsten and the results compared. The body of this discussion is divided into two distinct divisions: one section dealing with molecular sieves and their desulfurization characteristics and the other section is concerned with the noncrystalline supports and their promotions. In these two divisions the supports are listed by their sample number (see TABLES III and IV). For each sample support two, and usually three or more, promotions with the transition metals are given. Percent desulfurization is plotted versus the reciprocal liquid hourly space velocity at a given temperature. Thus for each sample and its promotions, three temperature plots are presented.

The molecular sieves and noncrystalline supports are compared as desulfurization catalysts without any promotion on three plots, one for each temperature. Both support types are also compared at the three percent cobalt fifteen percent molybdenum and five percent cobalt and ten percent molybdenum targets. The best catalyst of each sample class (examples: Norton 0081 with 3.5% Co 10.0% Mo, Norton 20072 with 5.1% Co 19.3% Mo, and Norton 0255 with 2.3% Co 12.3% Mo) are compared for each of the two support classifications.

Distillation curves are found with a number of catalyst promotions compared within a support family (example: Norton 0081 with 3.0% Co 14.3% Mo vs. 3.5% Co 10.0% Mo vs. 4.5% Co 9.3% Mo vs. 2.3% Co 18.9% Mo). Then sulfur analyses for each of the six distillation fractions of a ASTM distillation are plotted for each support sample and its promotions. A ^{o}API gravity table gives the results of hydrodesulfurization on the specific gravity change from the feed to the product. The higher the API number, the lower the specific gravity. This table lists selected supports and their promotions with the product obtained at the most severe operating conditions.

Desulfurization data taken from the two commercial catalyst made by Houdry and Harshaw are plotted with Percent Desulfurization versus 1/LHSV at the three temperatures 650, 725, and 800^{o}F. The products from the hydrodesulfurization treatment with the Houdry C catalyst are shown on a distillation curve.

In the noncrystalline support section three supports that have similar pore volumes are compared on three Percent Desulfurization vs. 1/LHSV plots at the three operating temperatures. Other than these exceptions, the desulfurization data for noncrystalline supports follows the molecular sieve data presentation.

B. Crystalline or Molecular Sieve Supports

1. Desulfurization data for nonpromoted support materials is

shown on FIGURES 5, 6, and 7. Six molecular sieves plus one noncrystalline support are plotted for their desulfurization ability. Only one noncrystalline support is used as a desulfurization catalyst without metal promotion so it is included with the crystalline supports in this series of three plots.

Noncrystalline Norton 6473 with a 50 to 60 Å pore diameter outperforms Linde's 13-X and the other Norton crystalline supports that have pore diameters between 7 and 10 Å. At 650°F 28 percent desulfurization is accomplished at the low feed rate with Norton 6473, and next in performance is the Linde molecular sieve with 18 percent removal at LHSV 1.5. The low LHSVs are at the right side of the plots thus the LHSV increases as attention is shifted to the left. Data for the 650°F temperature level is somewhat scattered indicating that steady state conditions within the catalyst system might not have been achieved. Higher temperatures, as examination of the three plots will indicate, favor more desulfurization at each of the three flow rates and more continuity to the data. At 650°F no general trend of desulfurization for a specific chemical composition of Norton's molecular sieves is apparent. The high surface are, high pore volume Linde 13-X molecular sieve gives the best results of the molecular sieve materials.

The 725 and 800°F plots give similar conclusions for Linde 13-X as compared to Norton molecular sieves. The Norton 6573 noncrystalline

base is in a class by itself and its most distinguishing property is its large pore diameter in comparison to the molecular sieves and the resulting higher desulfurization. Linde 13-X removes 30 weight percent sulfur at 725°F LHSV 1.5 and this is just three percent less than Norton 6473's performance. The bulk of the molecular sieves remove between 17 and 25 percent sulfur at 725°F LHSV 1.5. The Norton samples have approximately the same pore diameter as Linde 13-X, but one half of Linde's pore volume and a surface area two thirds as large. Base 20072 which is in the NH_4^+ form gives the lowest performance figures at 650 and 725°F. Release of ammonia from the base material could have suppressed its desulfurization effectiveness.

Relatively high desulfurization at the low feed rate for the 800°F plot is exhibited by the nonpromoted catalyst support materials. Each base retains its rank or hierarchy that was established at the lower test temperatures. The noncrystalline Norton 6473 exhibits the greater sulfur removal at the high feed rate (LHSV 7.0) but exhibits a decrease at LHSV 4.0 and then a slight increase at LHSV 1.5 with the desulfurization at the low space velocity less than at the high feed rate. This can be explained by saying possible coke laydown from cracking reduces the catalyst effectiveness. Base 0081 which is crystalline also exhibits this behavior. At this high temperature, the highest space velocity is checked first, then the intermediate

LHSV, and finally the lowest liquid hourly feed rate.

The results given for the six molecular sieves and the one non-crystalline support are not shown with the intention of predicting which catalyst support would be best in the promoted state.

2. Specific samples and their promoted families:

a. Norton's pure mordanite sample 0081 is presented on three desulfurization plots (FIGURES 8, 9, and 10). Three promotions are given for the 7 to 9 Å pore diameter molecular sieve. Cobalt promotion varies from 3.0 to 4.5 percent and molybdenum from 9.3 to 14.3 percent. Examination of the three plots shows that the 3.5% Co 10.0% Mo gives the best performance of the three promotions at each of the three temperatures studied. Those catalysts with the higher and the lower molybdenum compositions straddling the 10.0 percent molybdenum figure give comparable performance, but do not reach the desulfurization high exhibited by the 3.5% Co 10.0% Mo promotion even at the high temperature 800°F. This Norton molecular sieve gives the best performance of any Norton crystalline base in the promotion mentioned above. The 88.0 percent sulfur removal at 725°F LHSV 1.5 is obtained and not exceeded until the Linde 13-X molecular sieve is tested with various cobalt and molybdenum promotions.

More cobalt molybdate promotion levels would be needed to chart the absolute local and overall optimum promotions for this sample and the other base materials. This support leads the observer to suspect

there is an optimal composition between the two cobalt and molybdenum levels and the 3.5% Co 10.0% Mo composition falls near this maximum sulfur removal catalyst composition.

Desulfurization with promoted 0081 runs from 18 percent at LHSV 7.0 650°F to the 88 percent figure at LHSV 1.5 725°F. Optimum temperature for promoted 0081 falls near 725°F as both the 650 and 800°F plots exhibit decreases from the 725°F data. The desulfurization decrease is not so marked in the 75°F temperature change from 725 to 800°F as from 725 to 650°F.

b. Norton sample 0255 possessing 90 percent mordanite is shown with its two cobalt molybdate promotions on FIGURES 11, 12, and 13. Maximum desulfurization is given as 72 percent at LHSV 1.5 725°F with the 2.3% Co 12.3% Mo promotion. The two promotions give similar results over the 650 to 800°F temperature span. The 2.3% Co 12.3% Mo promotion appears to be the better catalyst composition as all data points excluding one give high desulfurization readings than the 5.8% Co 10.6% Mo promotion. However, the two promotions give identical data at two points (LHSV 1.5 725°F and LHSV 7.0 800°F) and the data points differ by five percent a several other conditions.

When the catalyst was made, it was difficult to obtain a required cobalt molybdenum promotion target exactly, so with the promotions listed for Norton 0255 and all the other samples the exact quantitative influence of increasing either the cobalt or the molyb-

denum was hard to separate.

The low cobalt, intermediate molybdenum amount appears to be the best promotion for molecular sieve support 0255. High amounts of cobalt appear to decrease catalyst activity slightly while the molybdenum amount differs by less than two percent for the two promotions studied.

c. Norton 0256 is a support sample with 60 percent mordanite and identical pore volume, surface area, and pore diameter with the preceding Norton supports. Maximum desulfurization occurs at 725°F LHSV 1.5 with 75 percent removal by 6.3% Co 11.1% Mo on this support. FIGURES 14, 15, and 16 present the data.

The 3.9% Co 15.1% Mo promotion is the leader for the 650°F and 725°F levels, then at 800°F the two promotions listed for this support change position. At 800°F the two promotions are 10 to 15 percent apart in performance as measured by desulfurization amounts, while at 650 and 725°F they are five to seven percent apart. Also at 800°F the 3.9% Co 15.1% Mo promotion falls 10 to 15 percent from its high desulfurization at 725°F. The higher cobalt, lower molybdenum (6.3% Co 11.1% Mo) promotion makes a five to ten percent gain in sulfur removal when going from 725 to 800°F. Both catalysts are temperature dependent with one listing a net gain with temperature increases as it progresses from 650 to 725 to 800°F (6.3% Co 11.1% Mo) while the other promotion with a higher molybdenum content shows a gain from

650 to 725°F, then a loss in sulfur removal between 725 and 800°F.

d. Sample 44001 is discussed next with its five promotions. Again this is a Norton base with the surface between 400 and 500 m^2/gm. as are all Norton's crystalline supports. This material has the highest silica to alumina ratio which is 44/1 and the base is a self bonded high silica support.

Cobalt and molybdenum form three promotions while a nickel and tungsten promotion is also tested. The testing of 44001 concludes with a single promoted support where nickel is the metal added. One cobalt molybdenum promotion is very similar in support loading to the nickel tungsten promotion. These double promoted catalysts contain 3.1% Ni 12.6% W and 3.1% Co 14.6% Mo and give maximum sulfur removals of 82 and 78 percent respectively at LHSV 1.5 725°F (FIGURES 17, 18, and 19).

The three cobalt molybdate promotions are clustered together at the intermediate and high space velocities for 650°F along with the single promoted nickel catalyst. One cobalt molybdate promoted support forms a straight line between the three flow rates for the desulfurization data; the other three promotions then diverge as they decrease their slope between LHSV 4.0 and 1.5. The nickel tungsten promotion leads the "pack" of four promotions by about ten percent more desulfurization at 650°F.

At the next higher temperature in the study, 725°F, a good separation between all five metal promotions for support 44001 is apparent. The nickel tungsten promotion heads the list for performance while the 3.1% Co 14.9% Mo promotion follows. The single promoted 9.4% Ni support leads the double promoted 6.9% Co 10.1% Mo support by four percent at LHSV 7.0 and the gap widens to 18 percent at LHSV 1.5. Notice too the straight line relationship between the three space velocities for each of the five promotions. Often at sulfur removals less than 90 percent this occurs. At higher hydrodesulfurization levels a more pronounced curve is found.

When the 800°F plot, FIGURE 19, is examined the rank ordering of the previous plot from 725°F is preserved, but the desulfurization does not increase as dramatically with the space velocity decrease. Gains are posted for LHSVs 7.0 and 4.0 while there is a decrease for LHSV 1.5. This decrease was mentioned earlier in the discussion and was then attributed to coke laydown and possible catalyst deactivation at the low feed rate when the relatively high 800°F temperature was run. The high feed rates appear to have a scrubbing effect plus the residence time is less at the higher flow rates with resultant less severe cracking conditions.

The optimum cobalt molybdate loading for support 44001 is 3.1% Co 14.9% Mo. When less cobalt or more cobalt is added with also a decline in molybdenum promotion, the desulfurization decreases.

The nickel tungsten and cobalt molybdenum promotions that are similar in catalyst weight compositions are the two best promotions for support 44001. The nickel tungsten promotion gives ten percent more desulfurization for seven of the nine data points associated with the three temperature and three liquid flow rates. For 650 and 800°F and LHSV 1.5 both catalyst promotions give the same results.

e. A wide variety of cobalt molybdate, nickel tungsten (FIGURES 20, 21, and 22), nickel ion exchanged cobalt molybdate (FIGURES 23, 24, and 25), and cobalt ion exchanged cobalt molybdate catalysts (FIGURES 26, 27, and 28) are presented for the ammonium ion molecular sieve 20072. This Norton product contains 83.6 percent mordanite.

Since support 44001 gave promising results with nickel tungsten promotion, two promotions of this combination and two cobalt molybdate deposition catalysts were made and compared.

There are both high and low nickel tungsten content catalysts and a high and low content cobalt molybdenum set of catalysts. When the 650 and 725°F plots are examined, both cobalt molybdate combinations fall below the nickel tungsten promotions in desulfurization performance. The 800°F plot finds the high nickel tungsten promotion and the high cobalt molybdate catalyst giving parallel lines and less than five percent different sulfur removal capabilities at the three space velocities. The lower content nickel tungsten and cobalt

molybdate catalyst are found to give up to thirty percent less desulfurization at 800°F depending on space velocity. These two last catalyst compositions give almost exactly the same results even though the promoting metals are different.

When nickel is ion exchanged for ammonia on the ammonium ion base, the decreasing amounts of the ion exchanged nickel and deposited cobalt and molybdenum give decreasing sulfur removal. Sulfur removal increases from 650 to 725°F, then decreases between 725 and 800°F for all catalyst compositions with the single exception of 0.7% Ni 2.0% Co 10.5% Mo on 20072 at 800°F. This nickel ion exchanged cobalt molybdate catalyst experiences a five percent increase at LHSV 4.0 and ten percent increase at LHSV 1.5 for the 800°F plot (FIGURE 25) versus the 725°F graph (FIGURE 24).

The cobalt ion exchanged 20072 support gives less desulfurization when the three promotions are compared to the nickel ion exchanged cobalt molybdate catalysts. All three promotions are grouped with a ten percent sulfur removal range for all three temperatures. The three curves parallel each other through the flow rate region investigated. The cobalt ion exchange effect is more difficult to obtain than the effect of changing the nickel ion exchange amount as the deposited cobalt increases on the promotions and the molybdenum decreases while the ion exchange cobalt increases. A number of ion

exchanged cobalt and cobalt molybdenum promotions would be needed to separate each influence. Since all three catalysts tested gave desulfurization figures confined to a rather narrow band, additional promotions were not made.

Nickel tungsten and cobalt molybdenum promotions for support 20072 gave desulfurization figures between 70 and 75 percent. Ion exchanged nickel gave 60 to 70 percent, while ion exchanged cobalt gave 40 to 60 percent. These figures or ranges were all for the low feed rate LHSV 1.5.

f. Linde 13-X is tested with four cobalt molybdenum depositions. This data plus the results for 13-X used as a catalyst without any promotion are given on FIGURES 29, 30, and 31. This base material contains double the pore volume of Norton's supports while it retains the same pore diameter. Surface area is estimaed at 750 square meters per gram.

Desulfurization increases for each Linde 13-X promotion between 650 and 725°F then decrease slightly when the temperature is raised to 800°F. This effect is noted in prior discussion on Norton's support materials.

Cobalt promotion is in the narrow 1.7 to 3.9 percent range. The molybdenum content goes from 13.0 to 17.8 weight percent. The 2.9% Co 17.8% Mo promotion is the best performer throughout the 150°F temper-

ature area studied. As molybdenum content falls, the desulfurization for the catalysts at a specific temperature also decreases.

The sulfur removal changes less than 20 percent for a specific space velocity for the entire cobalt molybdenum promotional range of Linde 13-X. The 800°F data gives more separation between the four double promoted catalysts.

3. Comparisons

a. Comparison of promoted molecular sieve supports around the 3% Co 15% Mo target:

One of the two promotion target areas for molecular sieves is discussed in this section. All six molecular sieves have promotions between 2.3 and 3.9 percent cobalt and 12.3 and 17.8 percent molybdenum. While most supports do not have promotions exactly at 3.0% Co 15.0% Mo, the promotion region is expanded to encompass at least one deposition near the target. Support 44001 has two depositions samples within this arbitrarily selected range. FIGURES 32, 33, and 34 present desulfurization vs. reciprocal space velocity data for the three temperatures. The legend for FIGURE 34 lists the promoted supports in their order of decreasing desulfurization. This rank order is interchanged for two supports at the lower 650 and 725°F operating temperatures.

Linde 13-X with the 0.67 cc./gm. pore volume is the desulfurization leader for all three temperatures. It is interesting to note

the curved line joining the three space velocities at 725°F for 13-X as compared to the straight line relationship for the 650 and 800°F temperature plots.

Desulfurization increases between 650 and 725°F, then decreases slightly for some promoted Linde 13-X supports at 800°F and slightly increases for others. Linde's 2.9% Co 17.0% Mo removes 84 percent of the sulfur at both 725 and 800°F while in contrast the 83.6 percent mordanite Norton 20072 removes just 52 percent.

b. Comparison for 5% Co 10% Mo on molecular sieves:

Norton's five samples have promotions near the 5% Co 10% Mo figure and are portrayed on FIGURES 35, 36, and 37. Cobalt promotion ranges from 4.5 weight percent to 6.9 percent while the molybdenum amount ranges from 9.3 to 11.1 percent. One support, Norton 20072, has 2.2 percent cobalt ion exchanged in addition to the 5.1 percent cobalt deposited. No data for 20072 is available for the 5% Co 10% Mo target, so the next closest sample is chosen and this is the ion exchanged shown on the desulfurization plots. Linde 13-X is not promoted near enough to the target figure to be presented on these graphs.

The high silica 44001 base containing 6.9% Co 10.1% Mo gives the lowest desulfurization points for the 725 and 800°F plots while the leader is base 0255 with 5.8% Co 10.6% Mo. This lead is for 650 and 725°F and at 800°F promoted 0255 falls below two other supports, 0256

and 0081. Desulfurization increases for the promoted supports between 650 and 800°F. The most sulfur removal is with 0256 promoted with 6.3% Co 11.1% Mo at 800°F. Sulfur removal is 70 percent.

c. Best promotions of molecular sieves:

The best molecular sieve cobalt molybdenum promotions are grouped together on FIGURES 38, 39, and 40. Linde 13-X which has twice the pore volume, but identical pore diameter with Norton molecular sieves in the nonpromoted state leads the list as it also does for the 3% Co 15% Mo plots already discussed.

Note the promotion amounts on the supports. One, Norton 0081 has 3.5% Co 10.0% Mo and exceeds Linde 13-X promoted with 2.9% Co 17.8% Mo for 650 and 725°F then drops down at 800°F where 13-X assumes the lead.

These molecular sieves cover a thirty percent desulfurization band as one looks at each temperature and follows the curves joining the results for each space velocity. Linde 13-X with the high pore volume and Norton 0081 with half of Linde's pore volume are top performers at 650 and 725°F. Then the Linde 13-X is ten percent better than any of Norton's at 800°F. Four and sometimes all five of Norton's bases with their varied promotions fall within a narrow ten percent wide band.

4. Product Distillation

Six distillation curves are given on FIGURES 41 through 46 for

the crystalline catalyst product analyses. The product is taken at 800°F LHSV 1.5 for each promoted catalyst support. The curve represents the original Husky gas oil feed while the symbols are for the products of the various catalyst samples. When more than two symbols fall very near the same point, only the high and low data points are shown.

Norton's mordanite supports all give distillation data that is almost identical. The promotion amounts do not significantly affect the product distribution. All Norton supports were run on the 1.62 weight percent sulfur feed of 31.1°API gravity while the Linde molecular sieve catalyst were tested on the 30.4°API gravity 1.82 weight percent sulfur feed. Also the initial boiling point is 50°F higher for the feed used to test the Norton promoted supports than the Linde 13-X feedstock. When a graph of Norton's promotions is superimposed on the Linde distillation data, the Norton symbols fall directly upon the feedstock used to test the Linde catalysts. The Norton supports have their greatest effect on product distribution at the light end between 450 and 525°F. The initial boiling point is decreased 100°F and the five and ten percent recovery points drop 70°F. This dramatic decrease is not repeated with the Linde 13-X as the IBP, five, and ten percent points drop only 30°F from the original product distribution. The Norton supports contain higher silica to alumina rations that the Linde 13-X.

Most data points for the basic support materials are coincident with one or more promoted supports, so the promotion and the amounts of metal deposition do not affect the final product distribution, rather the base material itself with its attendant pore volume, surface area, and pore diameters are determining factors. All these molecular sieves have silica as their major component and since high alumina sieves were not used, the effect of changing the silica alumina ratio radically could not be observed. Linde 13-X contains the most alumina of the sieves studied.

5. Sulfur Removed vs. Distillation Temperature

The sulfur removal for six distinct distillation fractions is presented for the promoted Norton bases 44001 and 20072 on FIGURES 47, 48, 49, and 50 while a similar plot for Linde 13-X and its promotions is on FIGURE 51.

The percent sulfur removal is expressed as the remaining sulfur in the product distillation divided by the amount of sulfur contained in the same feed fraction. The ASTM distillation is from the 800°F LHSV 1.5 product, and only two of Norton's supports are presented. Insufficient product samples for Norton 0081, 0256, and 0255 remained when the decision to obtain this data was made.

Nickel tungsten, cobalt molybdenum, and nickel promoted Norton 44001 supports are compared. The nickel tungsten 44001 is the best overall desulfurization catalyst for support 44001, and the FIGURE

47 top curve shows 85 percent sulfur removed at the low boiling fraction and that this removal slips to 65 percent at the high boiling end. The cobalt molybdate combination removes an even 66 to 68 percent through the distillation range. The single metal promoted 44001 support removes 43 to 48 percent as the product temperature scale is ascended.

Support 20072 with ion exchanged cobalt and the deposited cobalt and molybdenum has two parallel curves differing by four percent and showing a gradual decrease in desulfurization as heavier weight, higher boiling fractions are encountered (FIGURE 48). For nickel ion exchanged and deposited cobalt molybdenum promotions the comparison is on FIGURE 49. A gradual increase is apparent for the three lower curves which all have lower metal loadings than the top curve depicting the heavily promoted 20072 support. A decrease is noted between the middle distillation fractions and the high boiling components.

Linde 13-X with four cobalt molybdenum promotions gives the same shaped curves as do the Norton supports. As one progresses from the light to the heavy fraction, the sulfur removal decreases.

6. °API Gravity Product from Molecular Sieve Treatment

Three molecular sieve supports and their promotions have their 800°F LHSV 1.5 product listed by °API gravity. This petroleum standard measurement is an indication of specific gravity. The higher the number, the lower the specific gravity. TABLE VII gives the

listings.

The only support material with product specific gravity data for a nonpromoted support test is Linde 13-X. The 30.7 °API figure is close to the 30.4 °API feed. All the promoted Linde 13-X products give gravity figures greater than 31.0 and the average is 31.8 °API. When the feedstock is hydrodesulfurized the heavy sulfur is replaced with hydrogen plus some molecular cracking occurs. The added hydrogen weight is not enough to make up the difference for the sulfur removed.

Norton 44001 and 20072 have °API data just for the promoted catalyst products. Support 44001 gives a 31.4 °API reading for the nickel promoted base while 20072 gives °API readings in the 31 to 32 range. The average °API figure for all 20072 promotions is 32.0 while the extreme values are 31.0 and 32.8.

C. Noncrystalline Supports

1. Support Family Promotions

a. Promoted Nalcat 2910-A:

Nalcat's high silica, large pore volume, and large pore diameter base is depicted with its cobalt and molybdenum promotions on FIGURES 52, 53, and 54. The 180 Å pore size and 1.22 cc./gm. pore volume support gives desulfurization results better than 90 percent for the low flow rates and the 725 and 800°F temperatures. Catalyst perform-

ance measured by percent hydrodesulfurization increases slightly between 725 and 800°F. The top catalyst promotion composition is the 2.7% Co 16.0% Mo with over 95 percent desulfurization for all three temperatures and the LHSV 1.5.

Performance decreases as the total promotion weight increases. The highest cobalt and lowest molybdenum promotion gives the best results at all three flow rates and temperatures. Also response to increasing flow rates is not as drastic for the 2.7% Co 16.0% Mo promotion as for the other two with their heavier cobalt and molybdenum loadings.

This 75 percent silica support is easy to promote. Target cobalt and molybdenum promotions are 3 and 15 percent respectively, and the only problem is the ready adsorption and deposition of the MoO_3.

The sampling sequence is the same on 2910-A as for the molecular sieve catalyst runs. At 650 and 725°F the flow rates are checked in increasing order; at 800°F the flow rates and the samples collected are checked in decreasing order. The 1.7% Co 19.4% Mo promotion was checked in this manner, then the temperature was decreased from 800 to 725°F and the desulfurization samples checked for increasing LHSVs. This rerun gives 12 to 18 percent less desulfurization at 725°F than when the 725°F temperature level was originally checked. Catalyst deactivation, probably by carbon laydown on the active sites and/or blocking the catalyst pore structure, was done at the low 1.5 LHSV

feed rate at 800°F.

b. Nalcat 2910-B:

Nalcat high alumina support 2910-B contains a pore volume of 0.78 cc./gm. and pore diameter of 125 Å. The three cobalt molybdenum promotions are portrayed on FIGURES 55, 56, and 57. The 3.7% Co 17.4% Mo promoted support performs best at 650 and 725°F, then relinquishes the lead to the 0.8% Co 13.9% Mo promotion at 800°F. All promotions exceed 94 percent desulfurization for the three temperature levels at LHSV 1.5.

Between LHSV 4.0 and 7.0 there is a dramatic change in slope for the curve depicting a particular promotion. This effect appears for all three temperatures. Desulfurization at LHSV 7.0 rises from the 80 to 87 percent band at 650°F to 87 and 94 percent at 800°F. The LHSV 4.0 flow rate does not have that large a change over the 150°F temperature spread, while the three promotions give a desulfurization change of one to two percent at LHSV 1.5 between 650 and 800°F.

c. Harshaw 1802:

Harshaw 1802 is investigated for its desulfurization capability with three cobalt molybdate promotions. FIGURES 58, 59, and 60 show how the desulfurization capacity changes with temperature and flow rate. A high alumina noncrystalline support with pore volume 0.91 cc./gm., this material in the promoted state gives increased desulfurization as the temperature scale is ascended. A comparison for the

two high flow rates and the temperatures shows the 2.7% Co 20.4% Mo promotion possesses the desulfurization lead. At LHSV 1.5 the other two materials with lower overall cobalt and molybdenum loading do two to five percent better than the 2.7% Co 20.4% Mo promoted support.

At 725 and 800°F a sharp break in the slope of the curve depicting percent desulfurization with flow rate change occurs between LHSV 4.0 and 7.0. This change happens when the desulfurization at LHSV 4.0 is greater than 90 percent. The 2.8% Co 16.5% Mo on 1802 has a decrease in activity at 800°F for the high flow rates. Its performance at 800°F is comparable to the 650°F data. The slope change between LHSV 4.0 and 7.0 at 725°F does not occur at either 650 or 800°F with this specific promotion. This catalyst's total promotion weight is between the two other promotions. Over the entire temperature range all but one of the data points falls below the other two promoted supports.

d. Harshaw 1602:

Harshaw 1602 with 0.48 cc./gm. pore volume and high alumina content is promoted with varying amounts of cobalt and molybdenum. This support removes over 92 percent of the feed material's total sulfur content at LHSV 1.5 and the temperatures 650 through 800°F (FIGURES 61, 62, and 63).

A low cobalt, low molybdenum promotion is the best combination for all three temperatures and space velocities used. At LHSV 1.5 the

difference between the three promotions is three percent sulfur removal, at LHSV 4.0 seven percent is the spread, while at LHSV 7.0 the figure increases to twelve percent. At 725 and 800°F the sharp change in slope for the promotions occurs again between the LHSV 4.0 and 7.0.

Both increases in cobalt and molybdenum over the sample containing 0.8% Co 10.3% Mo bring decreases in sulfur removal when compared with the low cobalt, low molybdenum promotion. The desulfurization capability of each support increases more between 650 and 725°F than between 725 and 800°F.

e. Alcoa H-151:

Alcoa's 1/8 inch spherical pellets of high alumina are presented on FIGURES 64, 65, and 66 with three interesting cobalt molybdenum promotion amounts. This support with the 0.30 cc./gm. pore volume is the lowest pore volume noncrystalline support tested and also the only one not in tubular or cylindric form. Its surface area is 390 m^2./gm. and exceeds the other crystalline materials by 100 m^2./gm.

All three promotions of H-151 have about the same cobalt content, however the molybdenum promotion changes from 6.6% Mo to 13.5% Mo. This support is the most difficult to promote as thermal fracture occurring during the promotion and while drying limits the promotion amount applied.

The 2.3% Co 6.6% Mo combination is the best of the three promo-

tions tested. Desulfurization increases as the temperature increases from 650 to 800°F. The highest sulfur removal is with the low molybdenum promotion at 800°F LHSV 1.5 and is 95 percent. The three promotions follow a three percent wide band at LHSV 1.5 and the temperatures 725 and 800°F; this increases to six percent at LHSV 4.0 and to eleven percent at LHSV 7.0. No break or sharp change in slope appears between LHSV 4.0 and 7.0 for the respective promotion curves.

As the molybdenum content increases and the cobalt amounts remain static, the desulfurization decreases for promoted H-151.

f. Norton 6473:

Norton 6473 contains practically pure alumina, possesses a low pore volume of 0.45 cc./gm. and pore diameter around 60 Å. Three cobalt molybdate promotions are presented for the 225-250 m^2./gm. surface area support (FIGURES 67, 68, and 69).

Desulfurization increases with temperature to 800°F and the maximum sulfur removal of 97.5 percent is reached at LHSV 1.5 and with the 4.1% Co 9.4% Mo promotion.

Two supports, one with 4.1% Co 9.4% Mo and the other 2.9% Co 15.1% Mo lead the 2.3% Co 18.4% Mo promotion at 650°F substantially, but at higher temperatures this lead decreases. Desulfurization decreases as high molybdenum loadings are reached. The three promotions span a five to six percent wide band from LHSV 1.5 to 4.0, then this increases to 15 percent at LHSV 7.0 for both the 725 and 800°F

temperatures.

The curves slowly flatten out as the reciprocal space velocity increases. No sharp break is noted and at 725 and 800°F the curves for each promotion parallel each other.

g. Houdry C and Harshaw 4401-E:

Houdry C, a cobalt molybdenum catalyst, and Harshaw 4401-E, a nickel tungsten presulfided catalyst, have their performance characteristics charted on FIGURES 70, 71, and 72. The support for Houdry C has over 90 percent alumina content while silica takes 50 percent of 4401-E's support weight. These commercially prepared catalysts have pore volumes of 0.48 and 0.39 cc./gm. for Houdry C and Harshaw 4401-E respectively.

Performance at 800°F for both LHSVs 1.5 and 4.0 results in better than 90 percent sulfur removed; the LHSV 7.0 figure is 87 percent. Both catalyst give desulfurization data within one and two percent of each other for all space velocities at 800°F. Desulfurization values for the three LHSVs and two catalyst compositions are quite close, the only serious divergence is at 650°F LHSV 7.0 where Houdry C gives 75 percent and 4401-E gives 90 percent desulfurization. Since 4401-E is a presulfided catalyst and Houdry C is not and this temperature is first checked after sulfiding, the presulfided catalyst might possess superior desulfurization activity to the Houdry C catalyst until the Houdry C becomes adequately sulfided.

The close performance at all other data gathering points shows the nickel tungsten and cobalt molybdenum catalyst give comparable results on this specific feedstock. The nickel tungsten promotion curves do not show the tendency to level out between the intermediate and low flow rates as do the Houdry C cobalt molybdate curves. The Houdry C has a slightly larger pore volume than 4401-E and this may account for the curve shapes between the two higher space velocities.

2. Comparison

a. 3% Co 15% Mo

FIGURES 73, 74, and 75 contain data on the six promoted crystalline supports near the 3% Co 15% Mo target. One support, Harshaw 1802, has two promotions straddling the target figure and both compositions are presented. Since six supports and seven promotions are near the target, each graph is a mass of lines connecting points representing the results at the three flow rates.

All the noncrystalline supports give greater than 90 percent desulfurization at 725 and 800°F for the LHSV 1.5 while there is only one exception at 650°F. Seven percent separates the high and low performers at this low flow rate at 725 and 800°F. The separation increases to 15 percent at LHSV 4.0 and 18 percent at LHSV 7.0 800°F.

2910-A and 2910-B are supports with two of the largest pore diameters and pore volumes. These supports, when they are promoted,

are the top two performers of the six listed supports. Their performance over the flow rates checked is more uniform than those supports with lower pore volumes and smaller pore diameters. Norton 6473 when compared with Nalcat 2910-A and 2910-B illustrates this. The change in desulfurization as one progresses from a high feed rate to a lower feed rate for 6473 is more dramatic than for the larger pore diameter 2910-A.

b. 5% Co 10% Mo;

Only two noncrystalline supports have cobalt and molybdenum near the 5% Co 10% Mo figure. The two, Norton 6473 and Harshaw 1602, have their desulfurization characteristics graphed on FIGURES 76, 77, and 78. Both have pore volumes close to 0.45 cc./gm. and while 6473 is practically pure alumina, 1602 has six percent silica with the remainder alumina.

Promoted 6473 has one percent more cobalt and one percent less molybdenum than the promoted 1602. The Norton support provides the best desulfurization results, 97 percent sulfur removal occurs at 800°F LHSV 1.5. Desulfurization as measured at all three flow rates increases from 650 to 800°F. The performance gap between the two similar supports is held to less than three percent for all flow rates and temperatures.

This data shows that these two supports made by different manufacturers and having similar silica alumina compositions and physical

measurements can give similar results when promoted with equal amounts of the same transition metals.

c. Best Noncrystalline Promotions:

The best desulfurization results from promoted noncrystalline bases are cataloged on FIGURES 79, 80, and 81. The six supports with the one best promotion chosen for each support are graphed and compared.

As temperature increases, catalyst performance increases. The relative performance order for the promoted supports may change between temperature levels, but with these noncrystalline supports the individual performance levels are all very close. Note the wide cobalt promotion range that produces the best performers for each support material. The high alumina, low pore volume 6473 with 4.1% Co 9.4% Mo gives 97 percent sulfur removal at LHSV 1.5 800°F while the high silica, high pore volume, large pore diameter 2910-A with 2.7% Co 16.0% Mo gives one percent better at the same conditions. When the 800°F plot is examined (FIGURE 81) the six promoted supports are grouped in a four percent band at LHSV 1.5, five percent at LHSV 4.0, and six percent at LHSV 7.0. This narrow performance spread is also apparent at 725°F and increases at 650°F. Individual support characteristics cannot be readily identified within such a narrow region as some supports change their position relative to each other's performance while progressing from one temperature level to another.

The low pore volume bases, H-151, 1602, and 6473, with lower total cobalt and molybdenum loadings do give comparable performance to the higher promoted and larger pore volume supports such as 2910-A, 2910-B, and 1802 for the LHSVs 1.5 and 4.0.

d. Equal Pore Volume Comparison:

Houdry C, Harshaw 1602 and Norton 6473 are all high alumina supports that have pore volumes between 0.45 and 0.48 cc./gm. FIGURES 82, 83, and 84 cover the desulfurization ability of these catalysts over the 650 to 800°F temperature range. The three catalyst on these three graphs have cobalt and molybdenum promotions close to the 3% Co 15% Mo target. The commercially prepared Houdry C has slightly less cobalt and molybdenum composition than 1602 and 6473. Three percent between the high and low performers occurs for the LHSVs 1.5 and 4.0 at all temperatures and this increases to six percent for the high flow rate LHSV 7.0.

Support 6473 performs better than the other two catalysts at LHSV 1.5 and 4.0 for all temperatures but falls behind Houdry C by one to two percent at LHSV 7.0. The Houdry C tends to level off in desulfurization ability between LHSV 4.0 and 1.5; while for 6473, the high alumina support, there is a rapid slope change between LHSV 7.0 and 4.0, but desulfurization still appears to increase steadily as the flow rate decreases.

These three catalyst combinations give almost identical results

at both 725 and 800°F. There are several slight decreases in performance when the highest temperature 800°F is compared with the results at 750°F. The Houdry C has the largest surface area, 330 m^2./gm., while the 1602 support has 210-240 m^2./gm., and 6473 contains 225-250 m^2./gm. All these materials are made in 1/8 inch cylindric pellets.

This series of plots shows the author is able to make catalysts comparable to a commercial sample when equal promotion amounts and similar characteristics for bases are compared.

3. Distillation Curves for Products from Noncrystalline Supports:

Distillation data for the promoted noncrystalline supports is contained on FIGURES 85 through 91. Two or three promotions are listed for each support and the product for these support promotions may be compared with the Husky gas oil feed. The feed with the 1.82 weight percent sulfur is used with all the noncrystalline catalysts except Houdry C which is compared against the higher specific gravity 1.62 weight percent sulfur feed that also has a higher initial boiling point (IBP).

Nalcat 2910-A on FIGURE 85 shows that as the catalyst loading decreases, the product distribution increases at the low boiling fraction. This catalyst has the largest pore diameter and pore volume, so possibly cracking is permitted more readily as less of the pore volume is taken up by the metal promotions.

FIGURE 86 for Nalcat 2910-B presents a high alumina support, but

with less pore volume and smaller pore diameter than 2910-A. The cracking results are the same as the two higher cobalt molybdenum loadings of 2910-A. At the high boiling fraction very little separation between products from either the high or low cobalt promotion of 2910-B is evidenced.

Harshaw 1802 with 0.91 cc./gm. pore volume and slightly higher cobalt molybdenum promotion than the 0.78 cc./gm. pore volume Nalcat 2910-B gives slightly less cracking as shown on FIGURE 87 than the Nalcat support.

1602's promotions are slightly less than 1802's, but Harshaw 1602 also has a 0.48 cc./gm. pore volume. Its product distribution is different from 1802's and promoted 1602 shows a higher recovery at the low boiling end plus a changed product distribution throughout the whole recovery range while the previously discussed supports do not change the higher boiling fractions much.

Houdry C on FIGURE 89 gives the most radical product distribution change of any catalyst studied. The initial boiling point of the feed is higher than the feed used with the other noncrystalline catalyst tests, yet the product initial boiling point for Houdry C and the other catalysts is the same. The Houdry C surface area is larger than the other catalysts excepting H-151, but the pore volume is the same as Harshaw 1602 and Norton LA 6473. Cobalt and molybdenum promotions are comparable too.

Alcoa H-151 possesses the largest surface area for noncrystalline supports, 390 m^2./gm., and the lowest pore volume, 0.30 cc./gm. Its cracking activity is practically coincident with Norton 6473 support that has 225-250 m^2./gm. surface area and pore volume 0.45 cc./gm.

4. Sulfur Analyses of Distillations:

Six figures, FIGURES 92 through 97, give the sulfur analyses data on six fractions taken from an ASTM distillation. The graphs compare the sulfur content of a specific fraction with the same fraction from the untreated feed. The product samples at LHSV 1.5 800°F are for the three promotions made on the noncrystalline support materials.

All graphs indicate declining desulfurization as the higher molecular weight and higher boiling constituents of the sample are encountered. Some, such as Nalcat 2910-A and Harshaw 1602, experience a small increase in desulfurization between the low boiling fraction and the intermediate. This increase is usually close to two percent.

All these noncrystalline supports are in the high desulfurization range when compared to the molecular sieve supports. Overall sulfur removal is greater than 90 percent for all promotions. 2910-A with 1.7% Co 19.4% Mo on FIGURE 92 has the greatest removal range with 93 percent removed at the low boiling end, then decreases to 80 percent at the high boiling end. A definite slope is apparent for the samples taken from this promotion. All other samples and their

promotions exhibit a trend to lower desulfurization in the high boiling range and the percent desulfurization may change drastically for the two samples taken at the highest boiling temperatures (FIGURE 96). H-151 is one catalyst where the largest cobalt and molybdenum content gives the least desulfurization in the higher distillation range when compared with other promotions on the same base that represent lower cobalt and molybdenum loadings on this low pore volume support. Harshaw 1802 with its high metal loading on FIGURE 94 is in opposition to this claim, but all three promotions represent more than 18 percent of the catalyst weight. So the desulfurization activity for low metal content on the large pore volume bases cannot be predicted.

At the high boiling range all supports except 2910-A give results within a seven to eight percent range for all three promotions. Nalcat 2910-A has a 13 percent change between the high and low performing promotions for the high boiling fraction.

5. ^{o}API Gravity Discussion:

TABLE VIII lists the ^{o}API gravity for the promoted base materials operating on the 30.4^{o}API gravity Husky gas oil. All the promoted noncrystalline supports change the specific gravity of the oil to 32 and 33 ^{o}API. Only one nonpromoted support, 6473, is listed and there is little change in specific gravity between the feed and the product.

The desulfurization ability of this support is in the 30 percent area. The high desulfurization abilities of the promoted noncrystalline bases change the specific gravity reading of the feed to the product 2.5°API. In contrast the promoted molecular sieves with their less desulfurization activity change the °API reading about 1.5°API (TABLE VII). Desulfurization by molecular sieves is 20 to 30 percent less than for the noncrystalline promoted supports.

VII. CONCLUSIONS

A. Molecular Sieves as Catalyst Supports:

1. Increased pore volume, a one to two angstrom greater pore diameter, and different crystalline structure give better desulfurization with promoted molecular sieves when Linde 13-X is compared to Norton supports.

2. The amount of metal loading on the sieve does not appreciably affect product distribution as shown on the distillation curves. The product distribution is a function of the pore volume, crystalline structure, and surface area rather than metal deposition amount.

3. Molecular sieve performance reaches a peak at 725°F and decreases at 800°F. High silica content present in molecular sieves could influence cracking and coke laydown at 800°F.

4. Ion exhange cobalt and nickel on the deposited cobalt molybdate catalysts do not give an increase in desulfurization over the deposited cobalt molybdate catalysts.

B. Noncrystalline Supports:

1. Low pore volume supports with a low cobalt and molybdenum content compete favorably with high metal loadings on larger pore volume bases at the low feed flow rates. Those bases with low pore volumes and pore diameters near 50 Å exhibit less desulfurization ability than the larger pore volume, larger pore size supports at high

liquid space velocities.

2. A high pore volume, high silica support gives similar desulfurization results to a slightly lower pore volume, high alumina base when both are promoted with equal cobalt and molybdenum amounts.

3. A high pore volume, high silica base shifts the distillation product distribution toward the lower boiling region as the metal loading of the catalyst base decreases.

4. Bases that have equal pore volumes, the same cobalt and molybdenum promotions and span a 100 m^2./gm. surface area range give identical desulfurization results.

C. Comparison between Molecular Sieves and Noncrystalline Supports:

1. Noncrystalline supports with larger pore diameters than the molecular sieves perform better at all temperatures tested in spite of the larger surface areas molecular sieves possess.

2. The ^{o}API gravity change is greater for the hydrodesulfurization products obtained with noncrystalline promoted supports than promoted molecular sieves. This is expected as the noncrystalline supports with larger pore sizes desulfurize the gas oil feedstock more than the promoted molecular sieves.

3. Hydrodesulfurization decreases as the higher boiling fractions of the gas oil are encountered.

VIII. RECOMMENDATIONS

A. Two crystalline molecular sieve structures, faujasite and mordanite, are tested; other molecular sieve structures should be tested to determine crystalline structure effects on hydrodesulfuriation.

B. 10 Å is close to the upper limit for molecular sieve pore size. Obtain molecular sieves with smaller pore sizes and see if the desulfurization results are the same or less than the 10 Å pore diameter sieves.

C. Sieve supports that have equal pore dimensions but double the pore volume give 10 to 20 percent more desulfurization than supports with the smaller pore volumes. Try to obtain sieves with the same pore size and other pore volume figures.

D. Obtain noncrystalline support samples with equal pore diameters and different pore volumes, promote them, and evaluate their desulfurization characteristics.

IX. APPENDIX

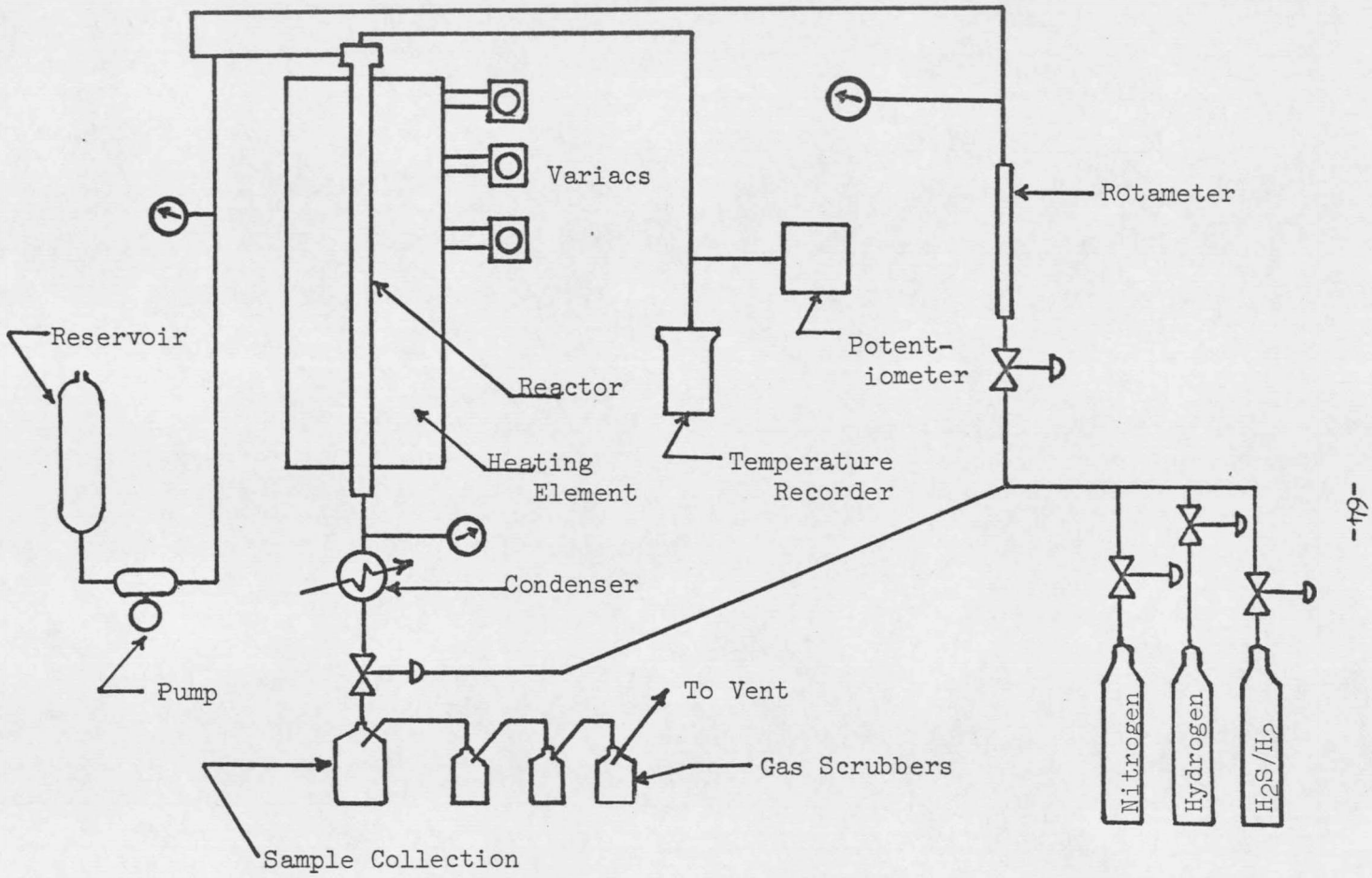


FIGURE 1
Equipment Schematic

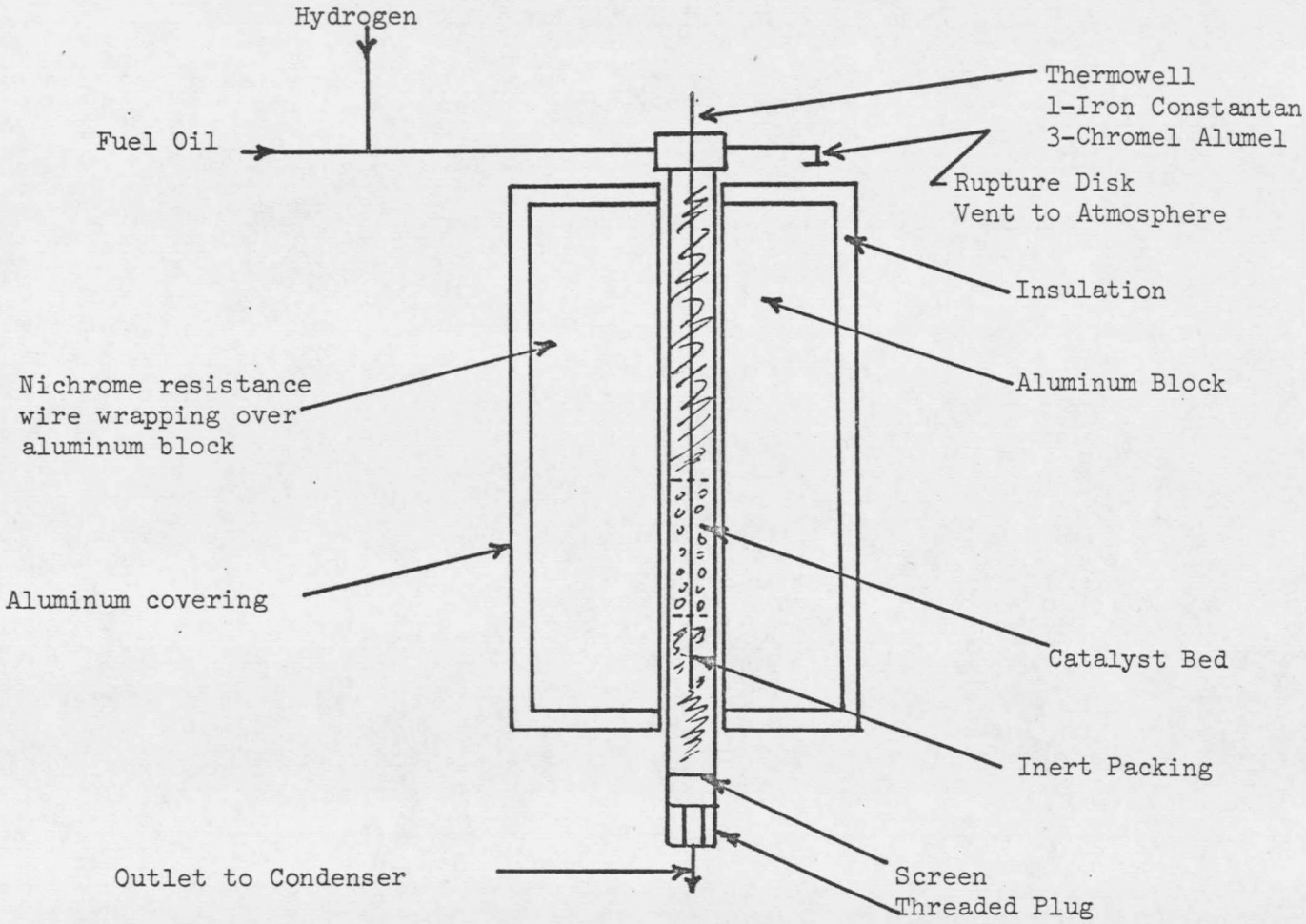


FIGURE 2
Schematic of Reactor and Heating Unit

TABLE I

Fuel Properties

Feed Runs 1-16		Feed Runs 17-57
API 31.1 @ 60°F		API 30.4 @ 60°F
Distillation		Distillation
IBP	459°F	IBP 398°F
10%	506	10% 464
50%	564	50% 541
90%	625	90% 667
EP	672	EP 664
		Flash Pt. 188°F
Sulfur wt. %	1.62	Sulfur wt. % 1.82
Data 641 mm Hg corrected to 760 mm Hg		Data 640 mm Hg corrected to 760 mm Hg

Sulfur Contained in Given Boiling Fraction

No Sample IBP too high	362-453°F	1.22 wt. %
1.12 wt. %	454-514	1.50
1.48	515-575	1.85
1.73	576-600	1.85
1.99	601-625	1.98
2.08	626-EP	2.28

TABLE II

Synopsis of Hydrodesulfurization Runs

Run	Purpose
1-16	Made on fuel #1 1.62 wt. % Sulfur 31.1 ^{o}API @ 60^{o}F
17-57	Made on fuel #2 1.82 wt. % Sulfur 30.4 ^{o}API @ 60^{o}F
1+2	Houdry C catalyst used to establish operating procedures and check equipment, however temperature problems caused run termination.
3	Harshaw 4401-E presulfided nickel tungsten catalyst used to check operating procedures.
4+5	Norton base materials used as catalysts.
6	Houdry C catalyst used to examine operating procedures with known catalyst and establish catalyst performance standards.
7	Norton base as catalyst
8	First promoted Norton base material tested.
9-14	Promoted Norton base materials evaluated.
15	Norton base as catalyst
16-19	Norton promoted base materials tested.
20	Norton base material only used as catalyst.
21-32	Co Mo, Ni W, and ion exchange promotions on Norton bases 44001 and 20072
33-57	Tests of promoted noncrystalline materials as hydrodesulfurization catalysts

TABLE II (Continued)

Run	Purpose
45	Support 2910-A with 1.7% Co 19.4% Mo rerun at 725°F to check activity decrease from most severe operating conditions (LHSV 1.5 800°F).
55	LA 6473 base material only used as catalyst.
56	Linde 13-X base material only used as catalyst.
35-57	Sulfiding done at 250 psig and lower to economize on H_2S-H_2 cylinders. No effect noted due to sulfiding pressures.
	All runs made as described in operating procedure.

TABLE III

Molecular Sieve Properties

Material	0081	0255	0256	44001	20072	13-X
Density (lb/ft^3)	40	40-45	40-45	40	40-45	42
Cation	H^+	H^+	H^+	H^+	NH_4^+	
Na_2O (%)	0.067	0.13	0.74	0.02	0.13	
SiO_2/Al_2O_3	10/1	10/1	10/1	44/1	10/1	1.2/1
Surface Area (m^2/gm)	400 to 500					750
Pore Volume (cc/gm)	0.33					0.67
Pore Diameter (Å)	7 to 9					10
Physical Appearance	1/16 inch tubular extrudates					
Manufacturer	Norton Company					Linde

TABLE IV

Properties of Commercially Available Noncrystalline Base Materials

Material	2910-A	2910-B	1802	1602	Houdry C	H-151	6473	4401-E
Density (g/cc)	0.36	0.50	0.53	0.83	0.85	0.86		
Surface Area (m^2/gm)	270	250	270	225	330	390	250	212
SiO_2 (%)	74.7	0.24	6.0	6.0				50.0
Al_2O_3 (%)	23.0	97.9			91.0	90.0	99.5	
Na_2O (%)	0.05	0.02		0.03			0.2	
Pore Volume (cc/gm)	1.22	0.78	0.91	0.48	0.45	0.30	0.45	0.39
Pore Diameter (Å)	180	125			55	50	55	
Physical Appearance	1/8 inch tubular pellets ———					1/8 in. spheres	1/8 in. pellets	
Manufacturer	Nalco ———		Harshaw ———		Houdry	Alcoa	Norton	Harshaw

TABLE V

Listing of Molecular Sieve
Supports, Promotions, and Best Results
At LHSV 1.5

Support	Promotion	Run	Sulfur Removal	Temp.
0081	3.5% Co 10.0% Mo	9	88.0%	725
	3.0 14.3	8	75.4	800
	7.3 18.9	16	72.4	725
	4.5 9.3	14	67.4	800
	Base Material	4	27.4	800
0255	2.3% Co 12.3% Mo	10	71.0	725
	5.8 10.6	11	70.5	800
	Base Material	5	30.0	800
0256	3.9% Co 15.1% Mo	13	73.5	725
	6.3 11.1	12	68.5	800
	Base Material	7	26.0	800
44001	3.1% Ni 12.6% W	32	82.8	725
	3.1 Co 14.9 Mo	19	74.5	800
	2.3 Co 13.8 Mo	18	61.0	725
	9.4 Ni	35	57.5	725
	6.9 Co 10.1 Mo	17	46.3	800
	Base Material	15	37.3	800
20072	5.1% Ni 19.3% W	31	75.8	800
1.3% Ni	3.5 Co 17.6 Mo	29	74.8	725
	3.5 Ni 17.5 W	30	72.8	725
	4.4 Co 19.8 Mo	23	72.5	800
0.6 Co	2.7 Co 13.5 Mo	24	65.6	800
1.2 Ni	2.7 Co 13.4 Mo	27	64.0	725
0.8 Ni	2.8 Co 13.7 Mo	26	63.0	725
4.3 Co	2.2 Co 11.1 Mo	25	60.5	800
2.2 Co	5.1 Co 10.3 Mo	21	58.7	800
	2.5 Co 13.0 Mo	22	55.6	800
0.7 Ni	2.0 Co 10.5 Mo	28	47.5	725
	Base Material	20	25.2	800

TABLE V (Continued)

Listing of Molecular Sieve
Supports, Promotions, and Best Results
At LHSV 1.5

Support	Promotion	Run	Sulfur Removal	Temp.
13-X	2.9% Co 17.8% Mo	43	86.2%	725
	1.7 16.3	52	85.0	725
	3.9 13.0	48	83.5	725
	1.8 13.7	46	81.5	725
	Base Material	56	36.5	800

TABLE VI

Noncrystalline Supports, Promotions, and Best Results for Lowest LHSV (1.5)

Base	Promotion	Run	Sulfur Removal	Temp.
1602	0.8% Co 10.3% Mo	36	97.4%	725°F
	3.0 10.5	37	95.7	800
	2.9 15.3	38	95.2	725
1802	2.7% Co 20.4% Mo	51	95.7	725
	3.5 14.6	34	95.6	800
	2.8 16.5	33	92.5	800
H-151	2.3% Co 6.6% Mo	40	96.8	800
	2.3 13.1	44	94.6	725
	2.8 13.5	57	94.0	800
6473	4.1% Co 9.4% Mo	47	97.6	800
	2.9 15.1	49	97.2	800
	2.3 18.4	53	94.0	725
	Base Material	55	33.8	725
2910-A	2.7% Co 16.0% Mo	39	97.8	800
	1.7 19.4	45	93.0	725
	0.9 21.8	50	94.8	725
2910-B	4.4% Co 13.0% Mo	42	97.4	800
	3.7 17.4	54	97.2	725
	0.8 13.9	41	96.8	800
Houdry C	3.2%CoO 14.6% MoO_3	6	95.8	725
4401-E	6.0% Ni 19.0% W	3	97.5	725

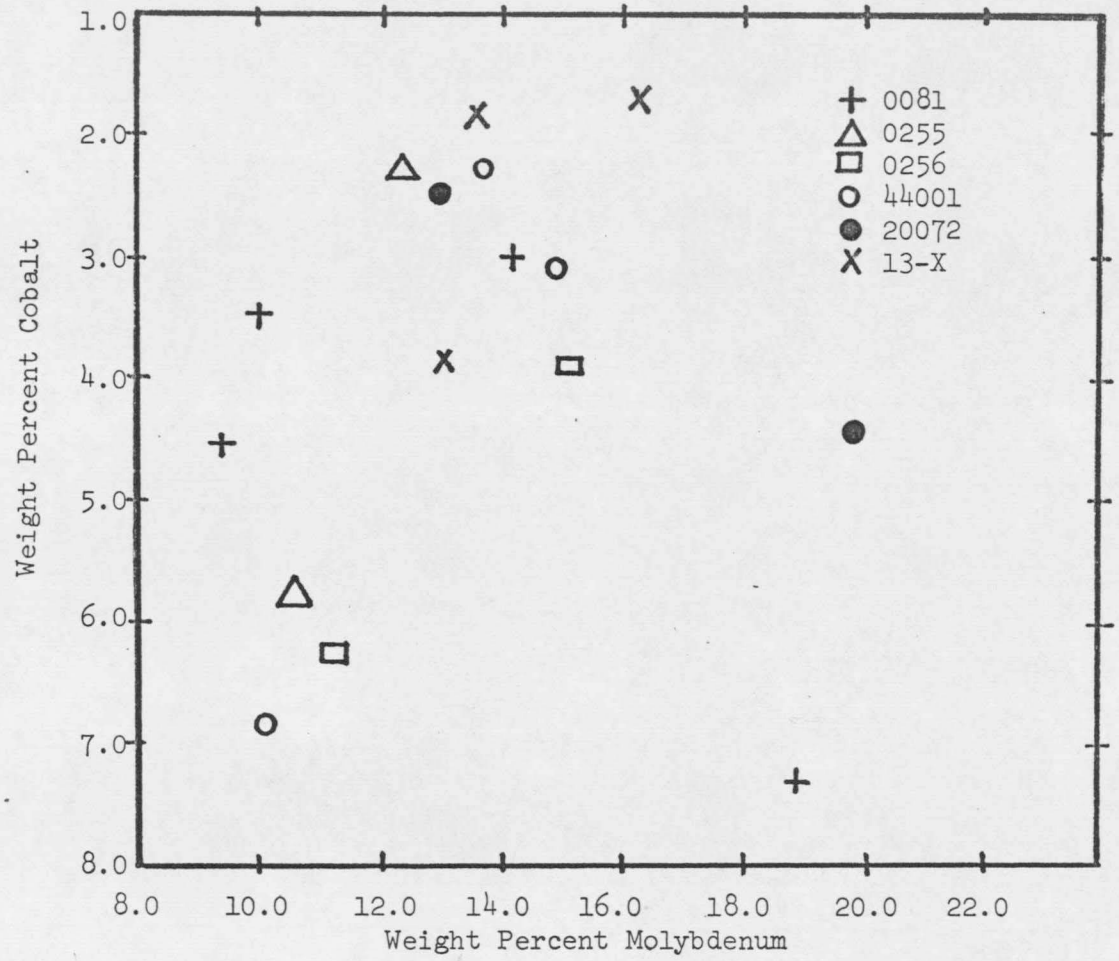


FIGURE 3
Weight Percent Cobalt vs. Weight Percent Molybdenum Promoted on Crystalline Base Materials

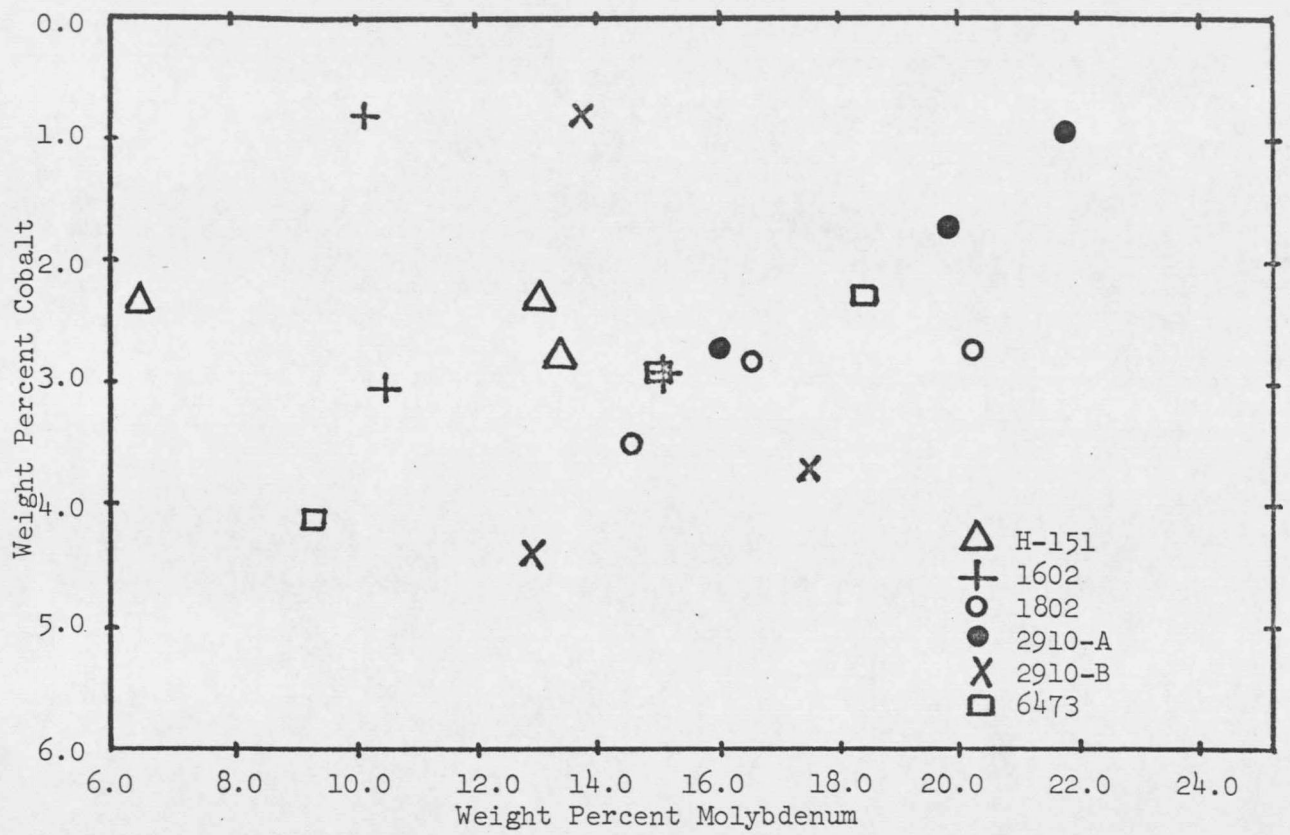


FIGURE 4

Weight Percent Cobalt vs. Weight Percent Molybdenum Promoted on Noncrystalline Catalyst Base Materials

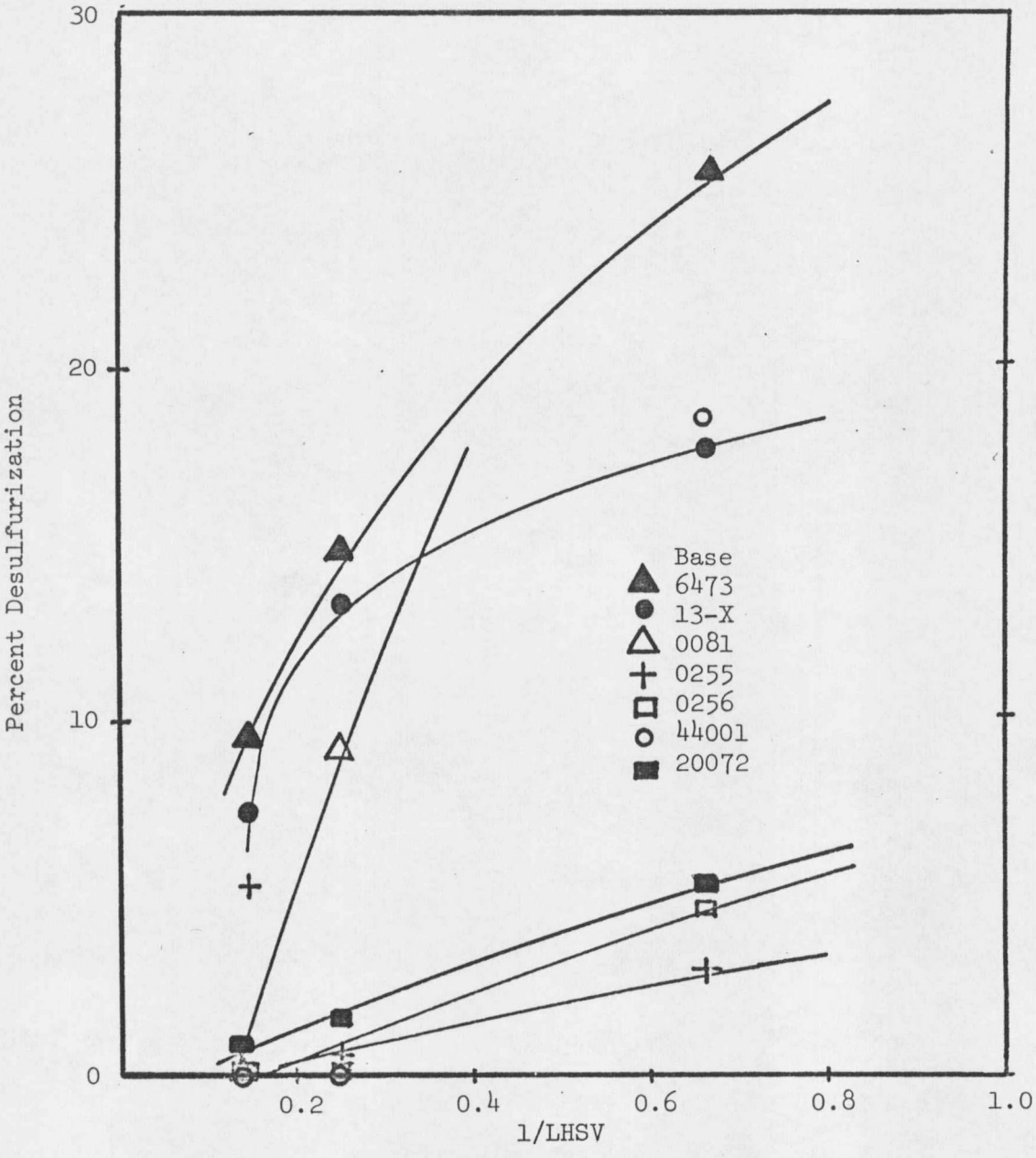


FIGURE 5
Percent Desulfurization vs. 1/LHSV at 650°F
Base Materials without Promotion

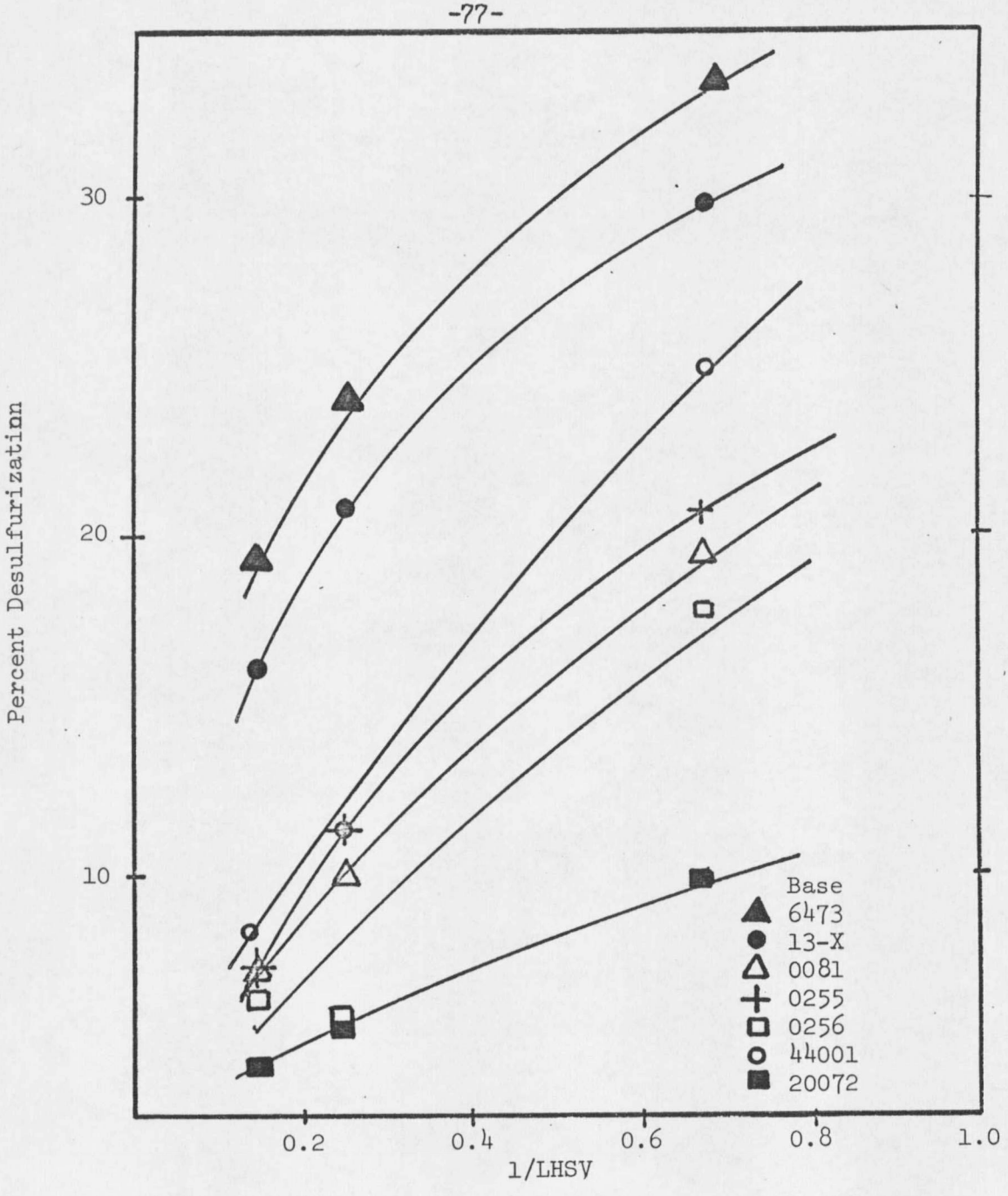


FIGURE 6
Percent Desulfurization vs. 1/LHSV at 725°F
Base Materials without Promotion

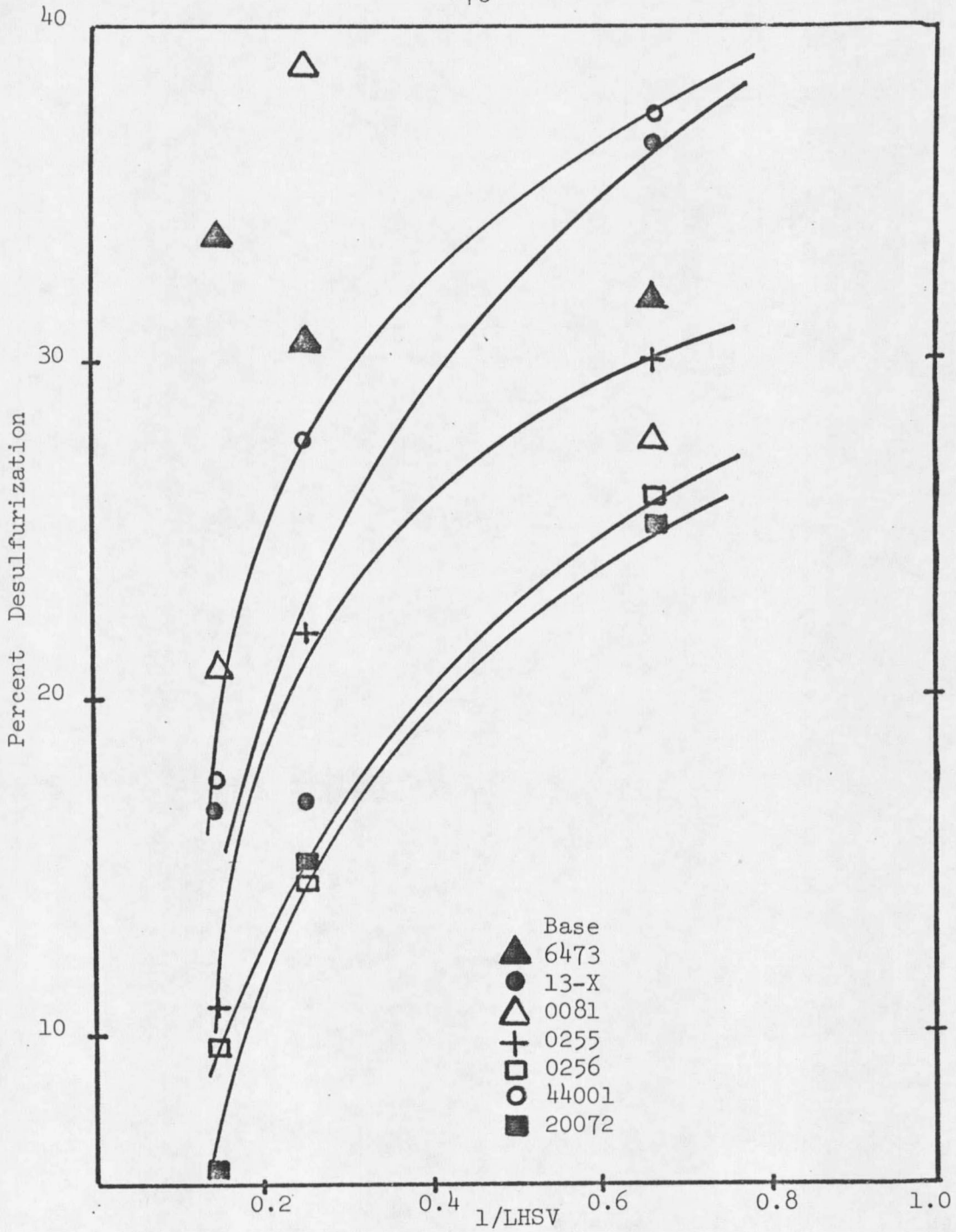


FIGURE 7
Percent Desulfurization vs. 1/LHSV at 800°F
Base Materials without Promotion

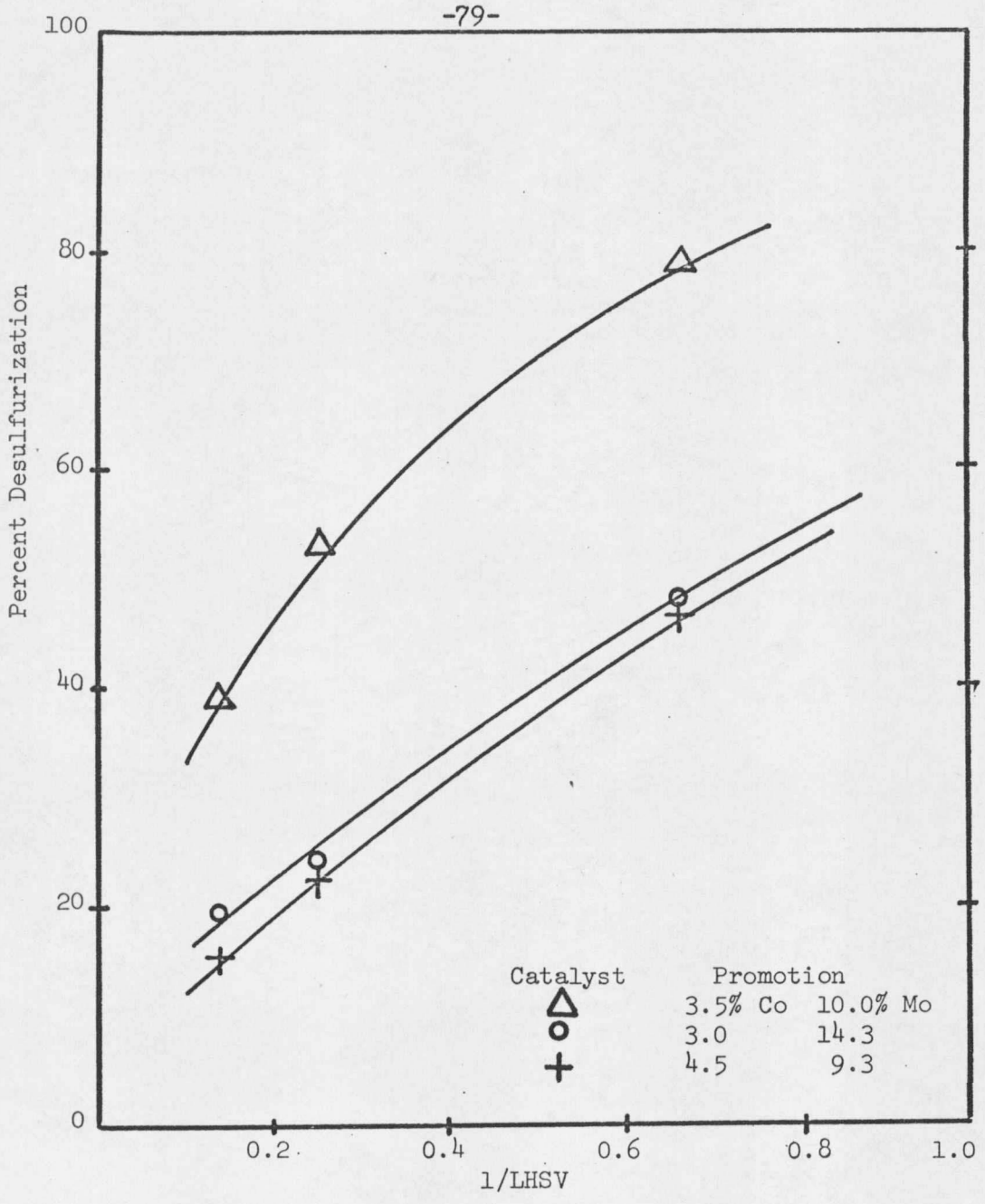


FIGURE 8
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 0081

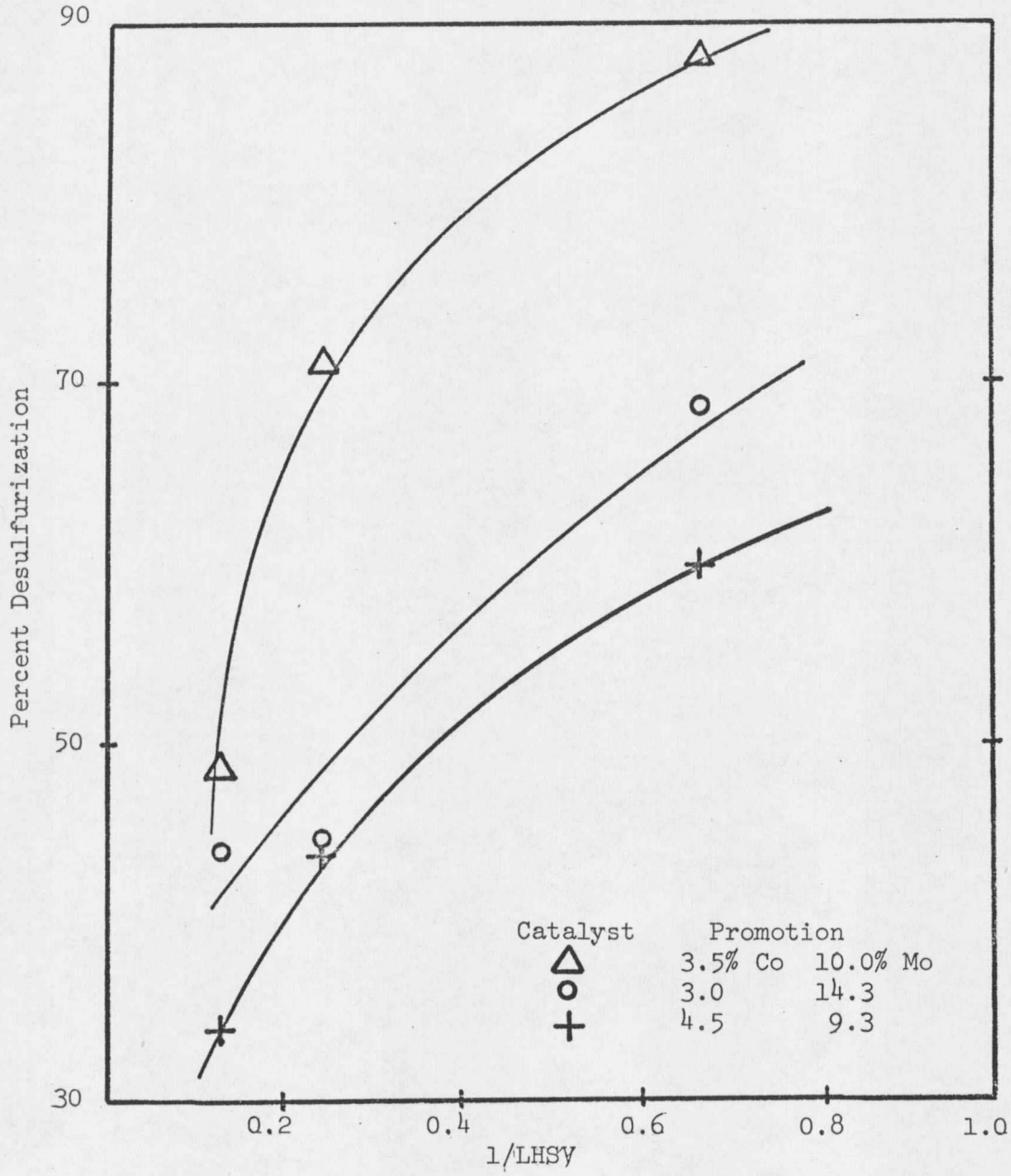


FIGURE 9
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 0081

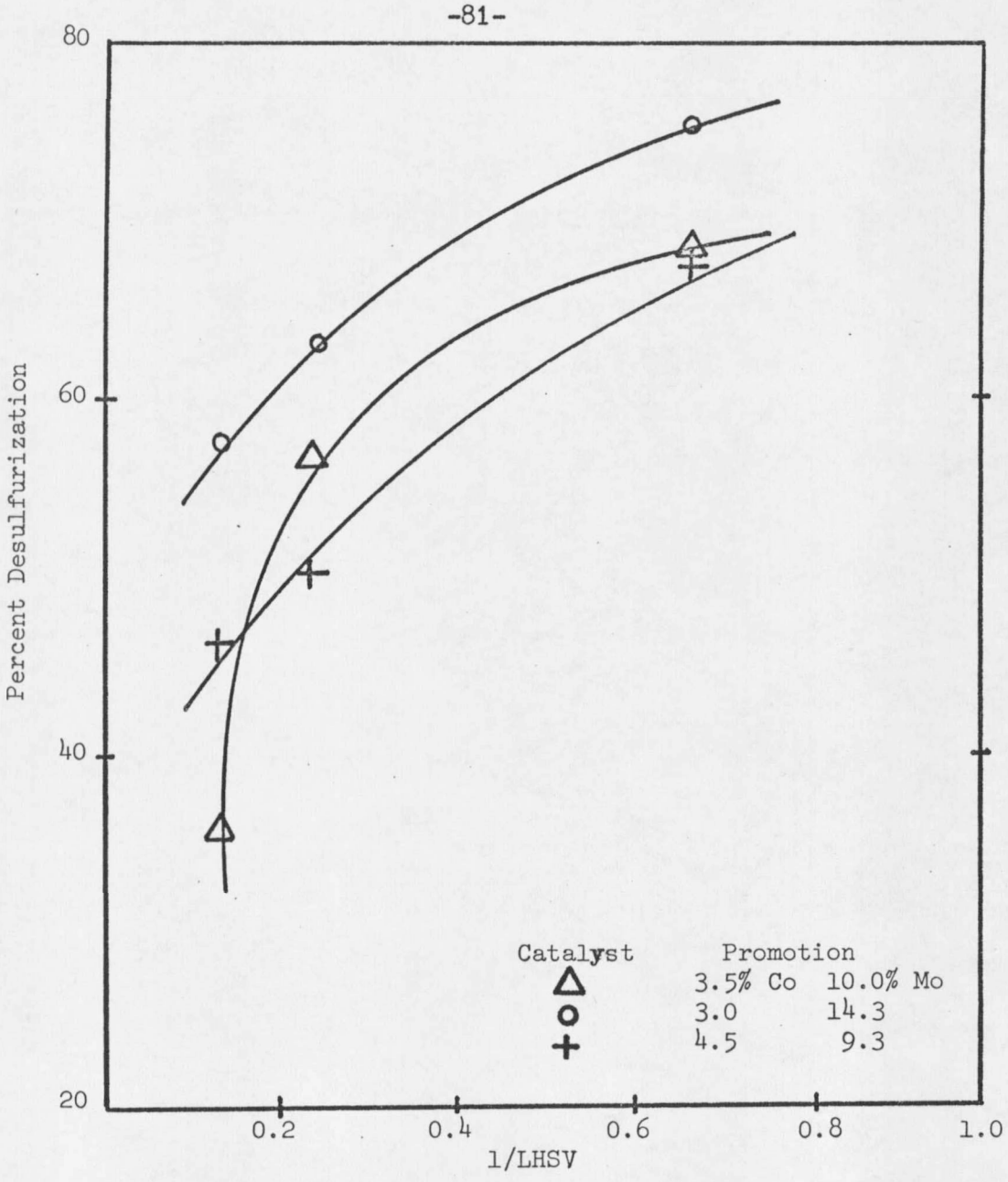


FIGURE 10
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 0081

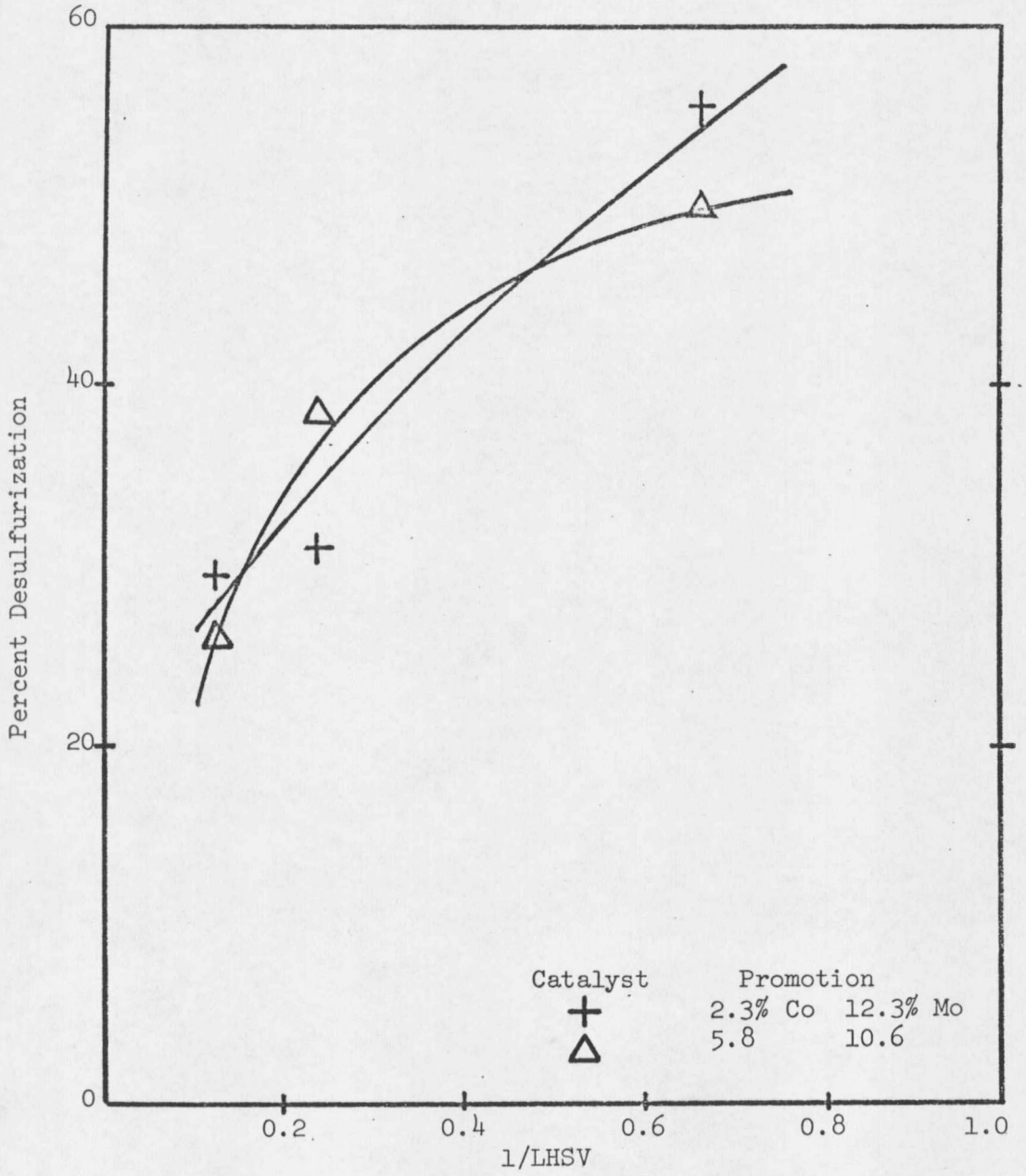


FIGURE 11
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 0255

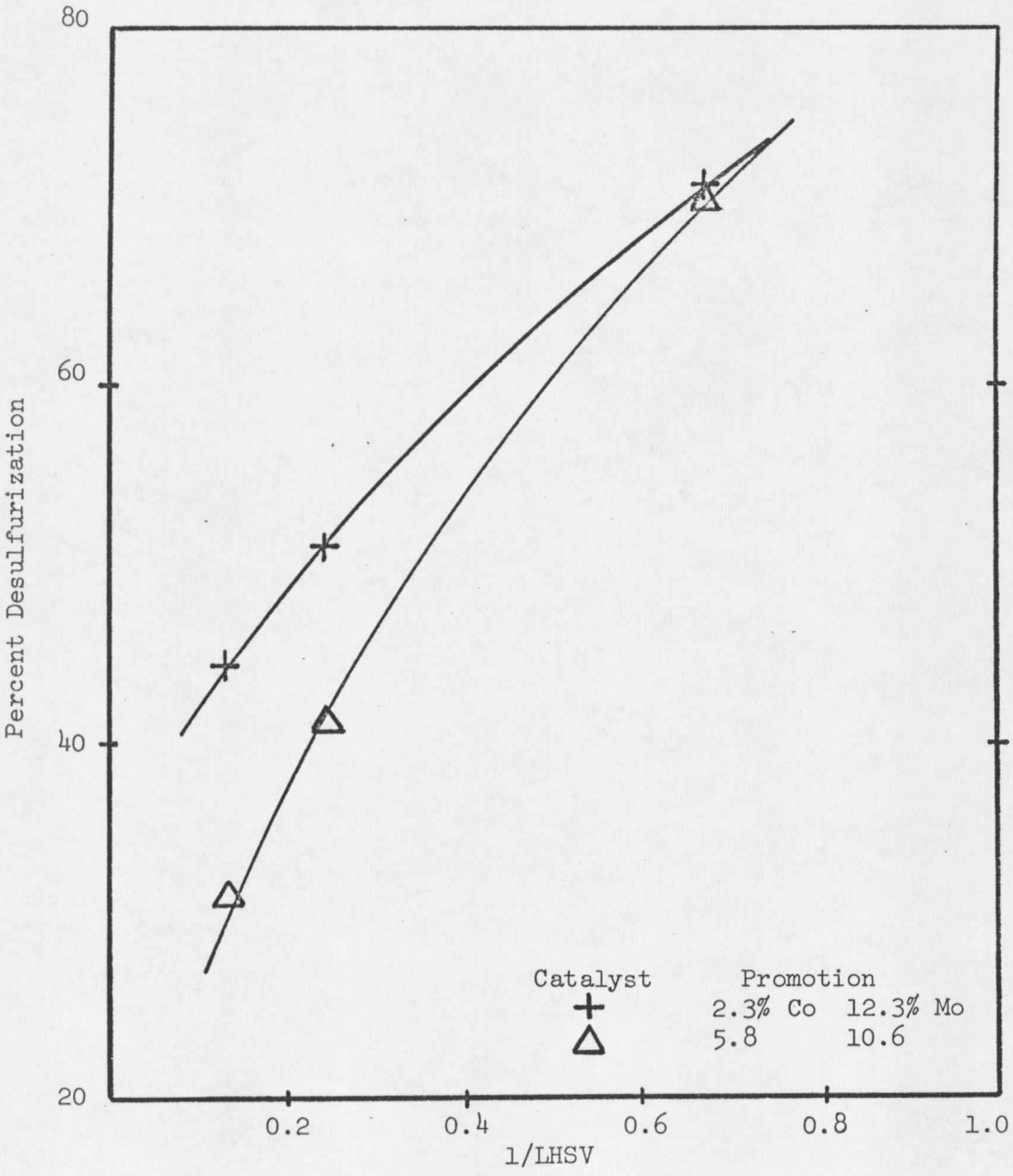


FIGURE 12
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 0255

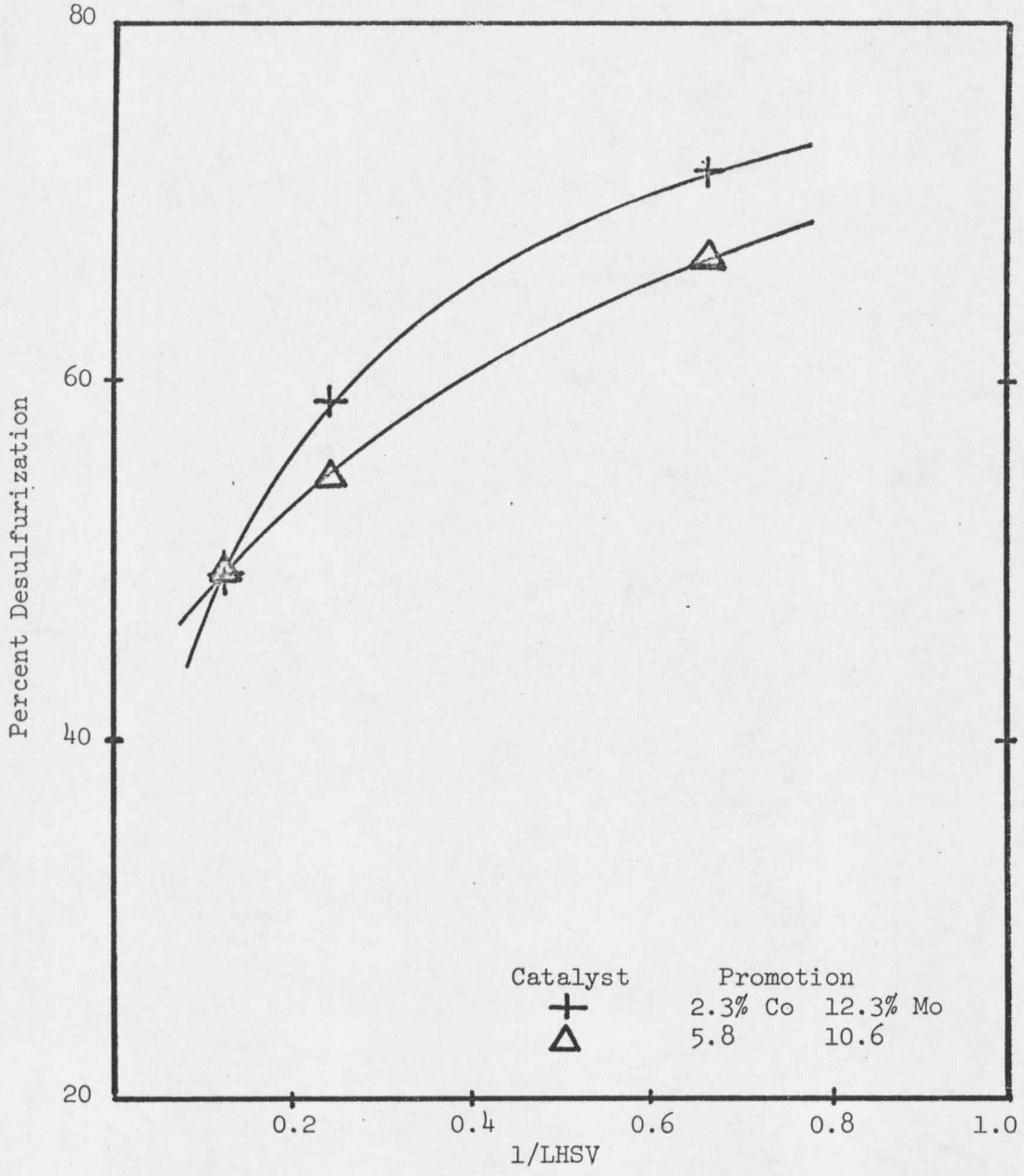


FIGURE 13
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 0255

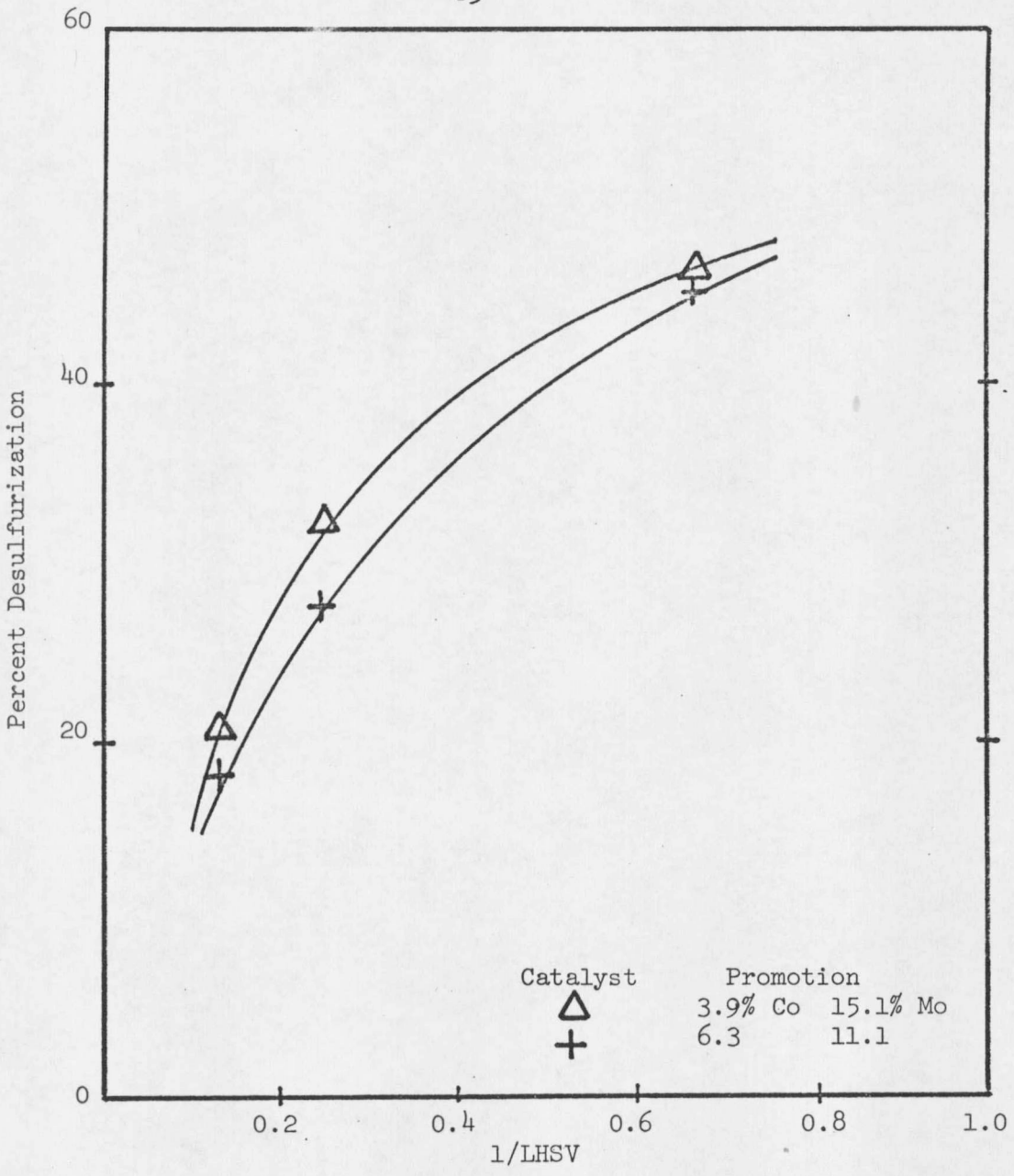


FIGURE 14
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 0256

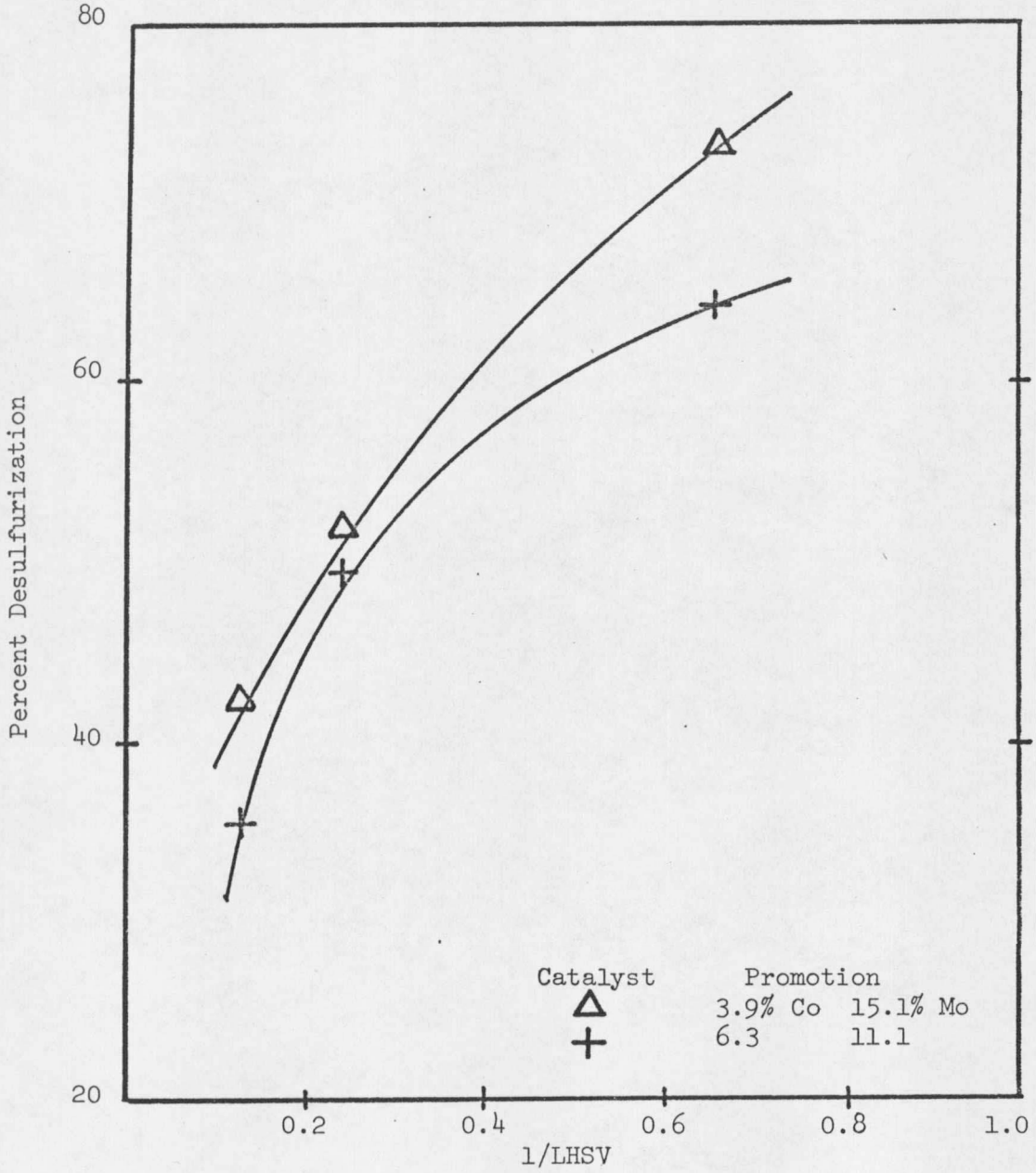


FIGURE 15
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 0256

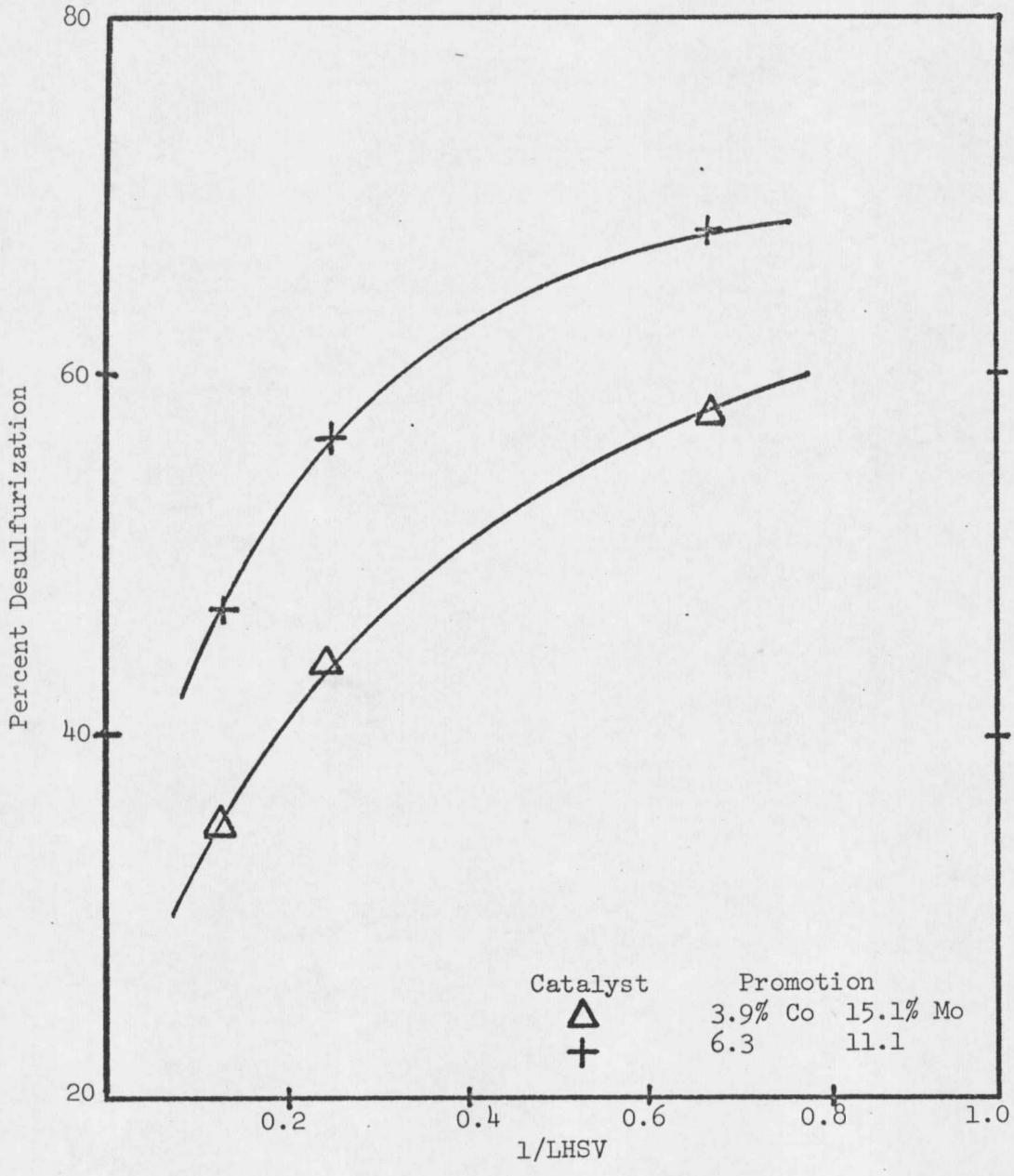


FIGURE 16
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 0256

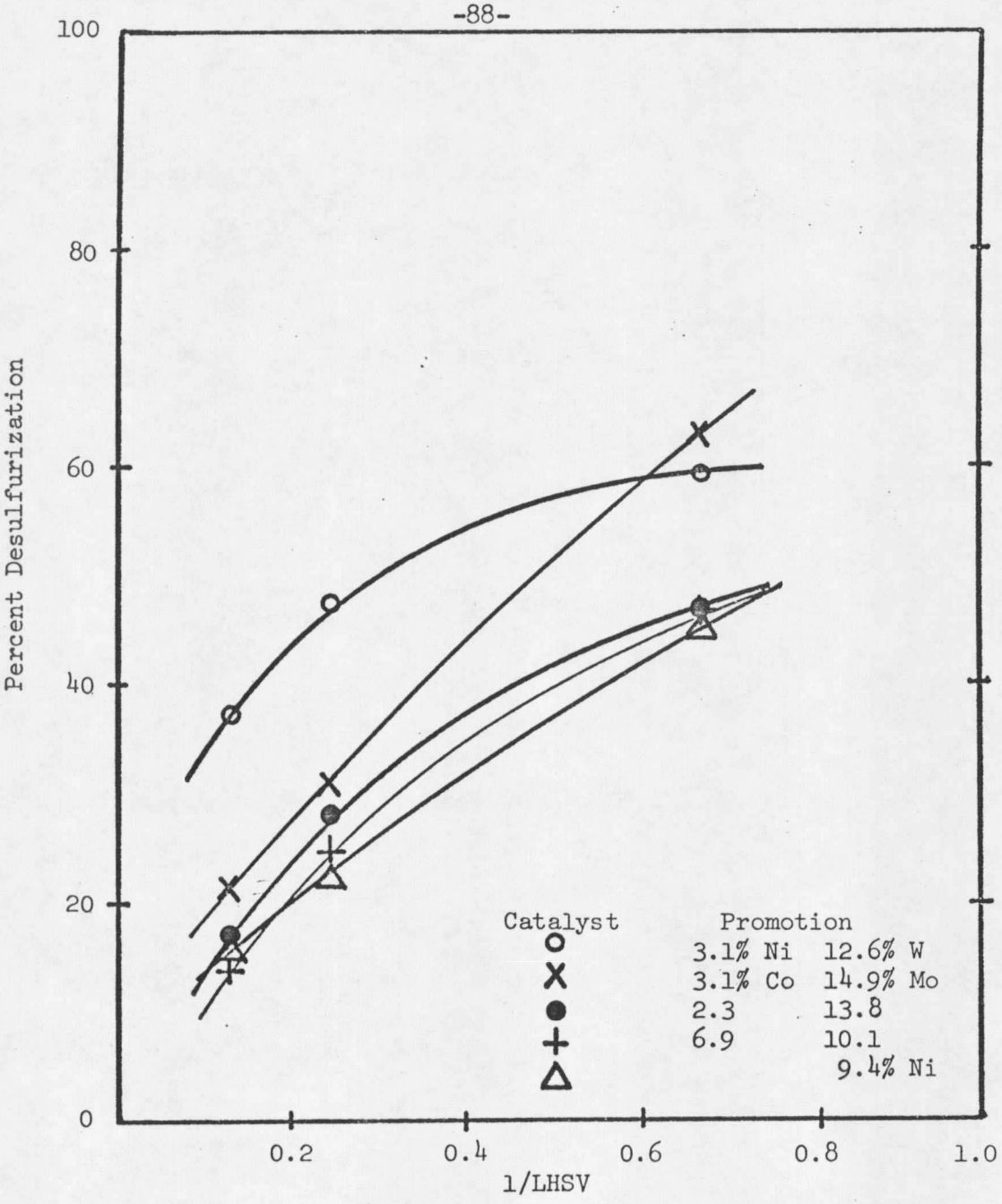


FIGURE 17
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 44001

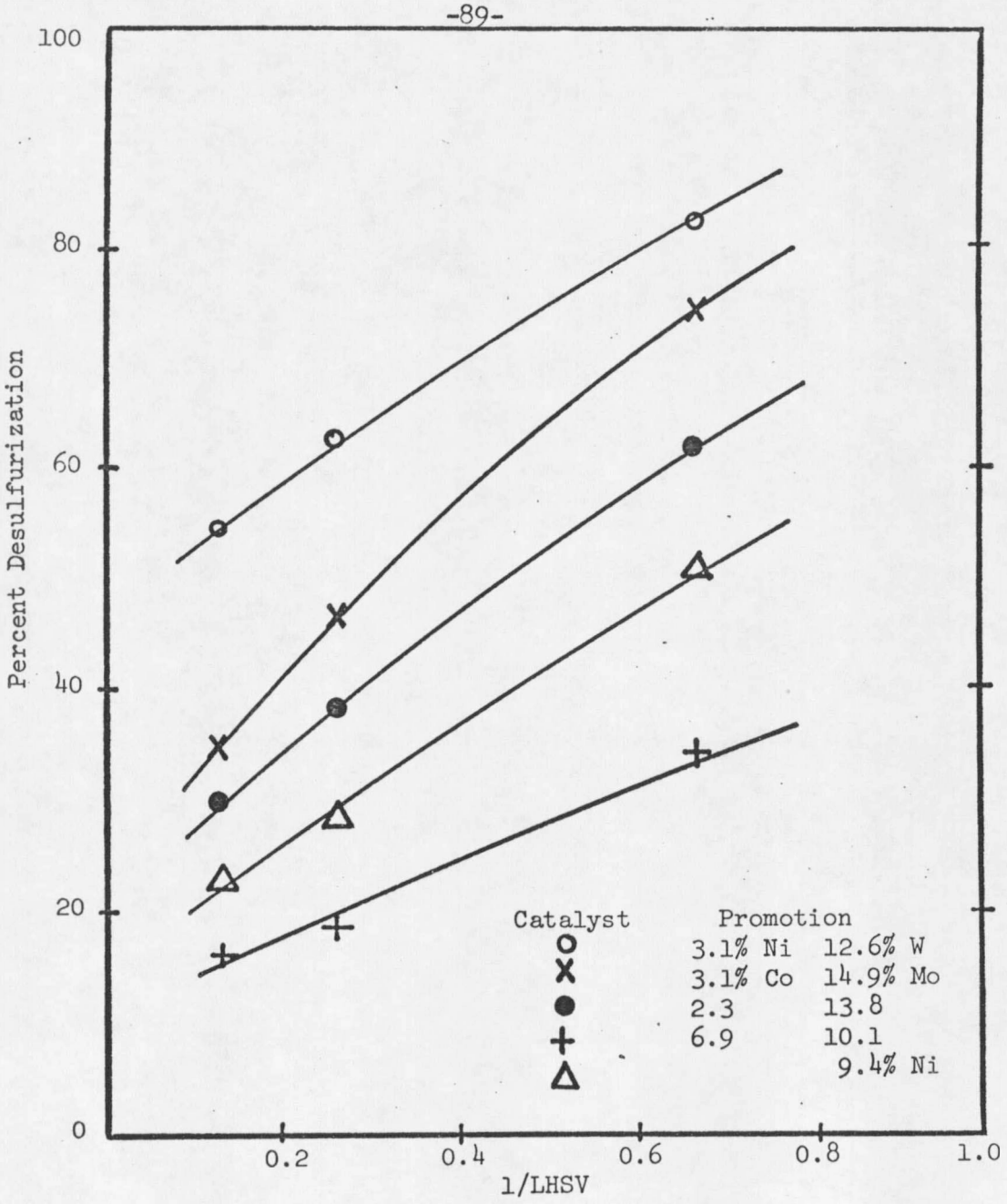


FIGURE 18
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 44001

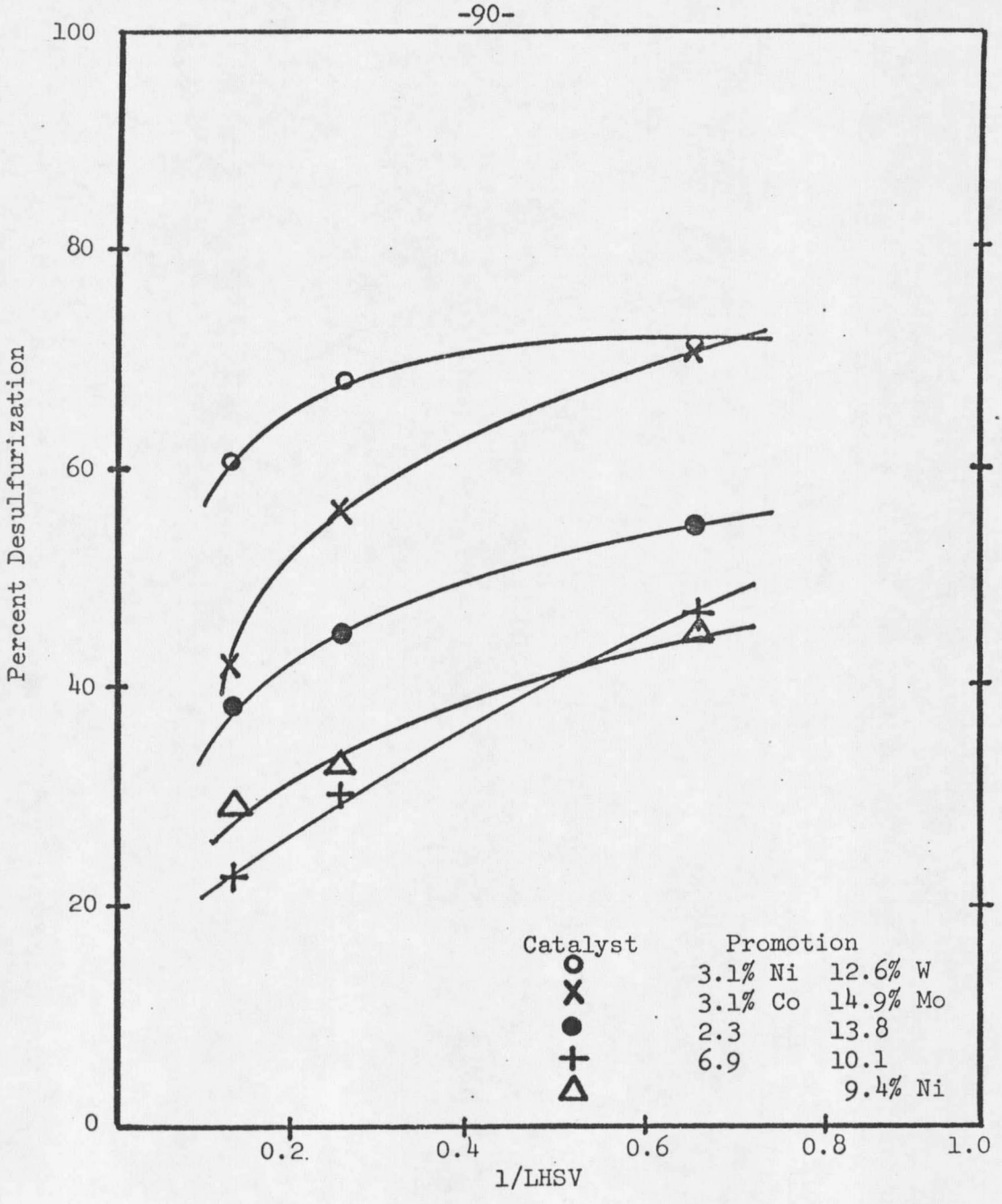


FIGURE 19
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 44001

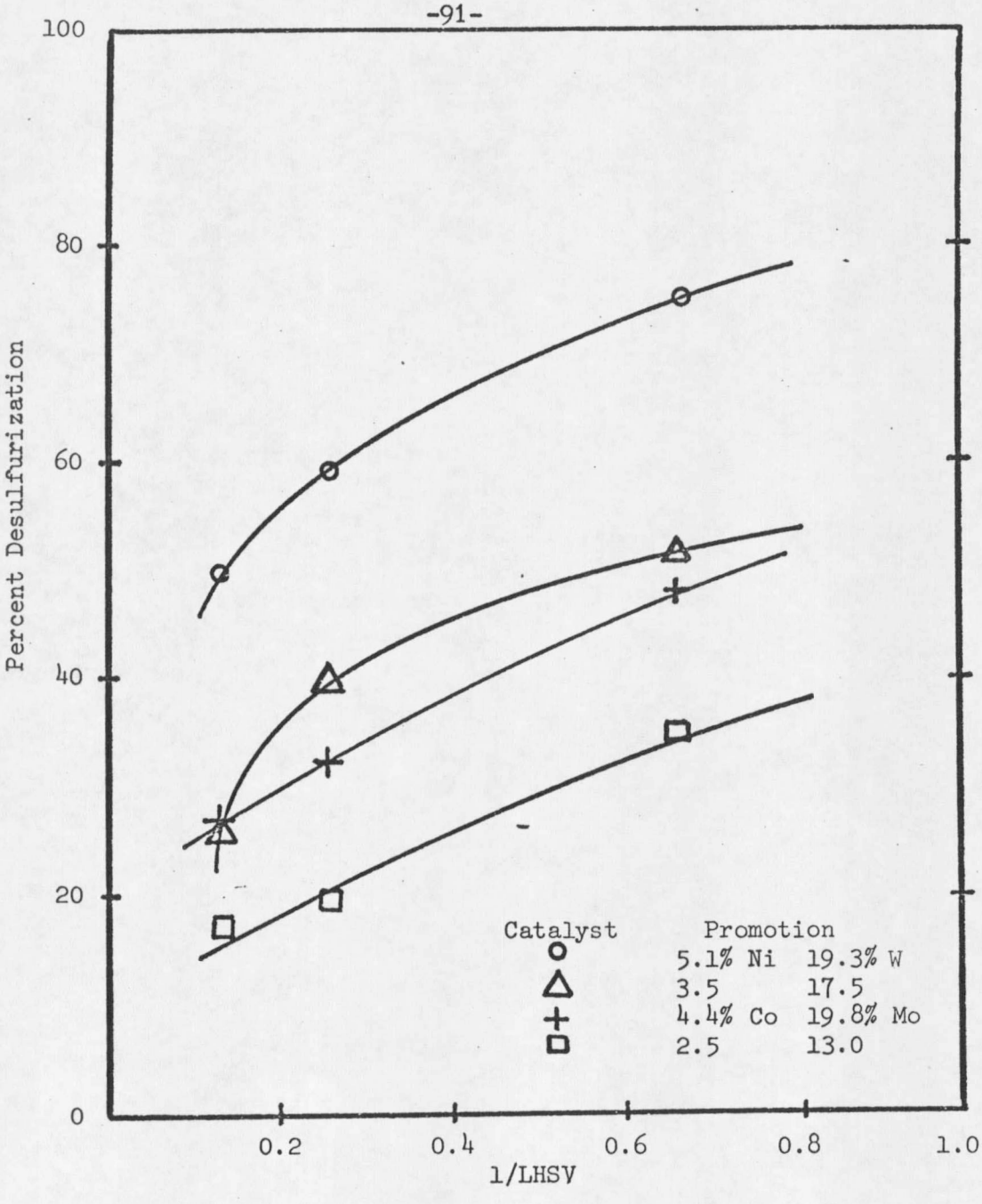


FIGURE 20
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 20072

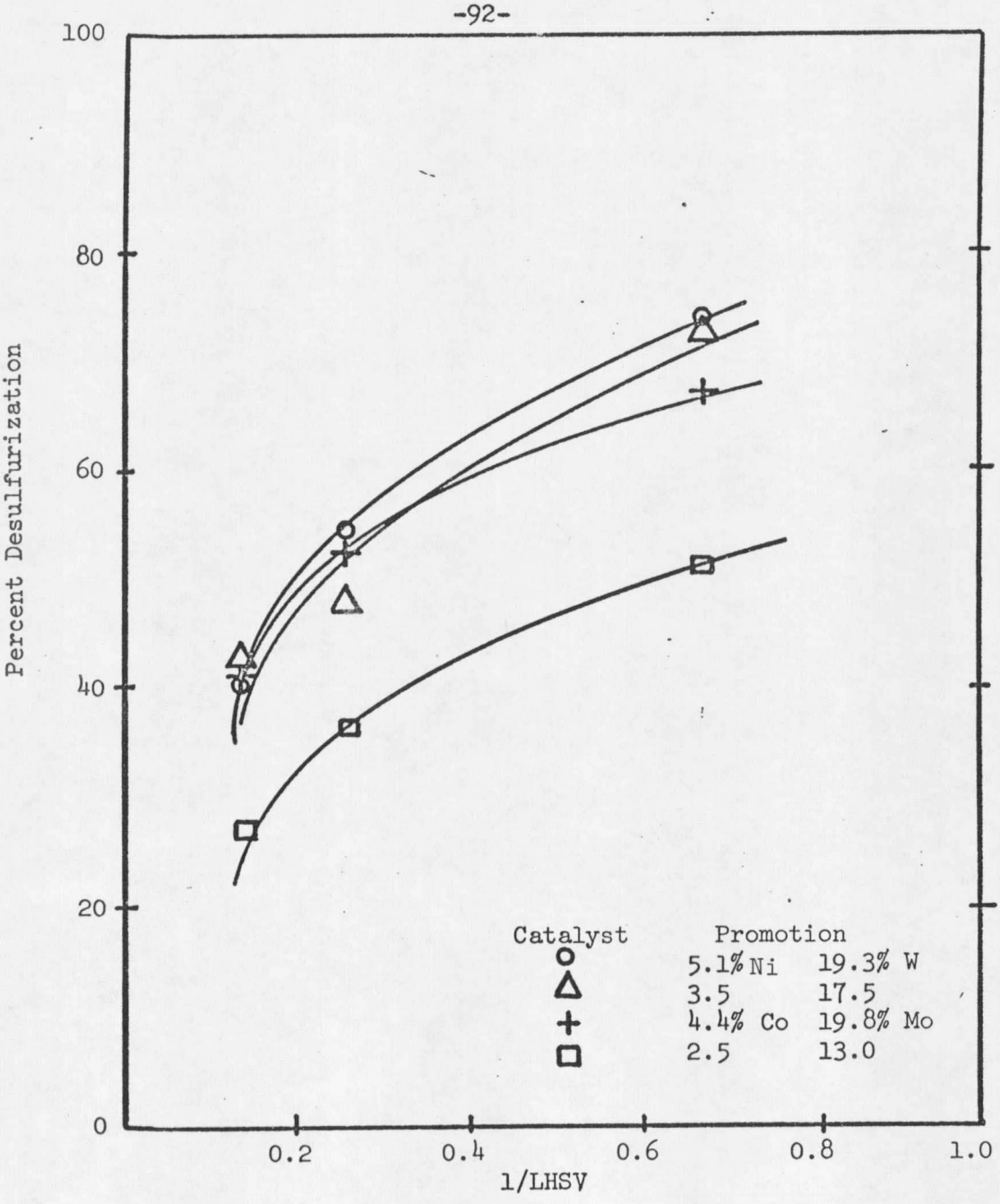


FIGURE 20
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 20072

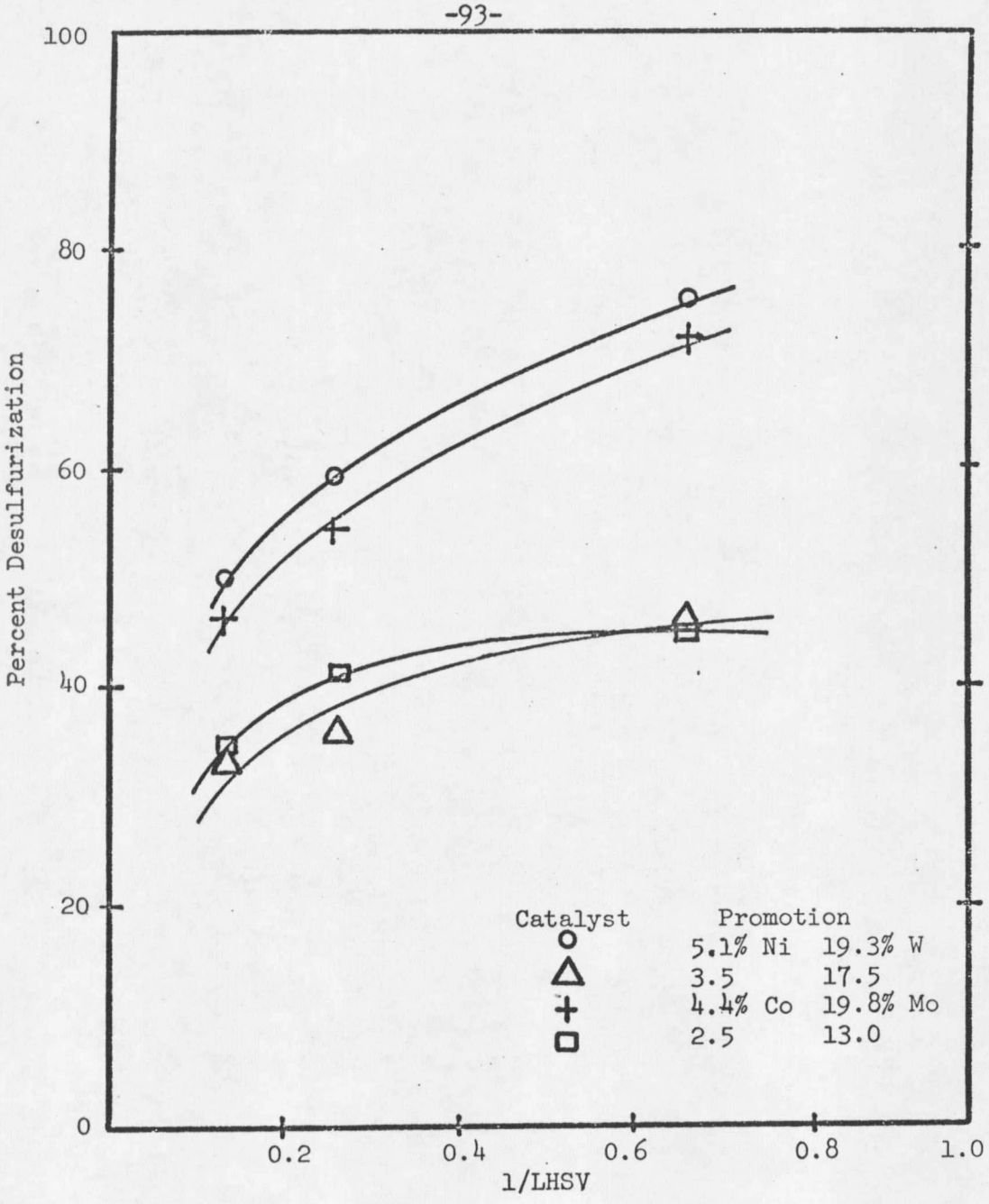


FIGURE 22
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 20072

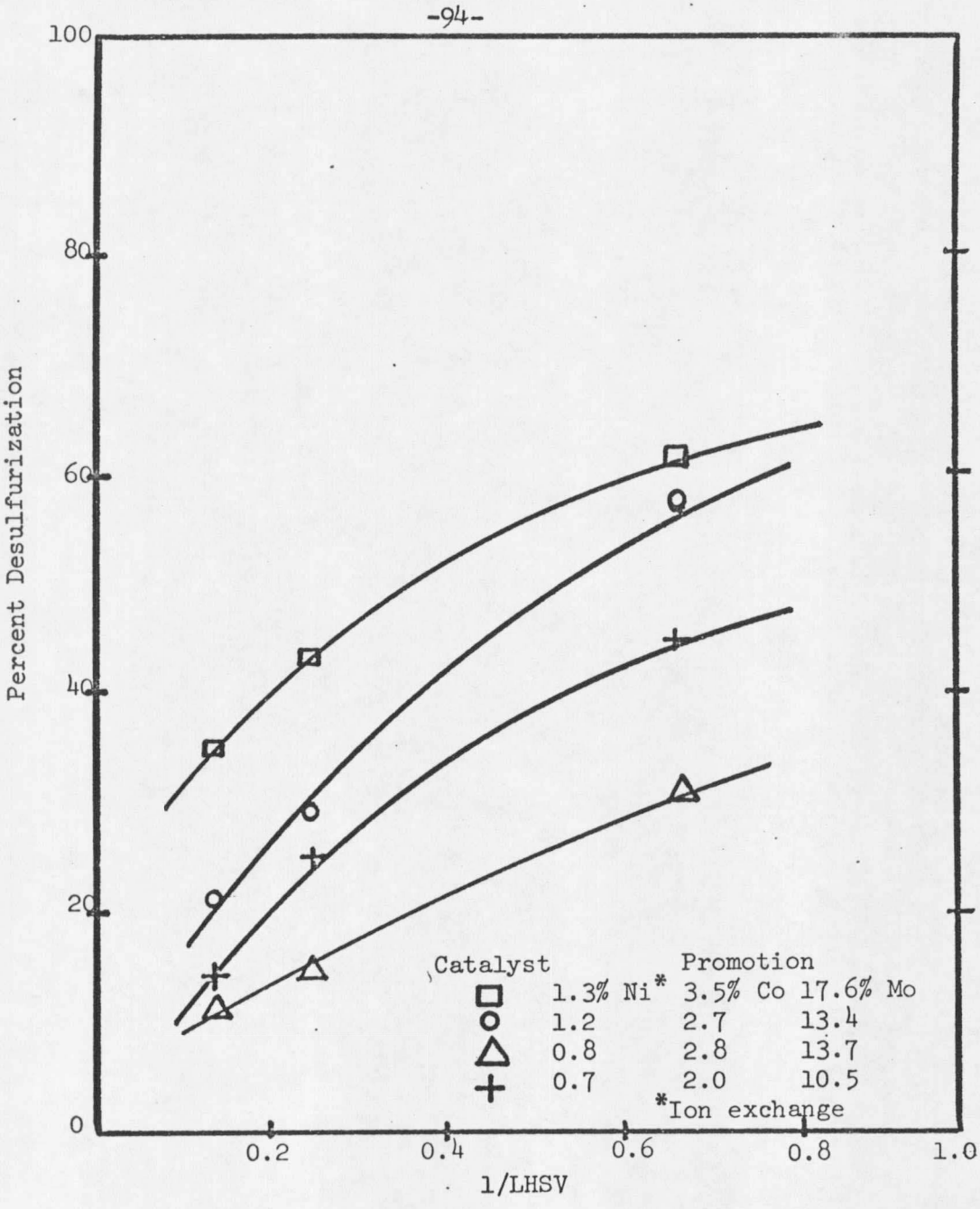


FIGURE 23
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 20072

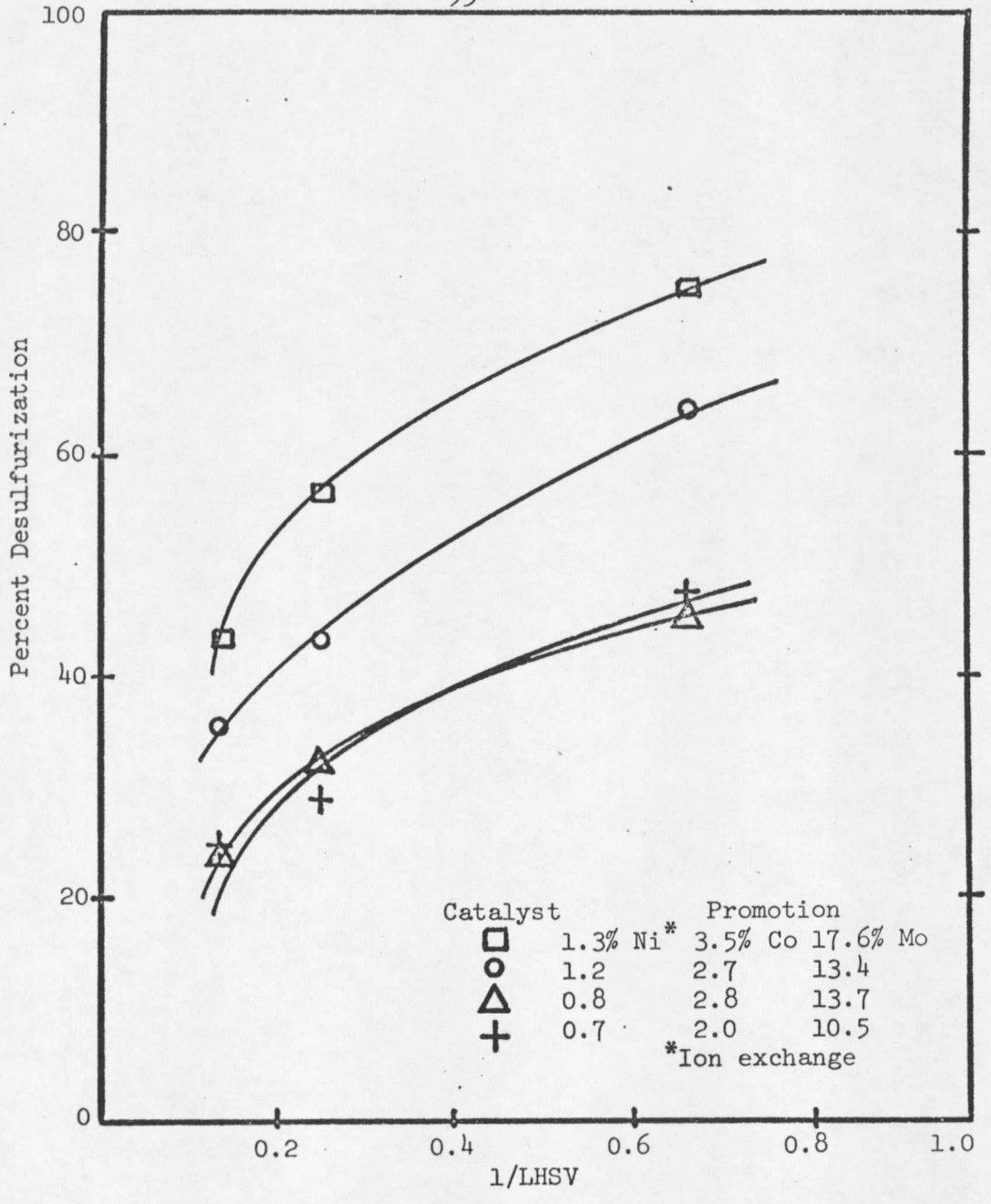


FIGURE 24
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 20072

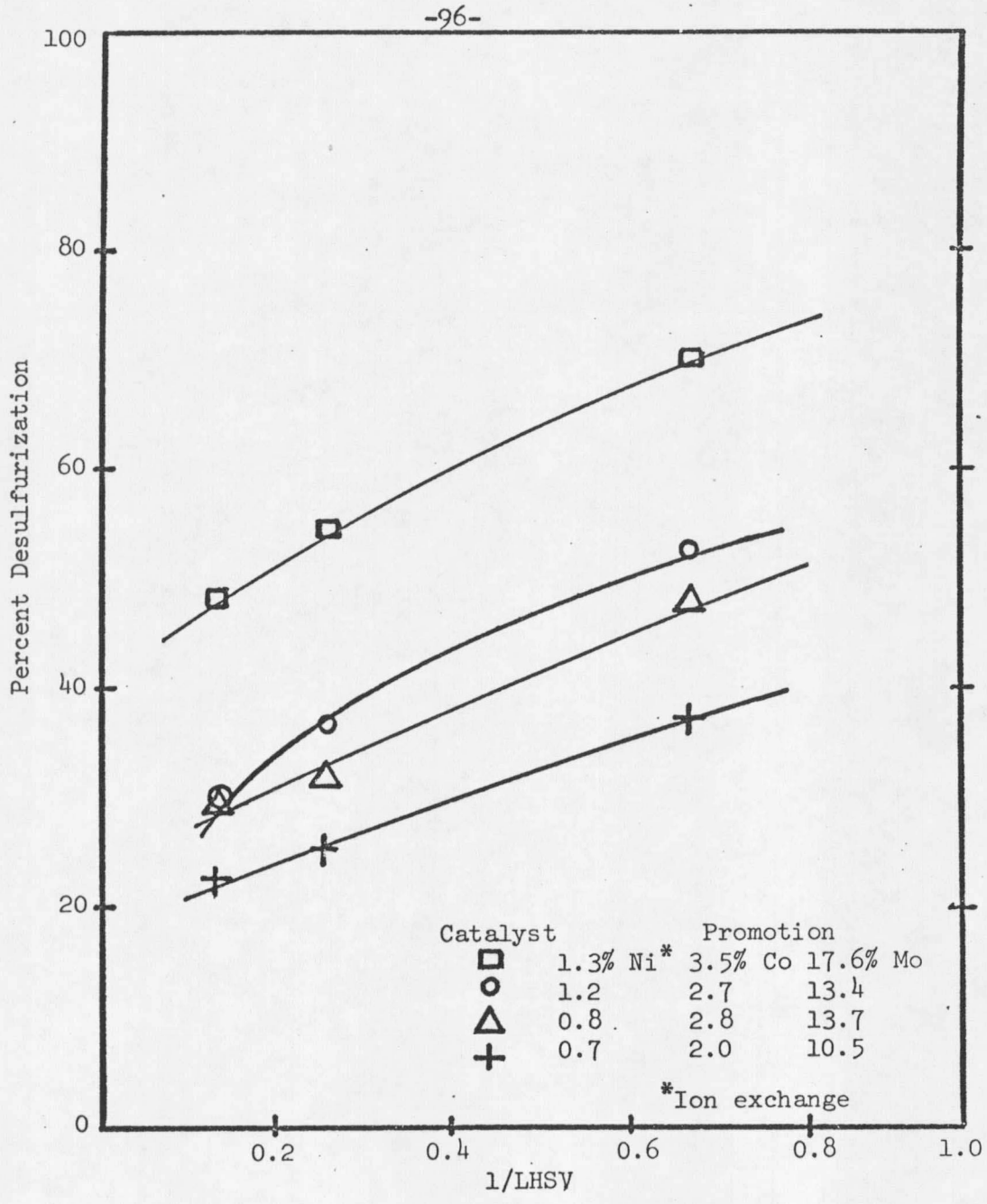


FIGURE 25
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 20072

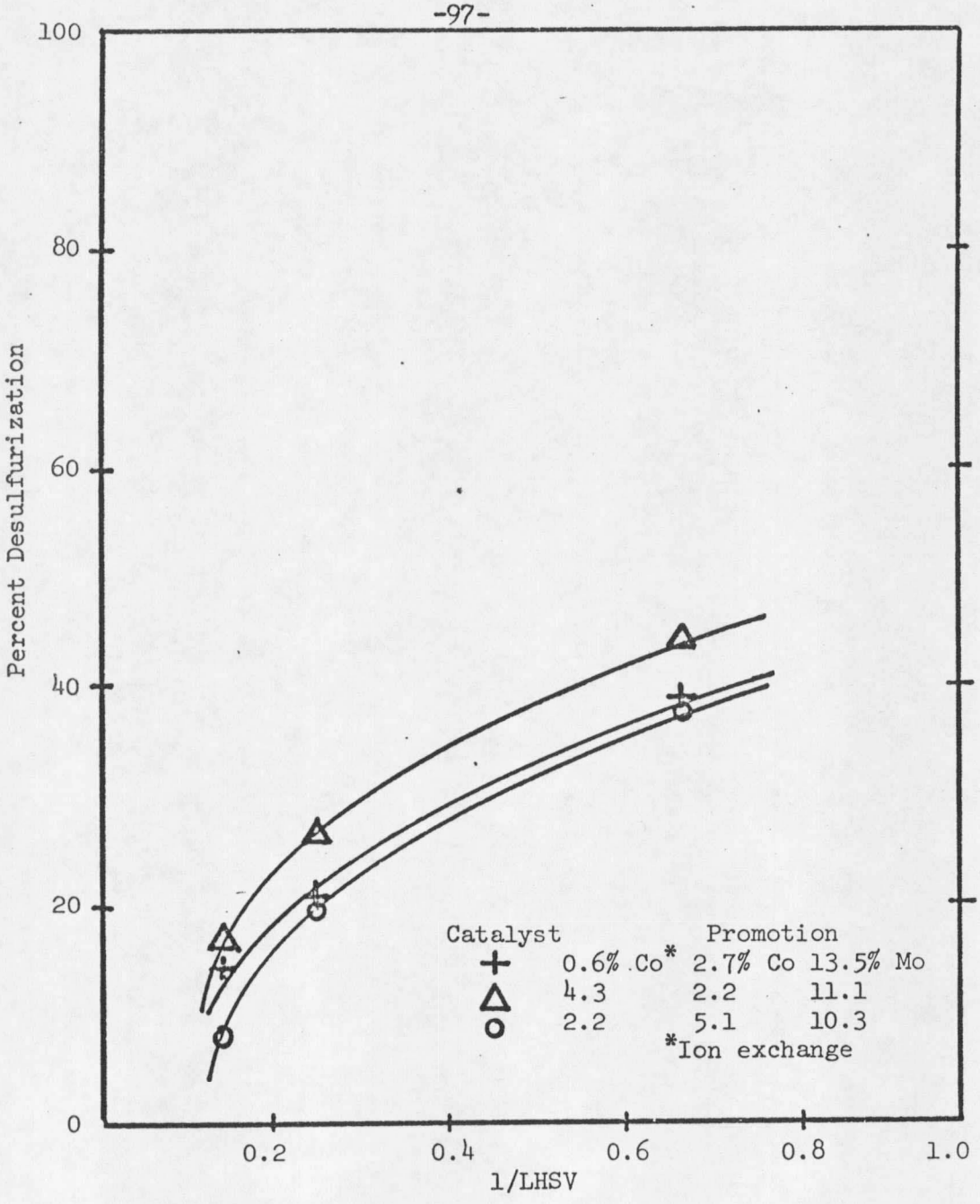


FIGURE 26
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 20072

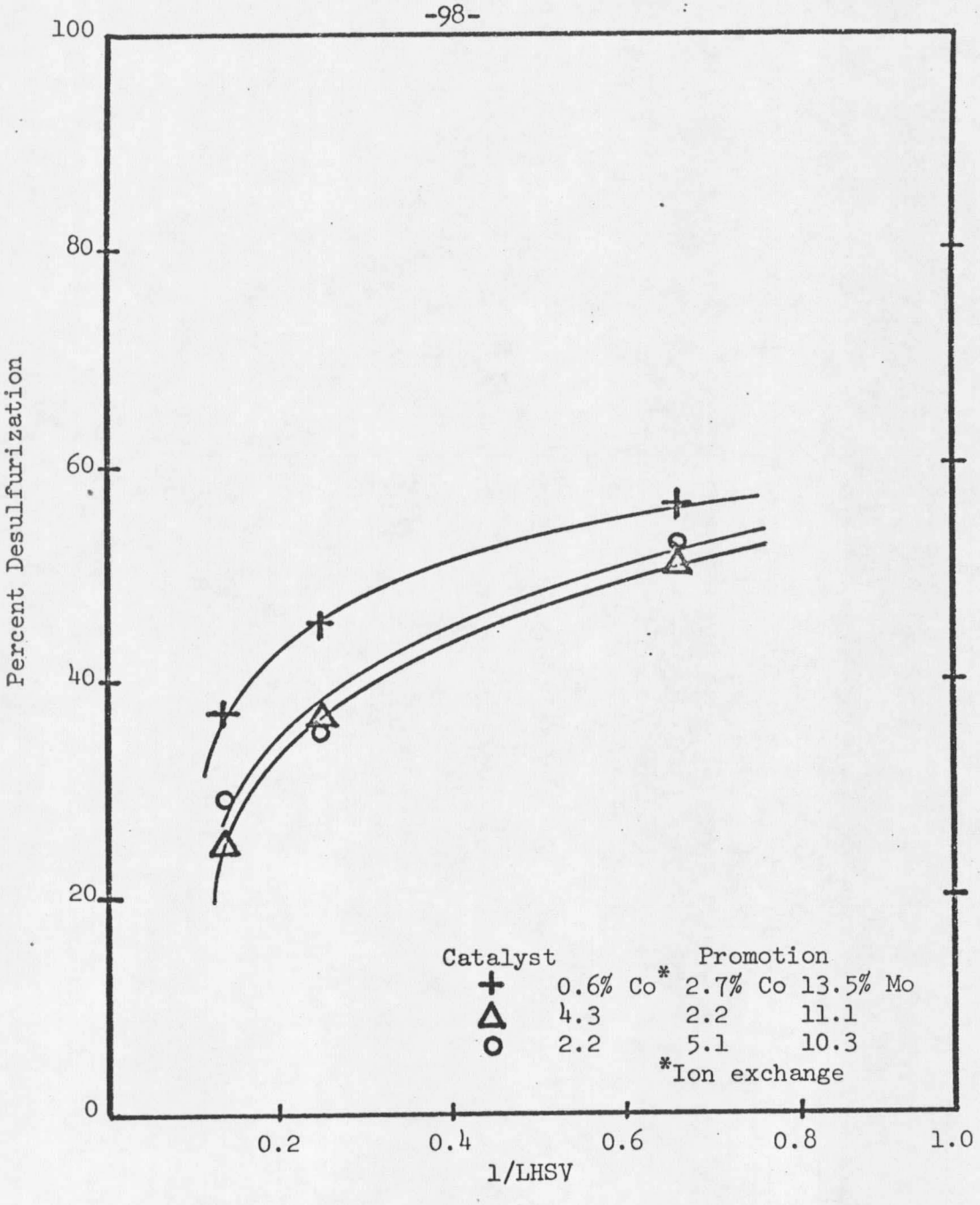


FIGURE 27
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 20072

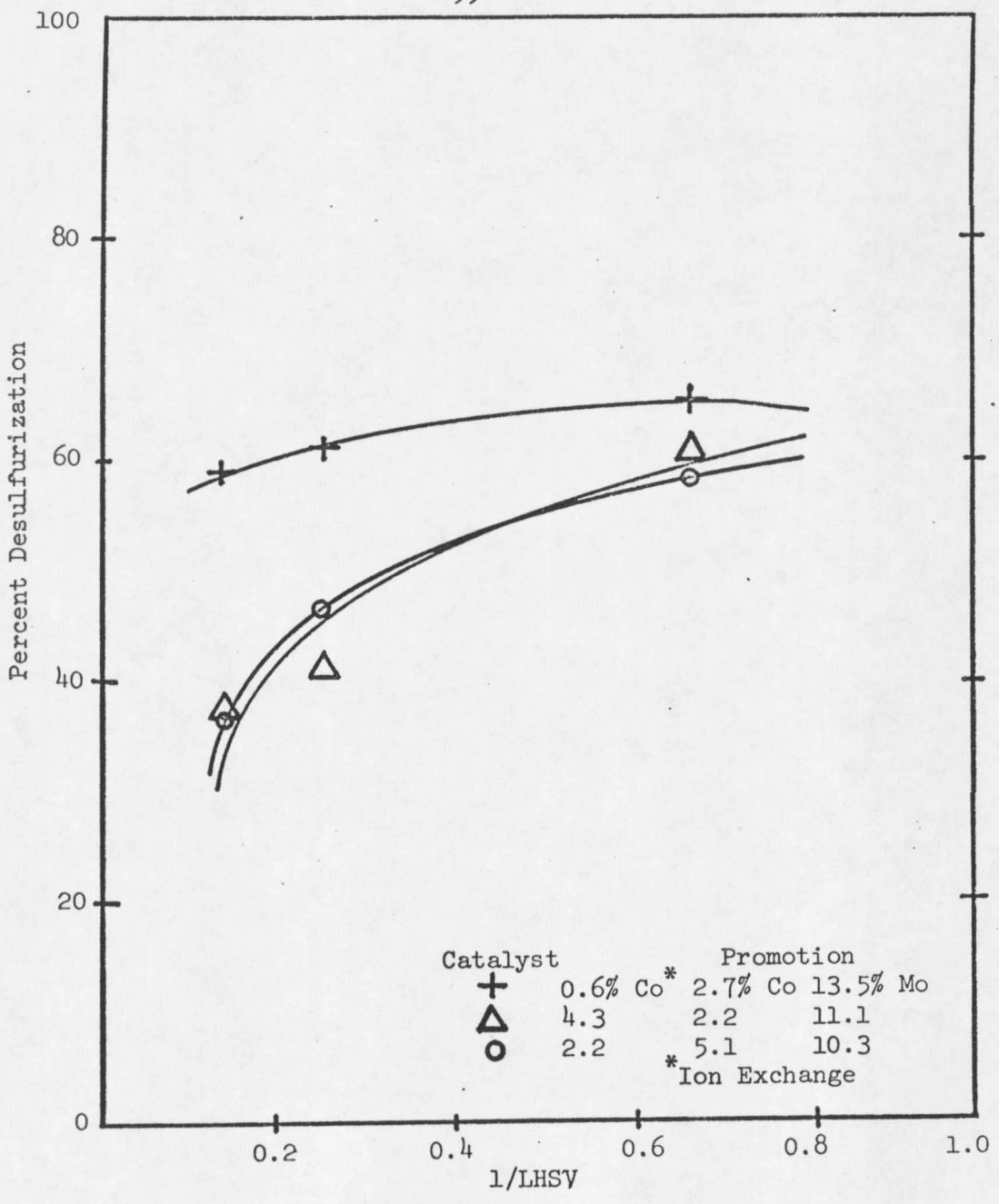


FIGURE 28
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 20072

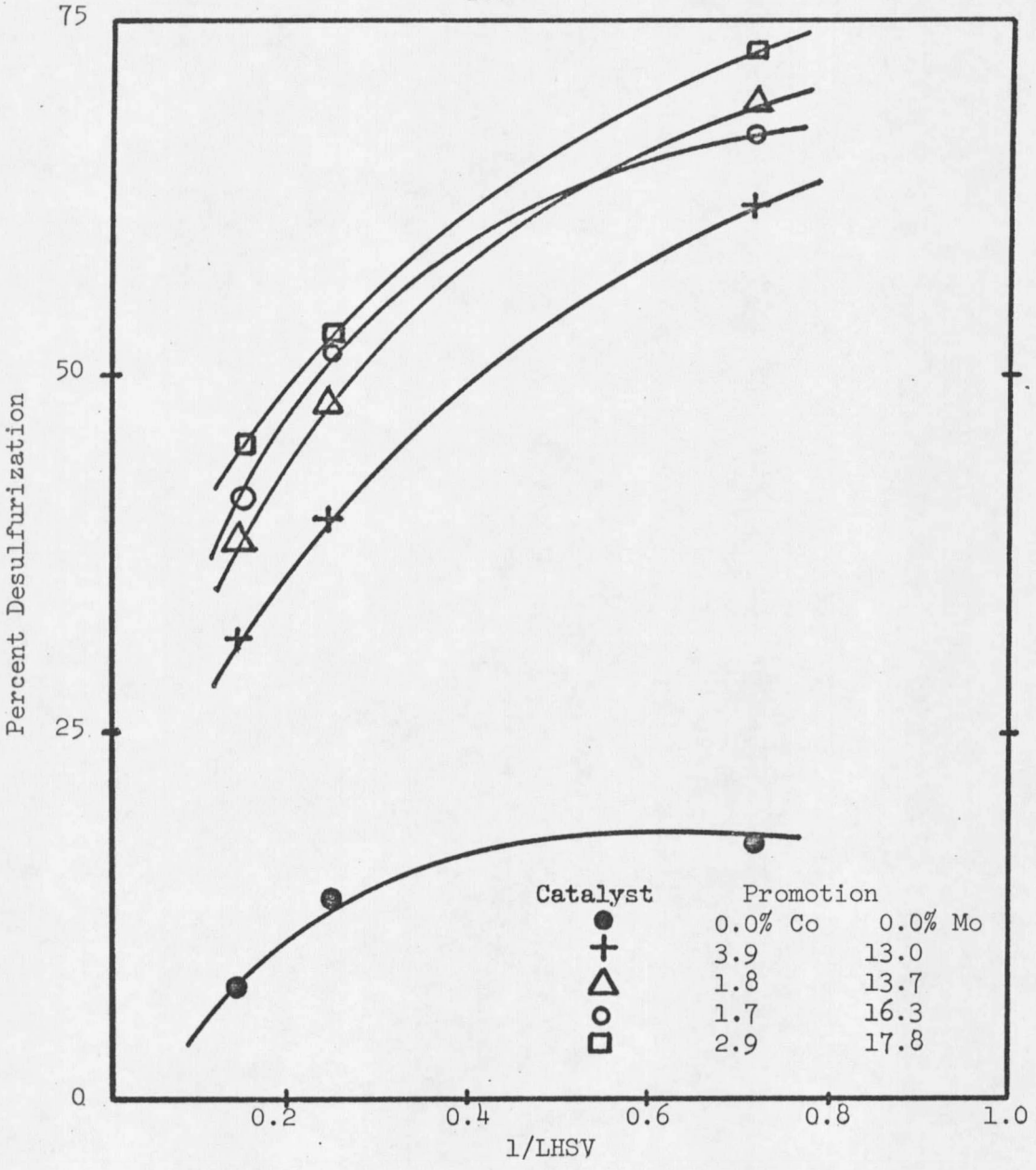


FIGURE 29
Percent Desulfurization vs. 1/LHSV at 650°F
for Linde 13-X

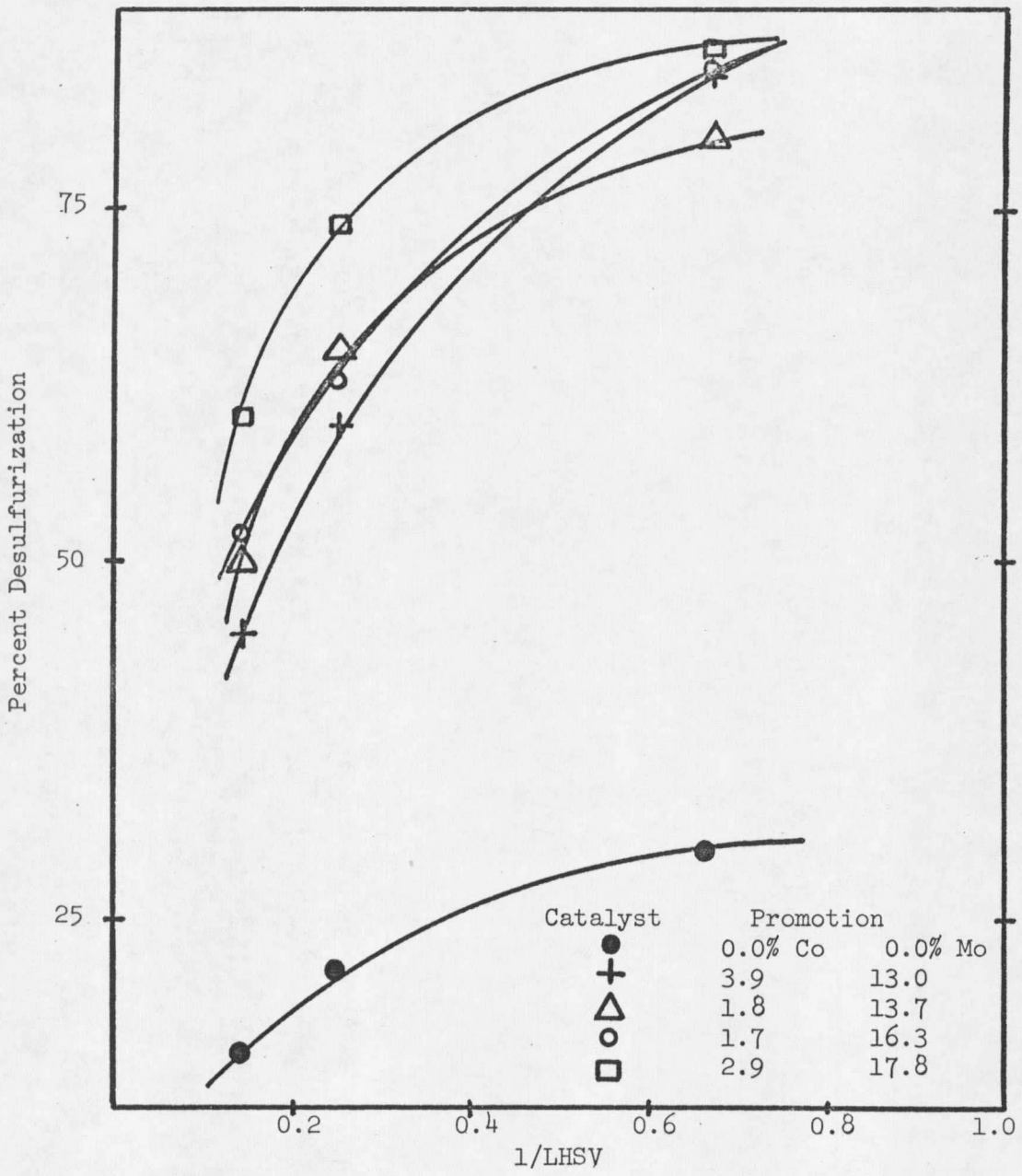


FIGURE 30
Percent Desulfurization vs. 1/LHSV at 725°F
for Linde 13-X

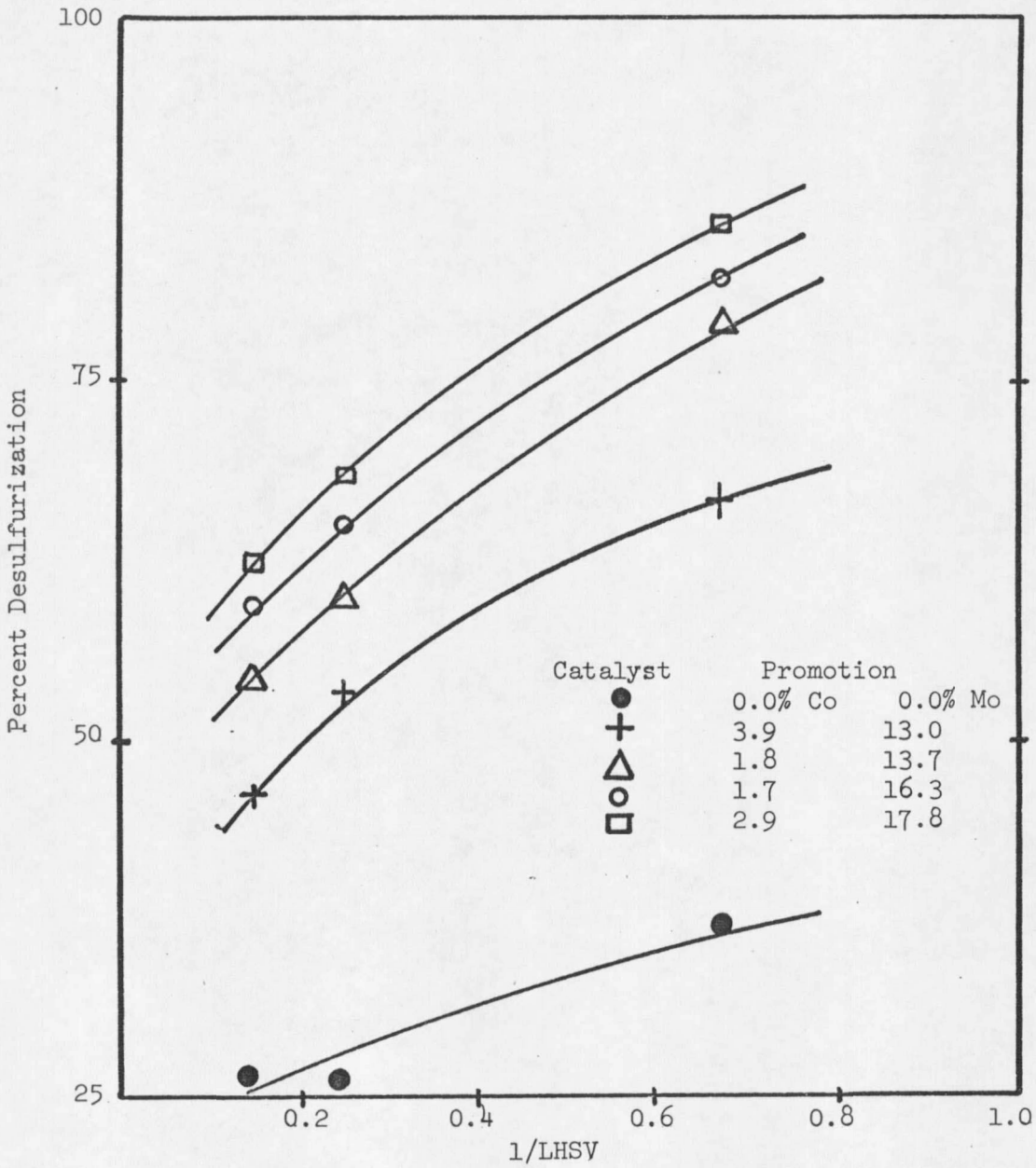


FIGURE 31
Percent Desulfurization vs. 1/LHSV at 800°F
for Linde 13-X

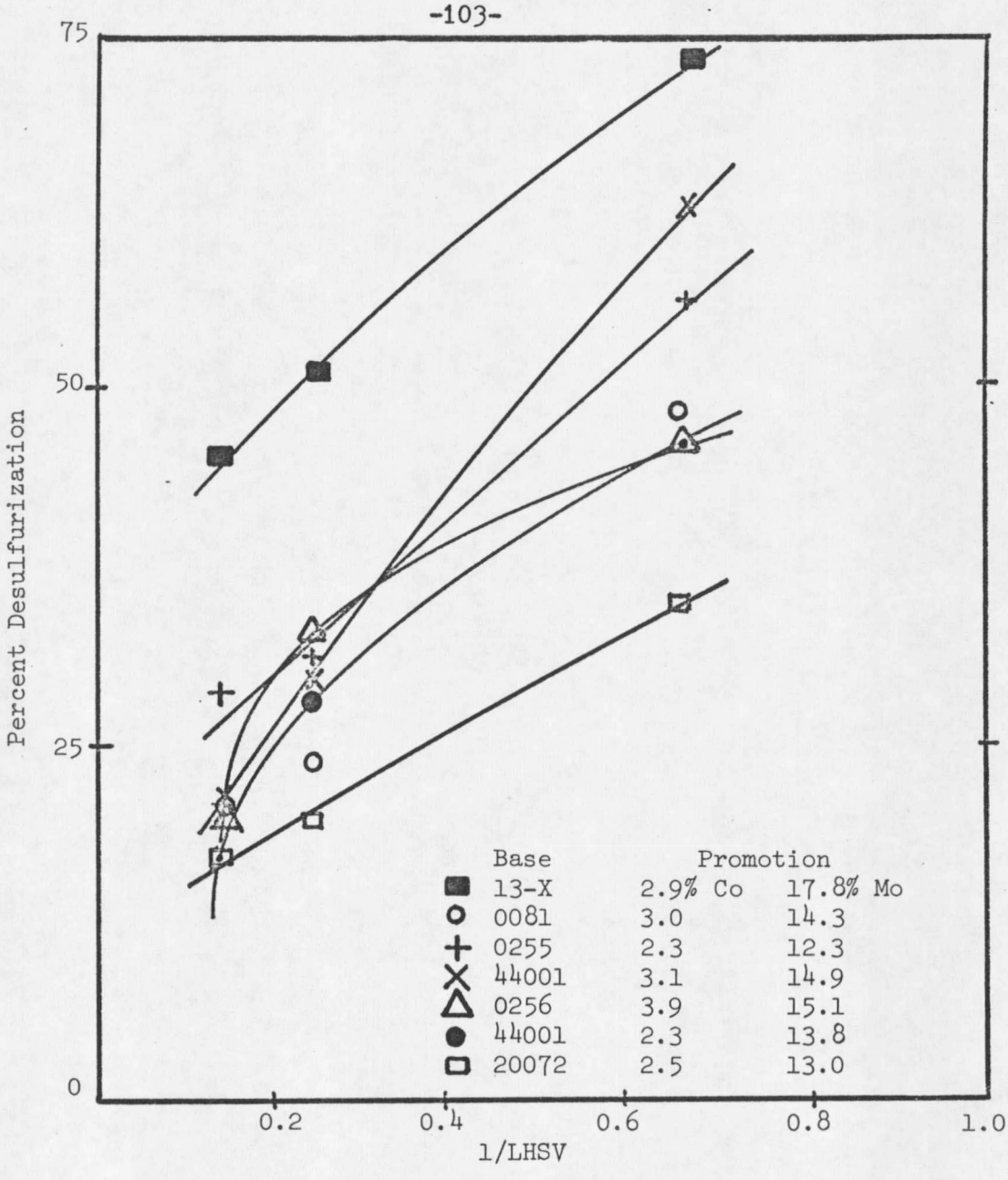


FIGURE 32
Percent Desulfurization vs. 1/LHSV at 650°F for
Crystalline Bases 3% Co 15% Mo Range

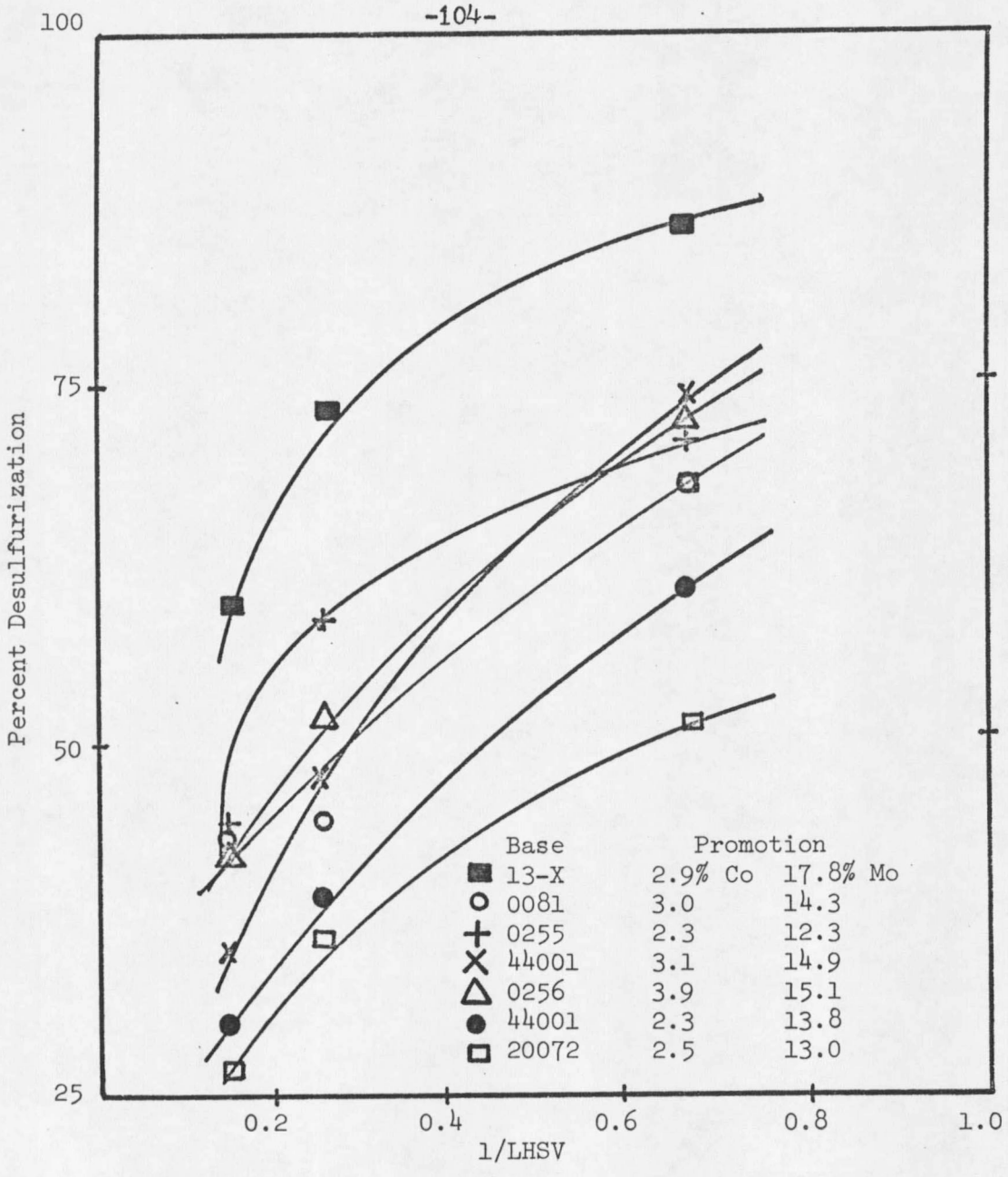


FIGURE 33
Percent Desulfurization vs. 1/LHSV at 725°F for
Crystalline Bases 3% Co 15% Mo Range

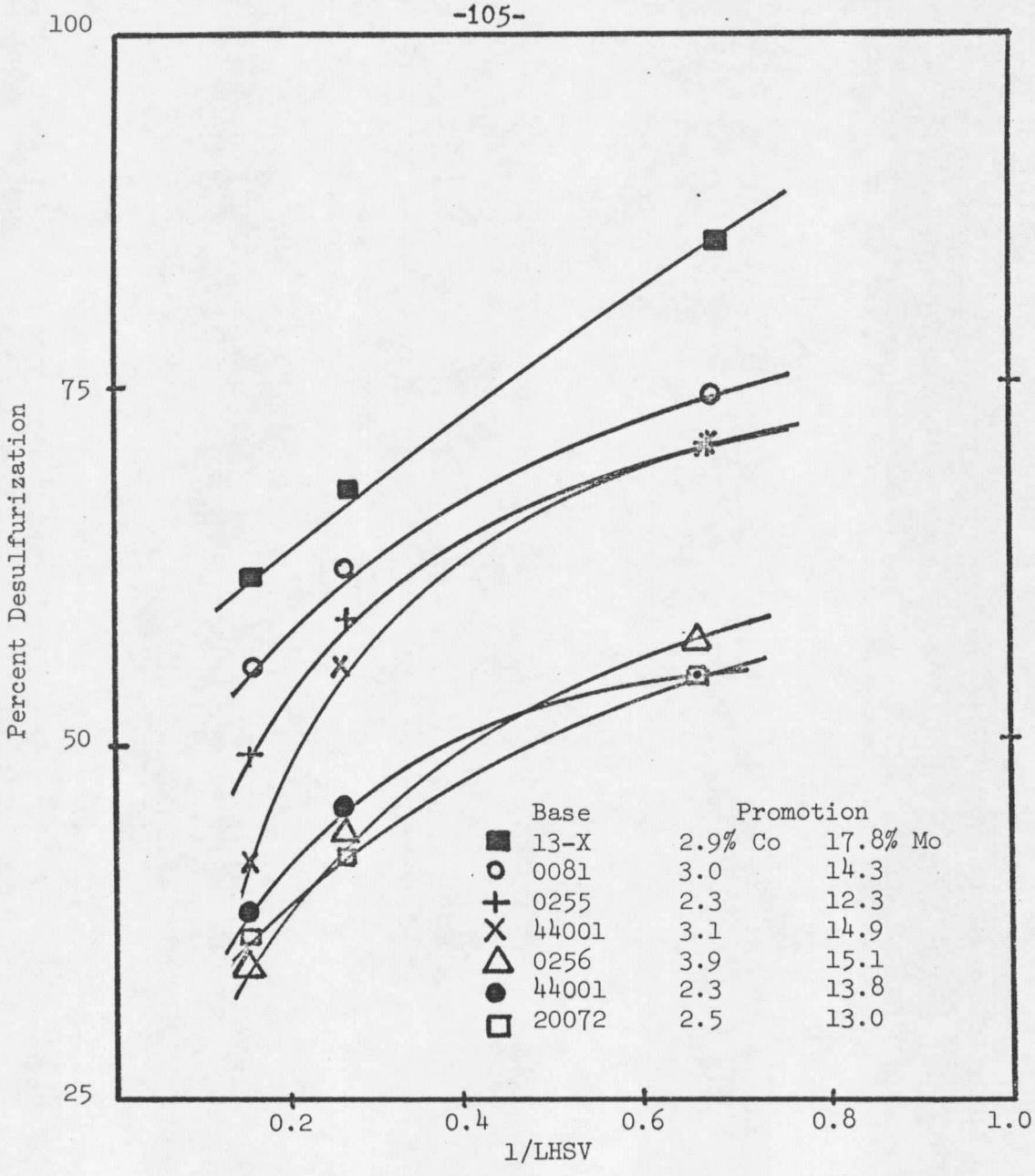


FIGURE 34
Percent Desulfurization vs. 1/LHSV at 800°F for
Crystalline Bases 3% Co 15% Mo Range

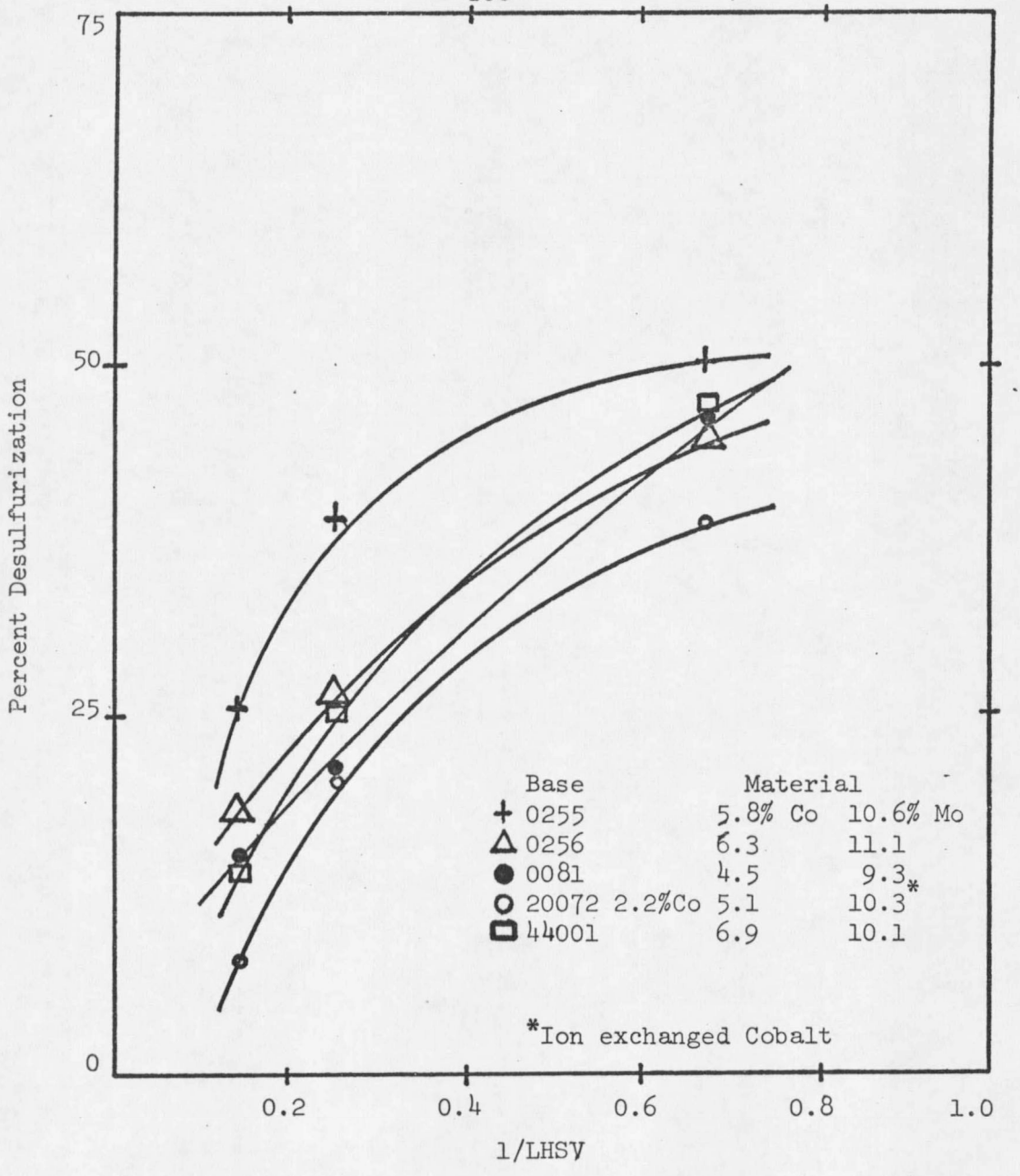


FIGURE 35
Percent Desulfurization vs. 1/LHSV at 650°F
For Crystalline Bases 5 % Co 10% Mo Range

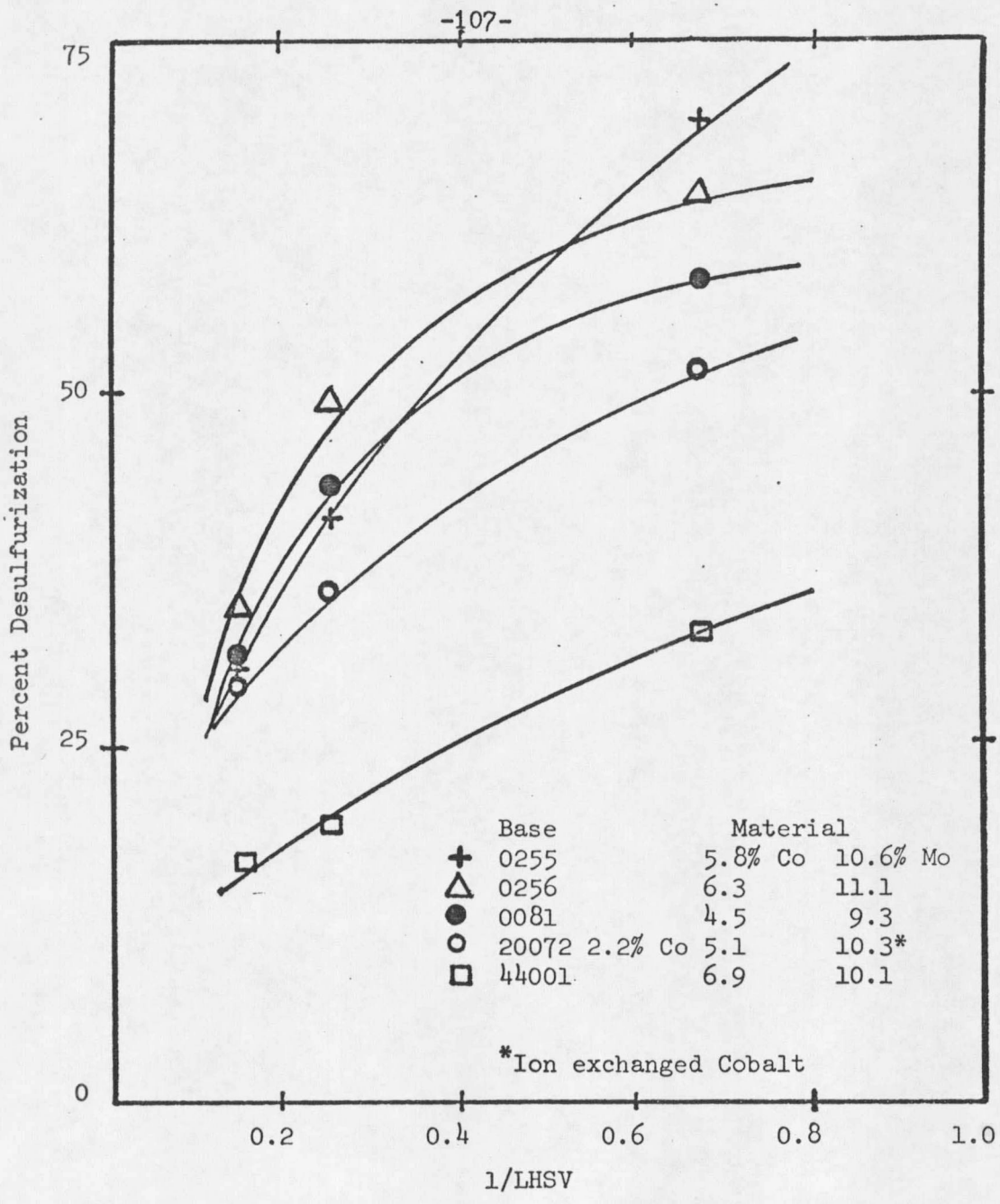


FIGURE 36
Percent Desulfurization vs. 1/LHSV at 725°F
For Crystalline Bases 5 % Co 10% Mo Range

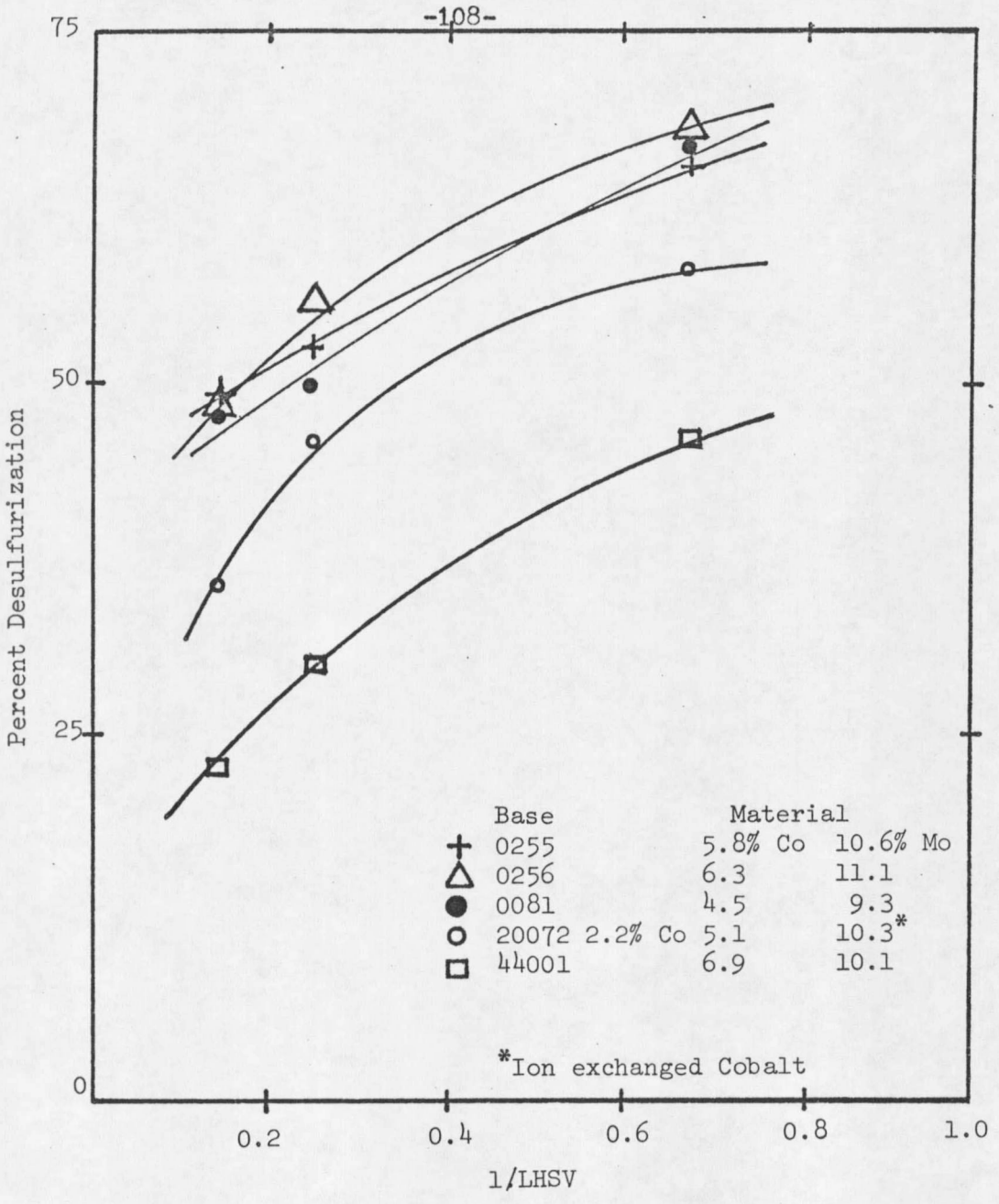


FIGURE 37
Percent Desulfurization vs. 1/LHSV at 800°F
For Crystalline Bases 5 % Co 10% Mo Range

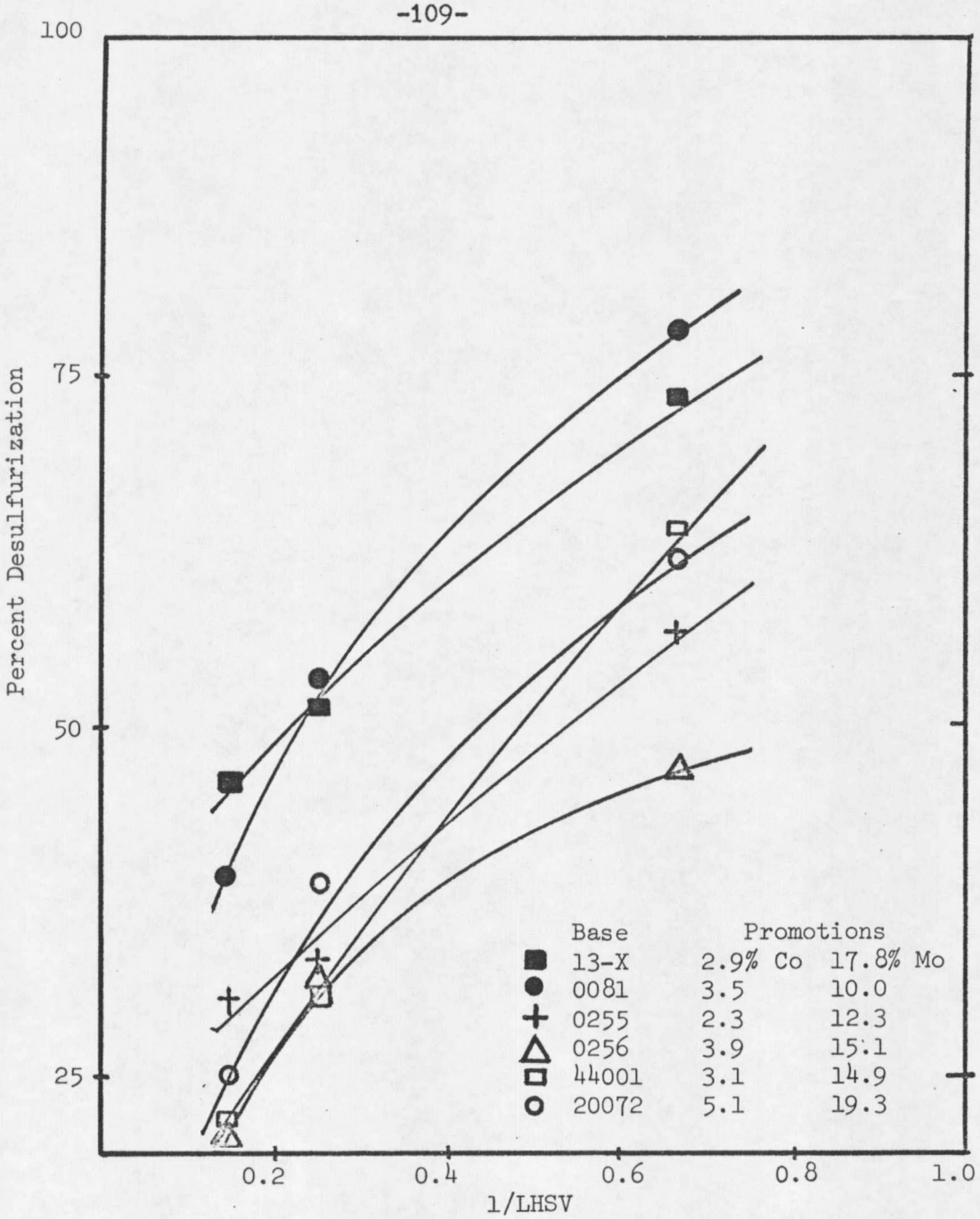


FIGURE 38
Percent Desulfurization vs. 1/LHSV at 650°F
for Best Catalyst Promotions

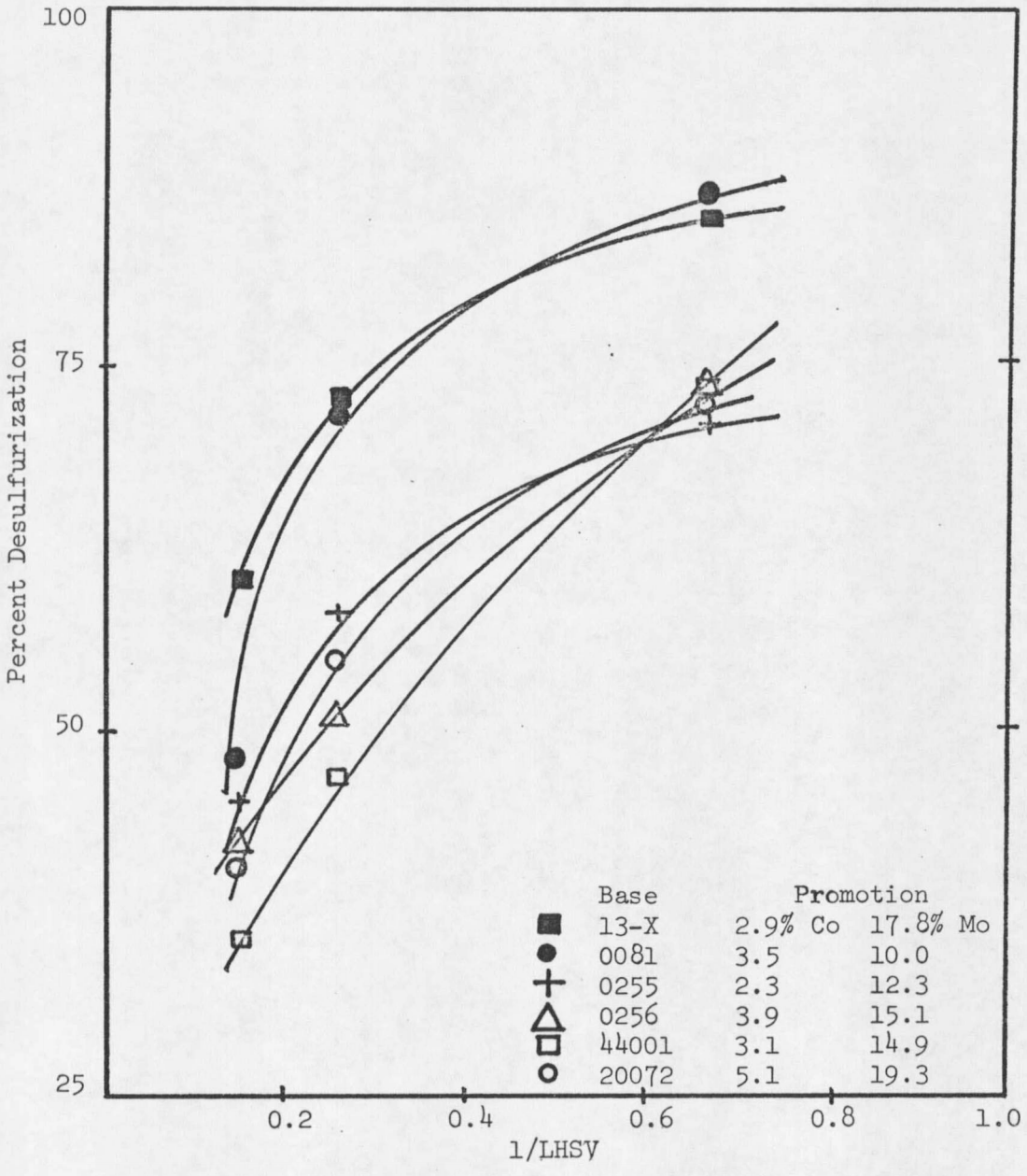


FIGURE 39
Percent Desulfurization vs. 1/LHSV at 725°F
for Best Catalyst Promotions

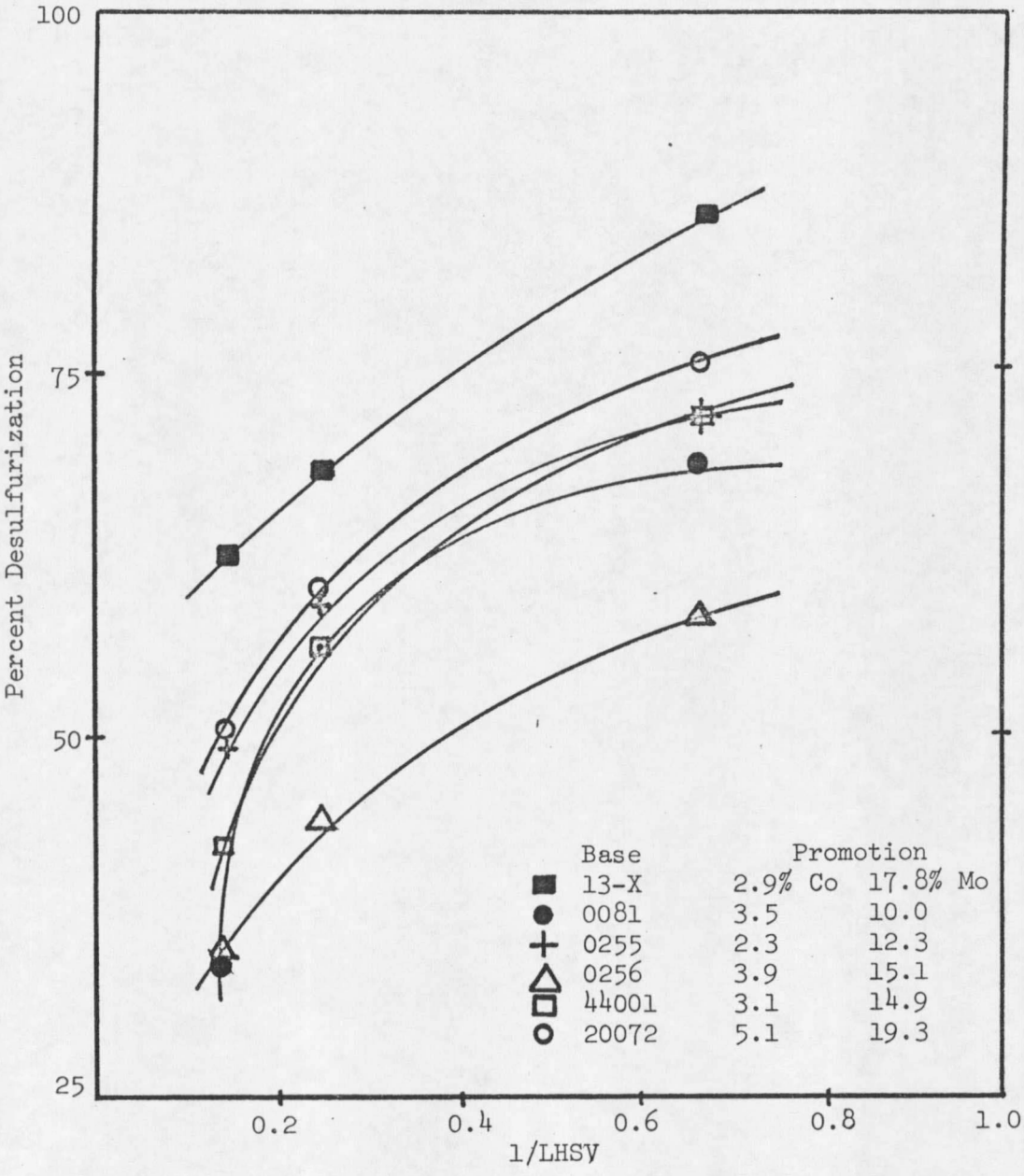


FIGURE 40
Percent Desulfurization vs. 1/LHSV at 800°F
for Best Catalyst Promotions

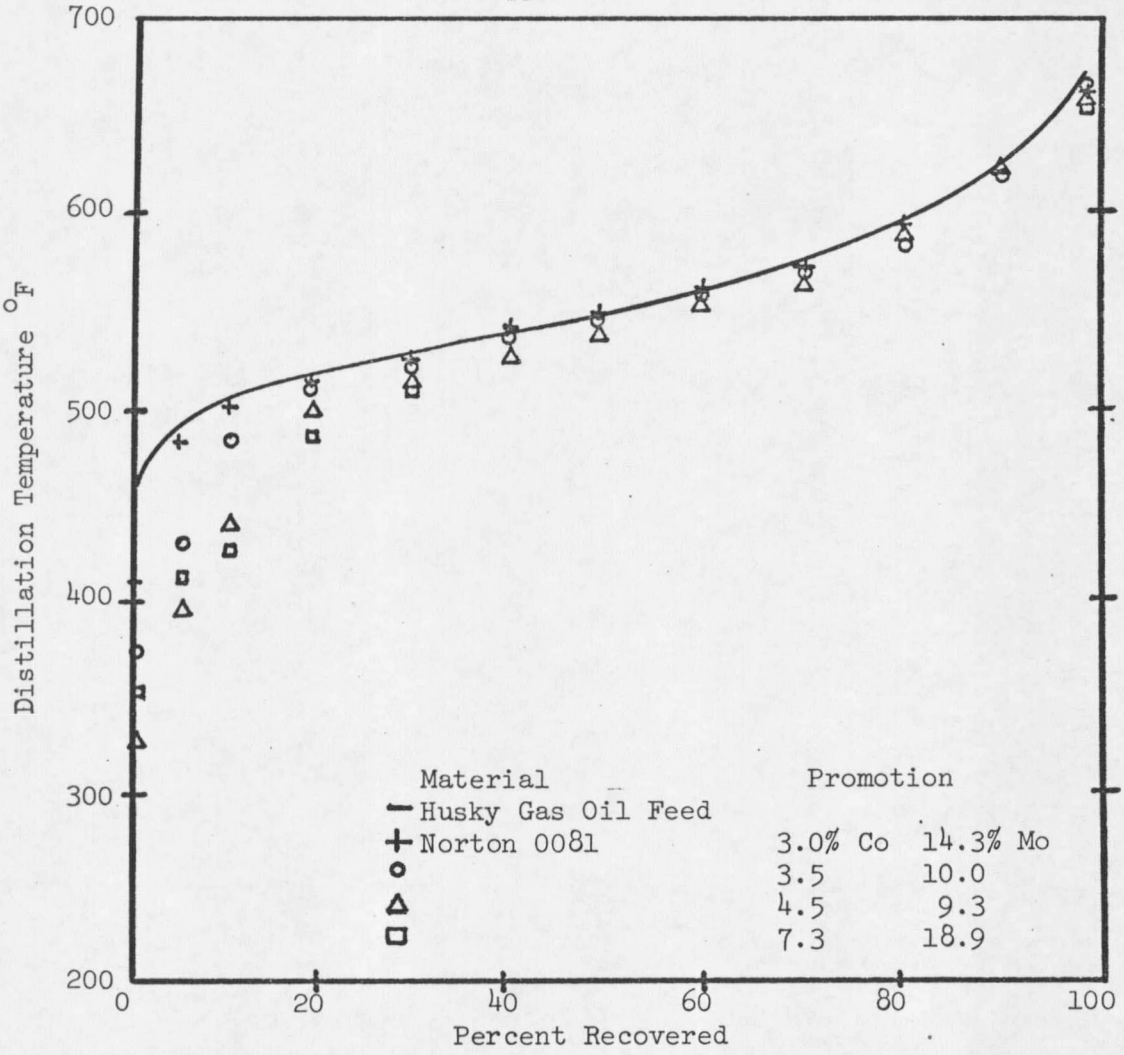


FIGURE 41
Distillation Temperature vs. Percent Recovered
for Norton 0081

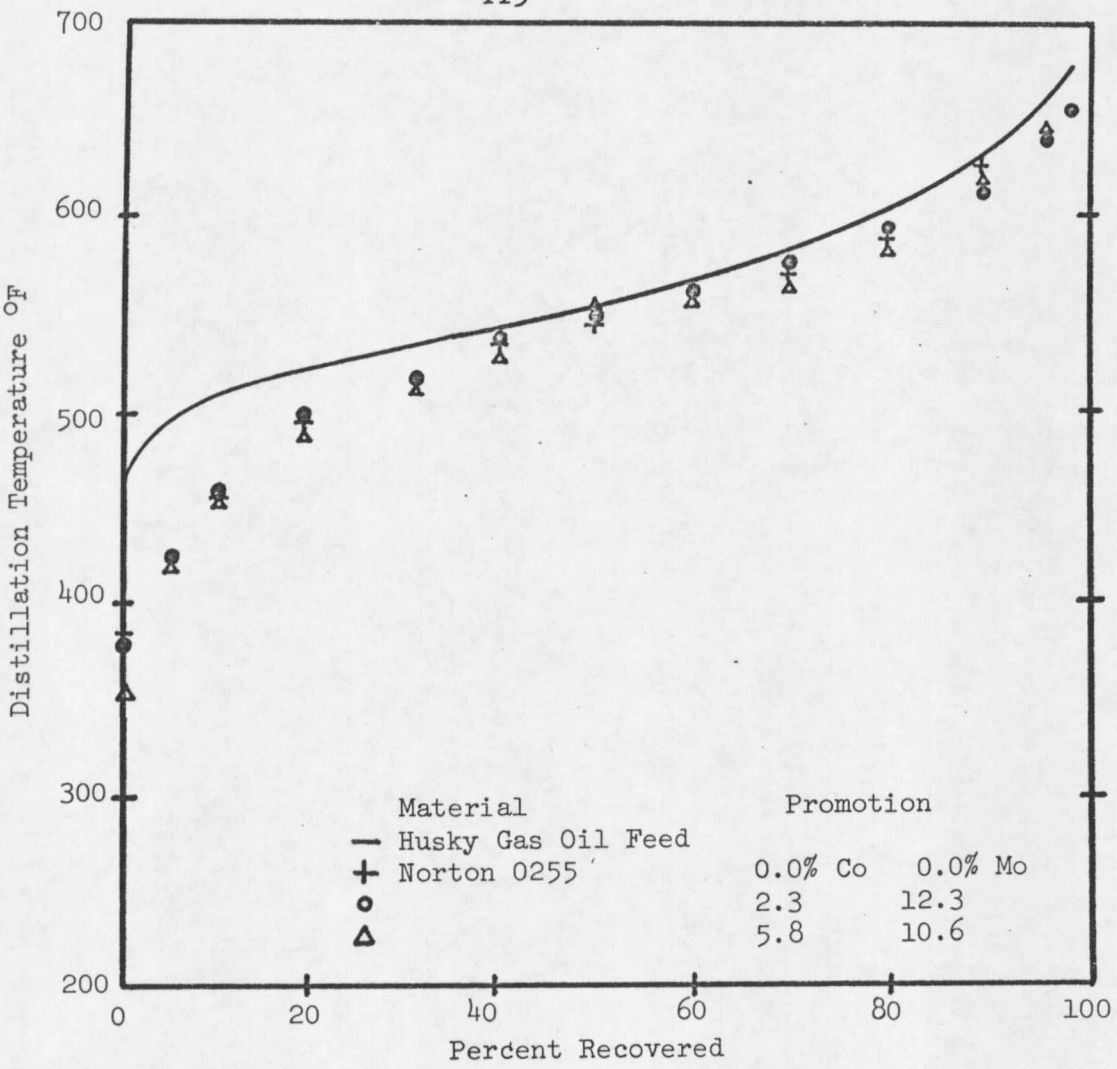


FIGURE 42
Distillation Temperature vs. Percent Recovered
for Norton 0255

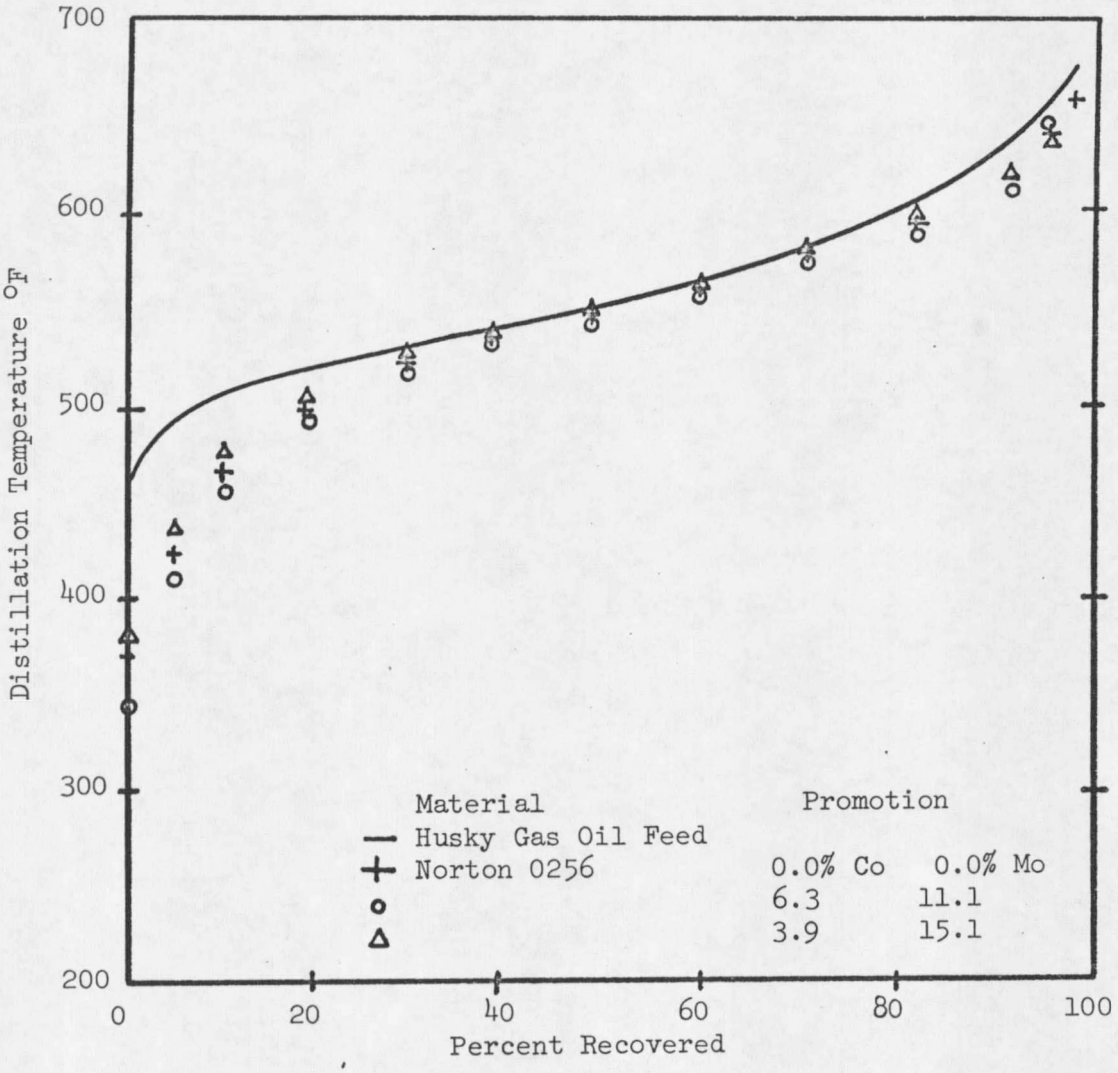


FIGURE 43
Distillation Temperature vs. Percent Recovered
for Norton 0256

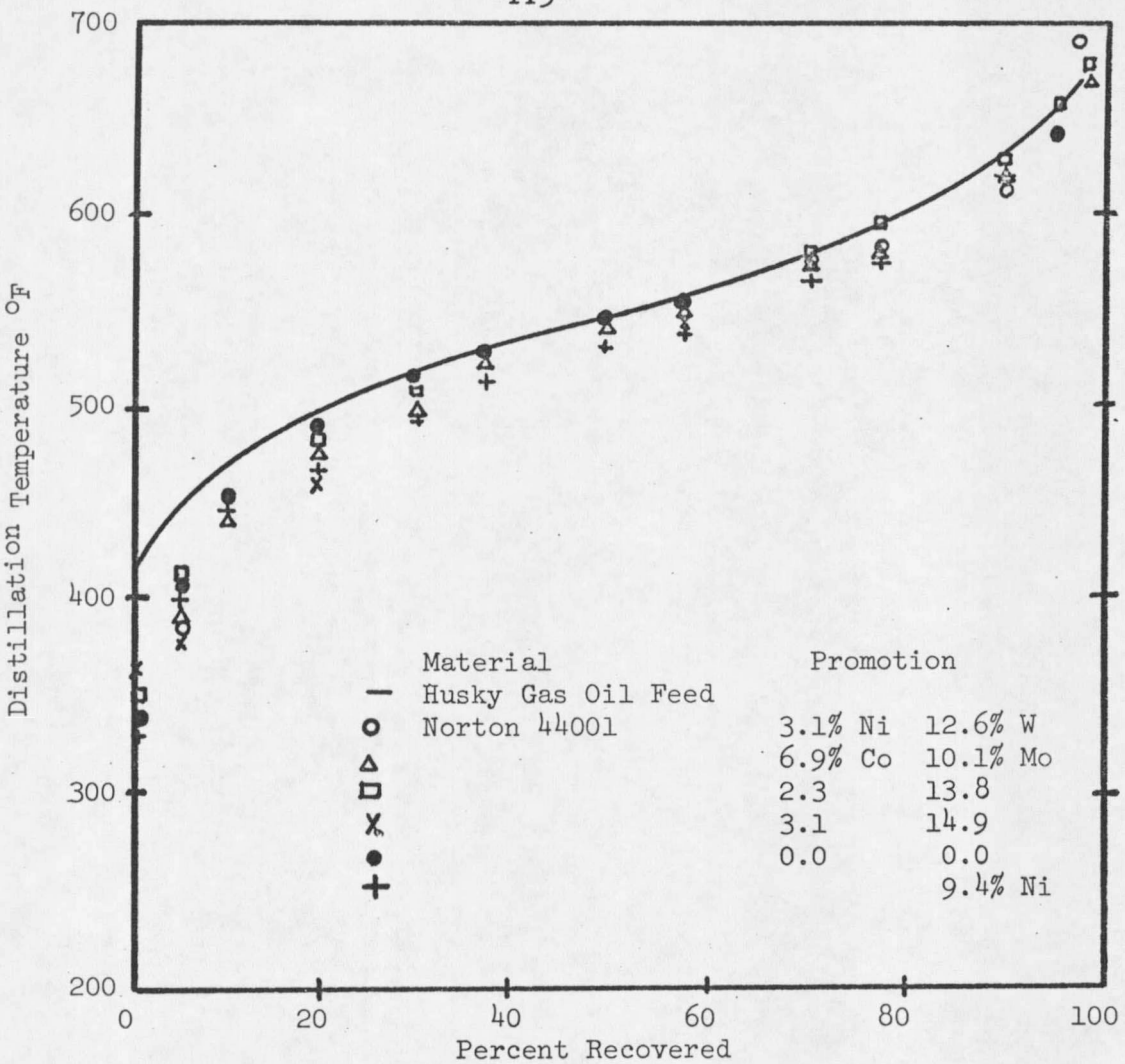


FIGURE 44
Distillation Temperature vs. Percent Recovered
for Norton 44001

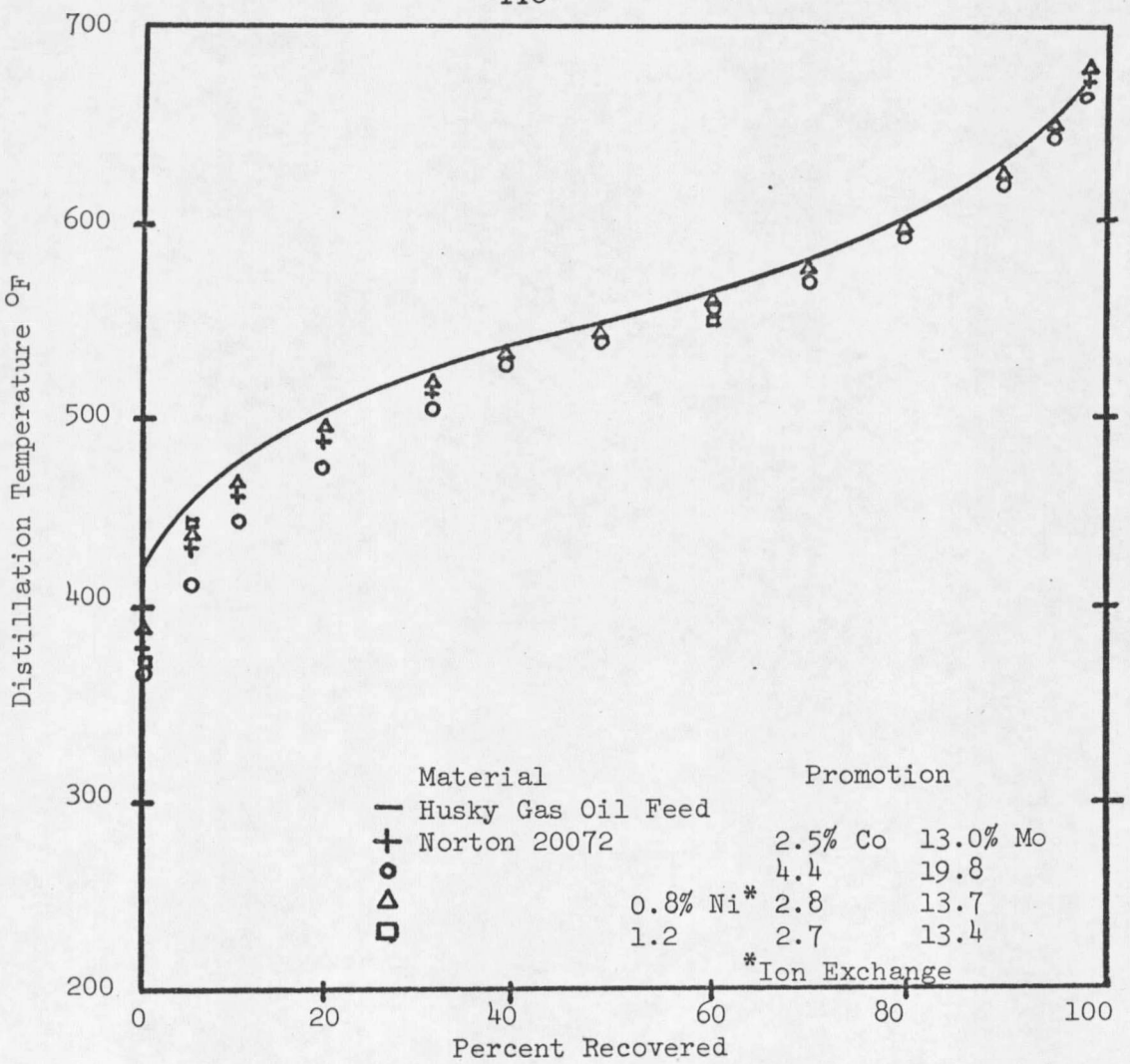


FIGURE 45
Distillation Temperature vs. Percent Recovered
for Norton 20072

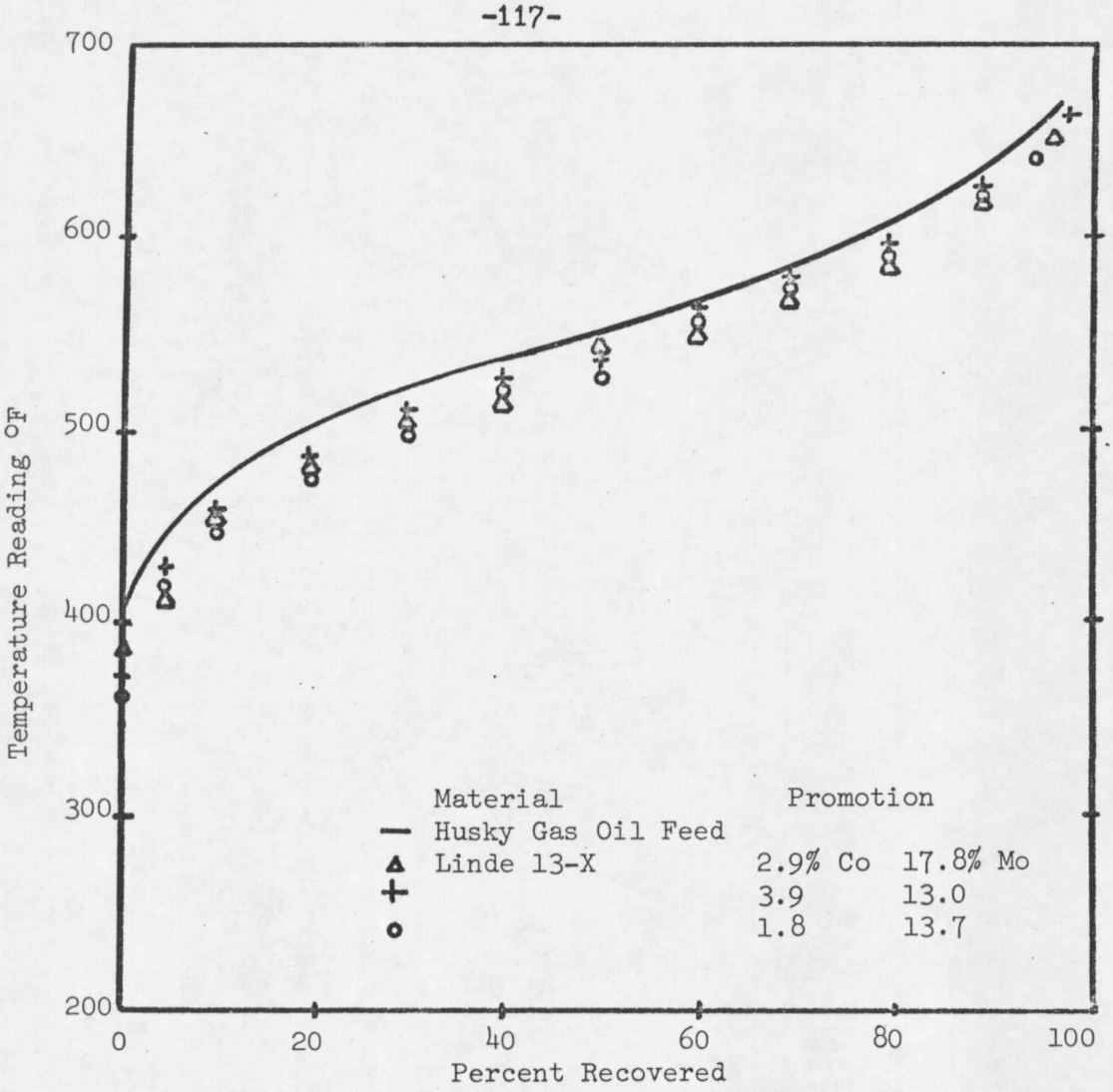


FIGURE 46
Distillation Temperature vs. Percent Recovered
for Linde 13-X

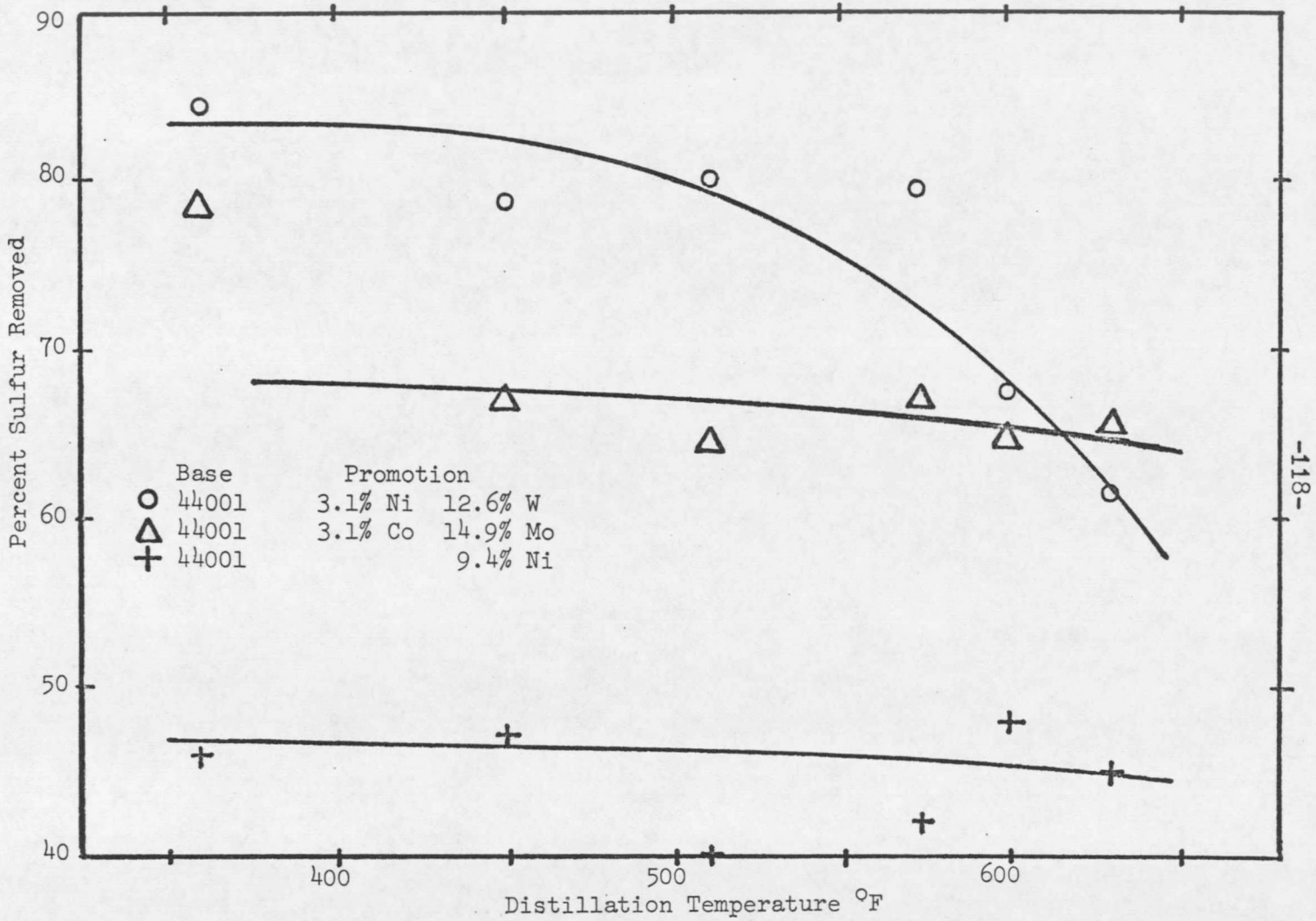


FIGURE 47

Percent Sulfur Removed vs. Distillation Temperature for Samples taken at LHSV 1.5 800°F

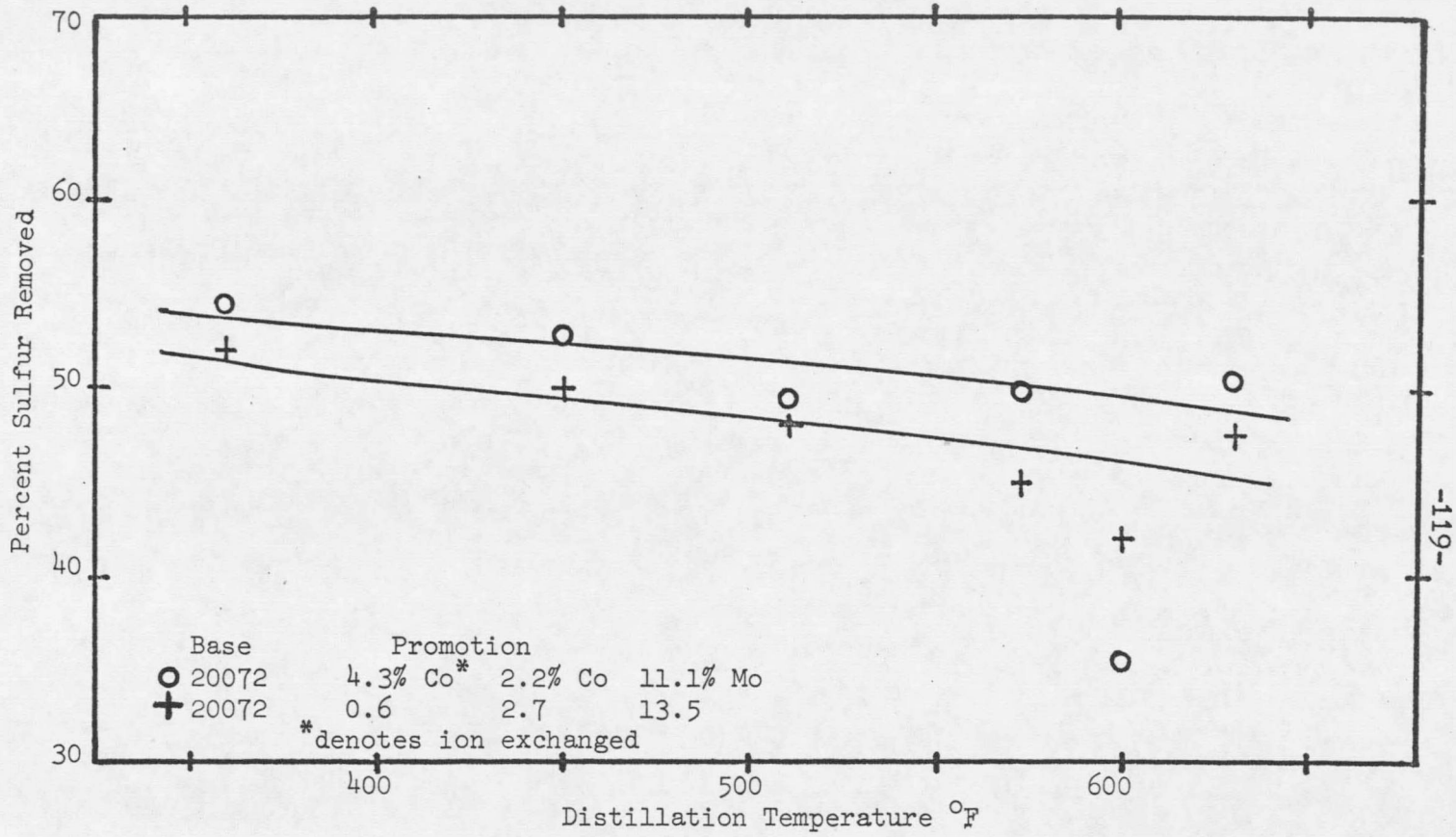


FIGURE 48
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

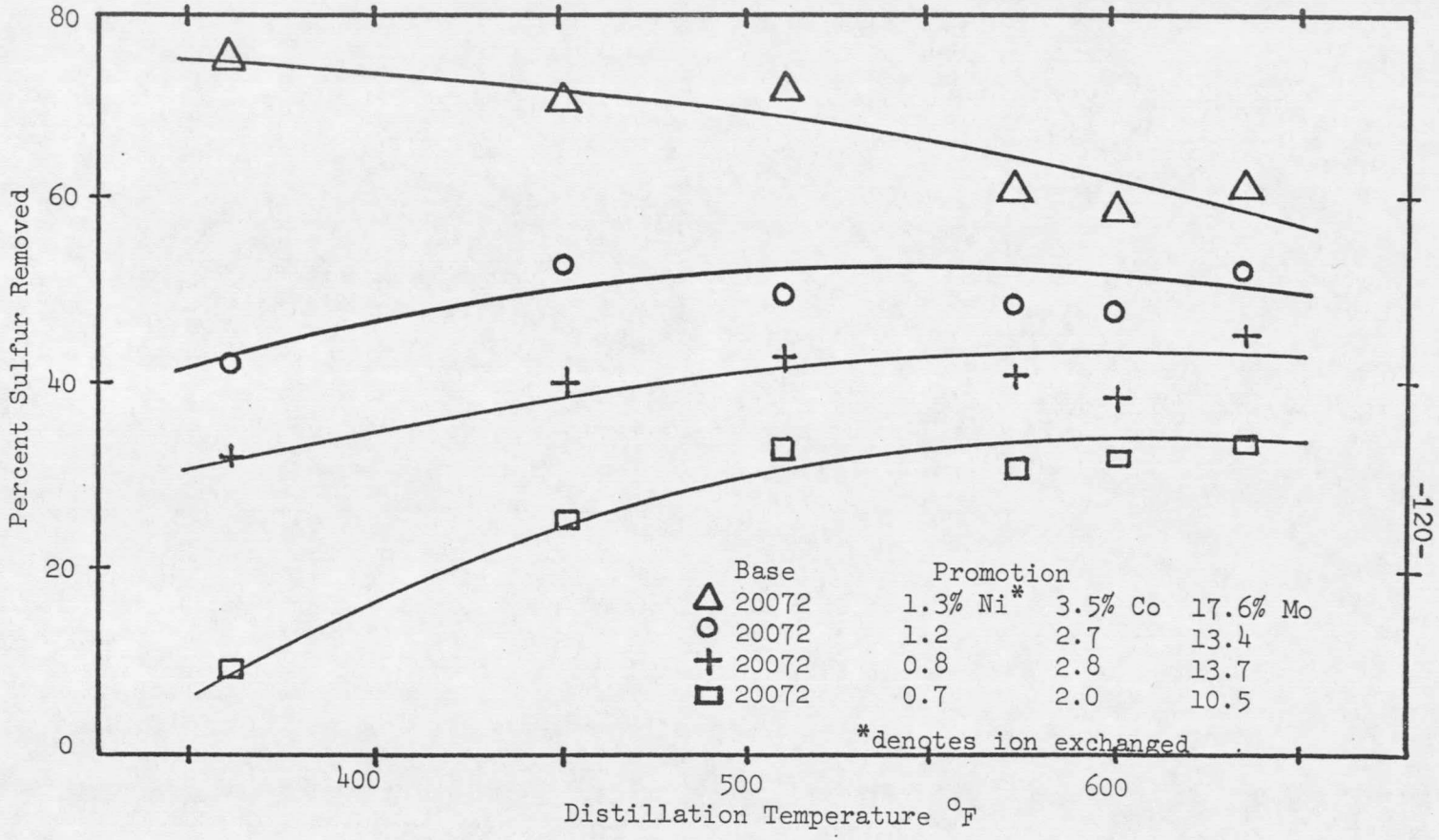


FIGURE 49
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

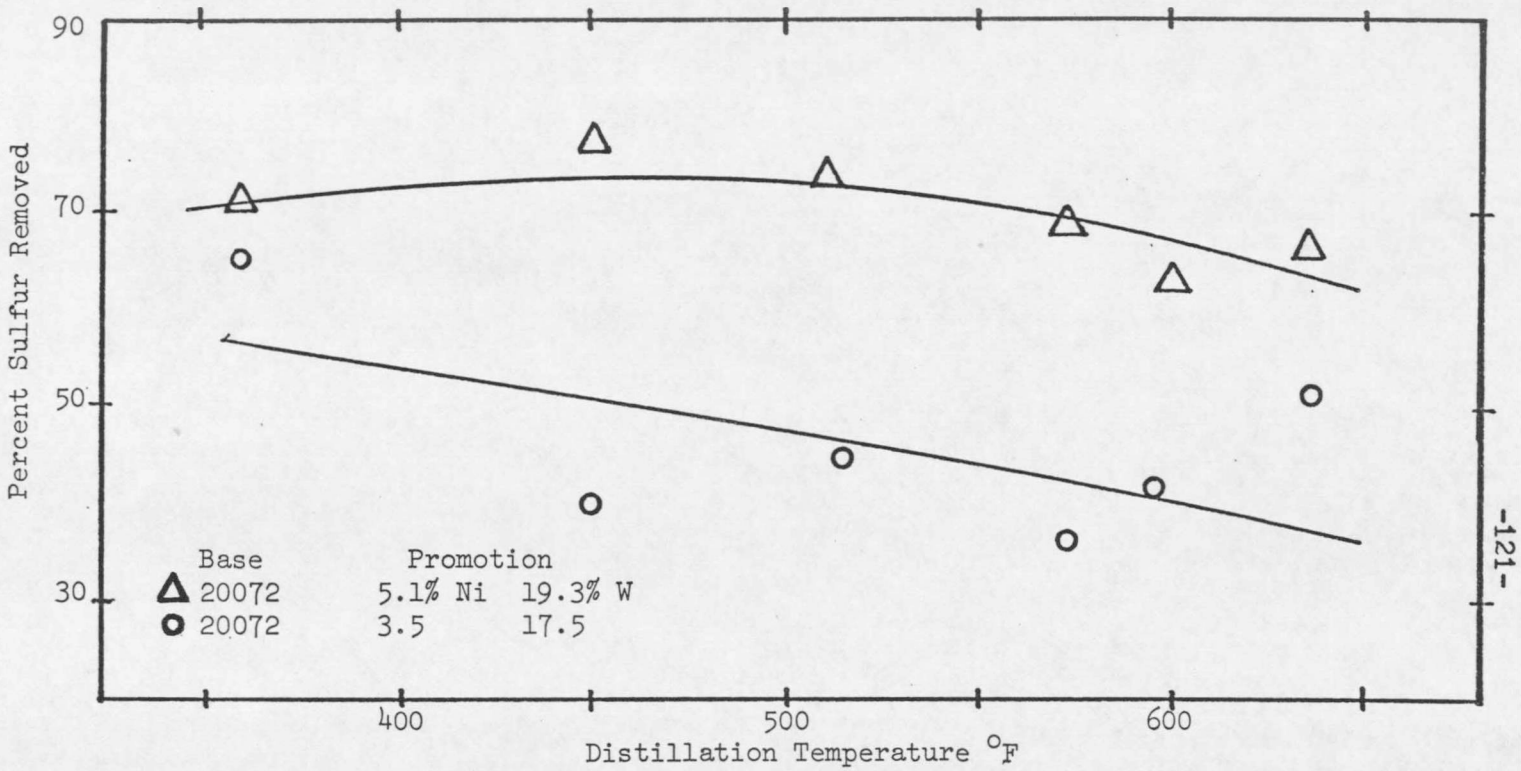


FIGURE 50
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

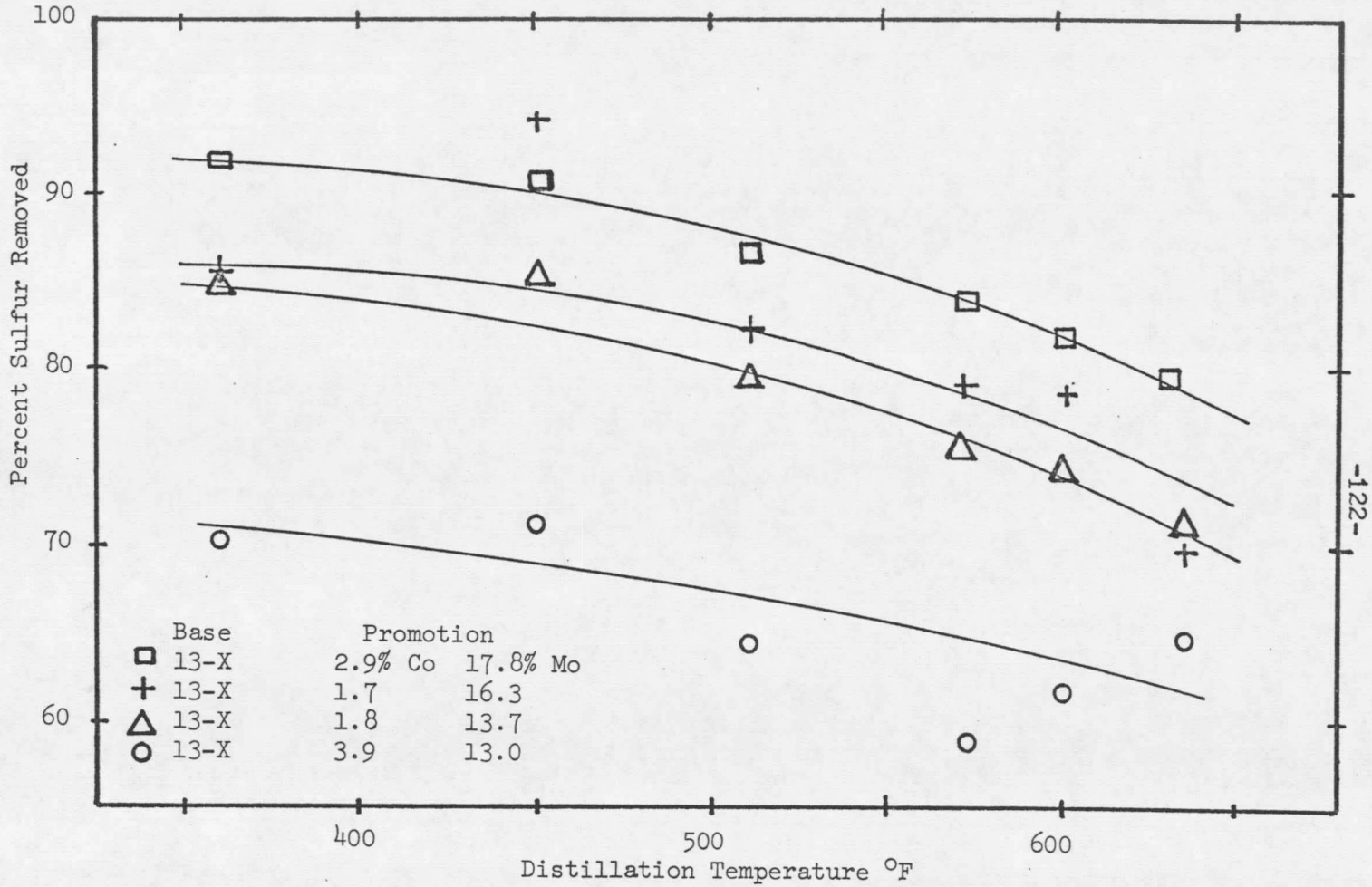


FIGURE 51
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

TABLE VII

Molecular Sieve Base Materials
°API Gravity Product

Base	Promotion	°API
13-X	None-Base Material	30.7
	3.9% Co 13.0% Mo	31.4
	1.8 13.7	31.3
	1.7 16.3	32.1
	2.9 17.8	32.5
44001	9.4% Ni	31.4
20072	2.5% Co 13.0% Mo	31.1
	4.4 Co 19.8 Mo	32.4
	3.5 Ni 17.5 W	31.0
	5.1 Ni 19.3 W	32.3
	0.7% Ni 2.0 Co 10.5 Mo	31.9
	1.2 Ni 2.7 Co 13.4 Mo	32.8
	1.3 Ni 3.5 Co 17.6 Mo	32.3
	4.3 Co 2.2 Co 11.1 Mo	31.6
	0.6 Co 2.7 Co 13.5 Mo	31.5

Feed 30.4 °API @ 60°F

Samples taken at LHSV 1.5 800°F

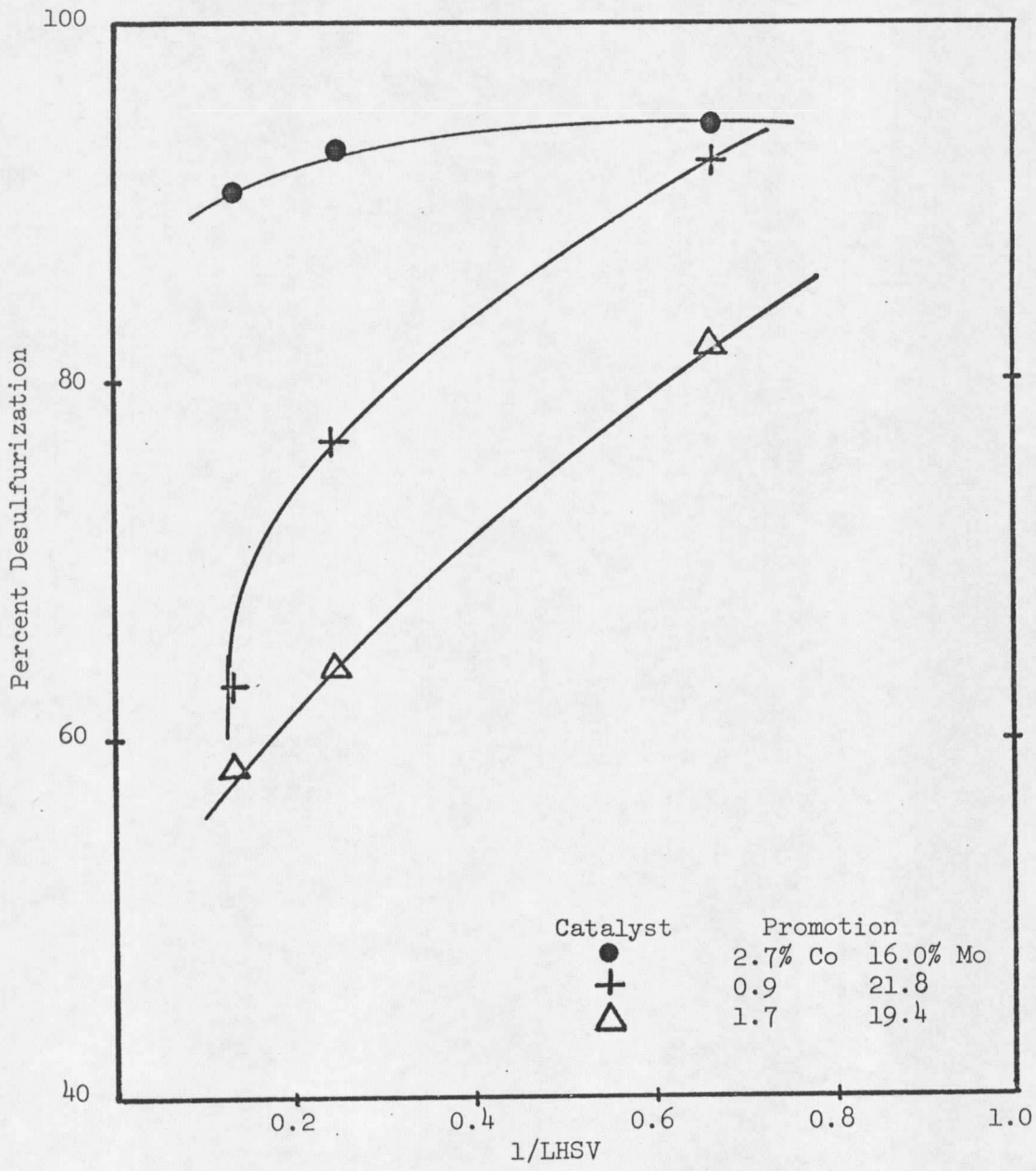


FIGURE 52
Percent Desulfurization vs. 1/LHSV at 650°F
for Nalcat 2910-A

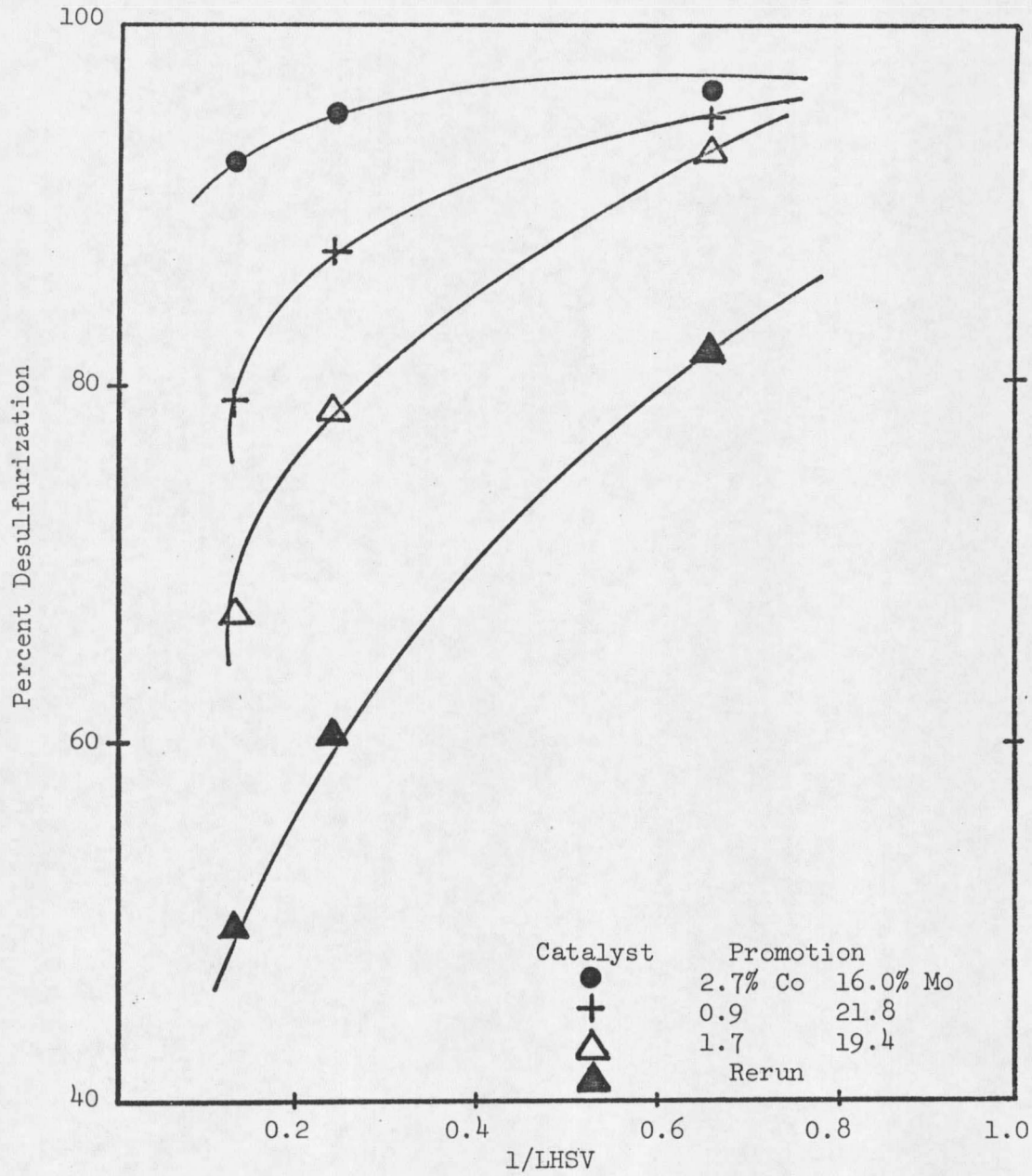


FIGURE 53
Percent Desulfurization vs. 1/LHSV at 725°F
for Nalcat 2910-A

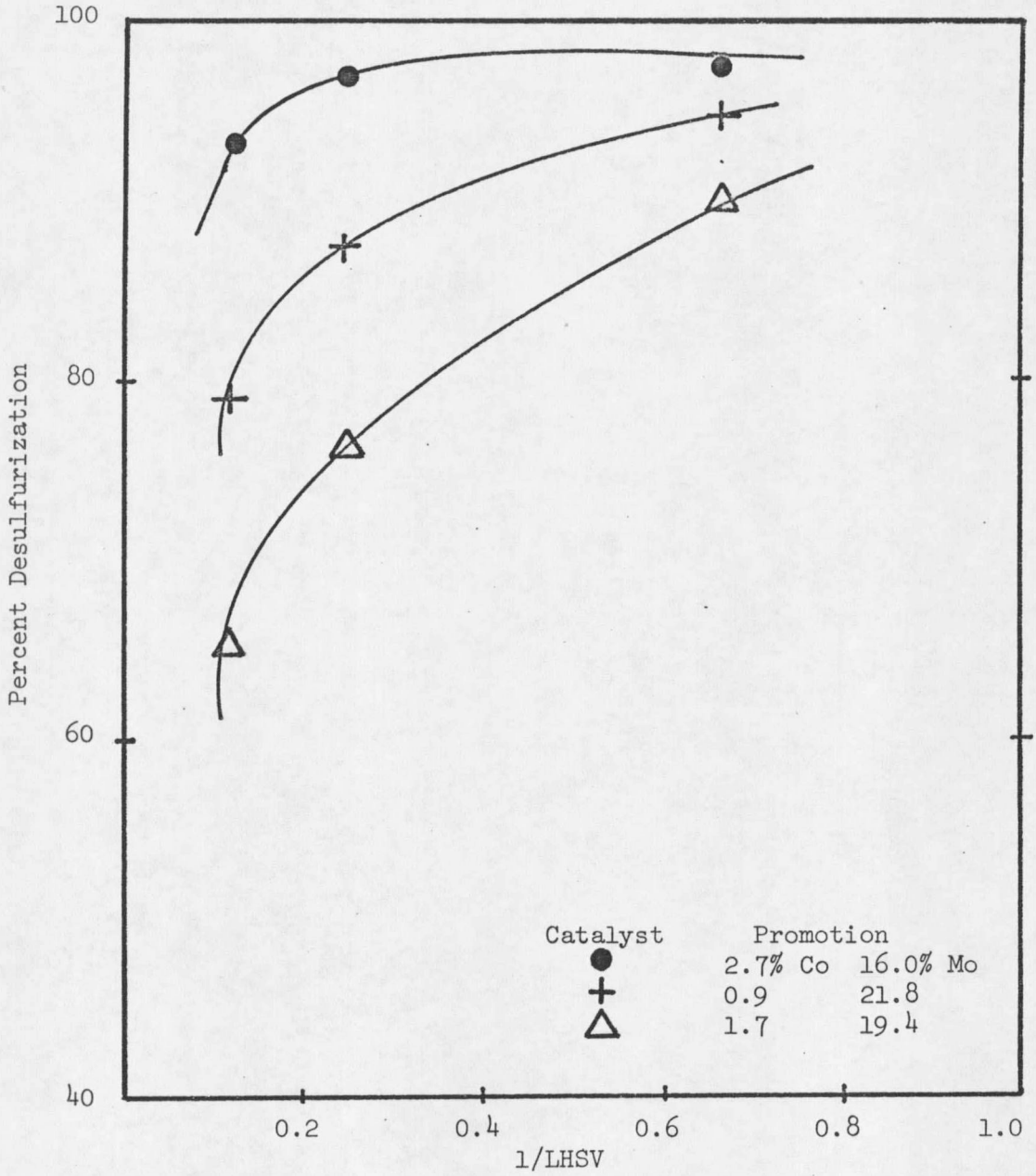


FIGURE 54
Percent Desulfurization vs. 1/LHSV at 800°F
for Nalcat 2910-A

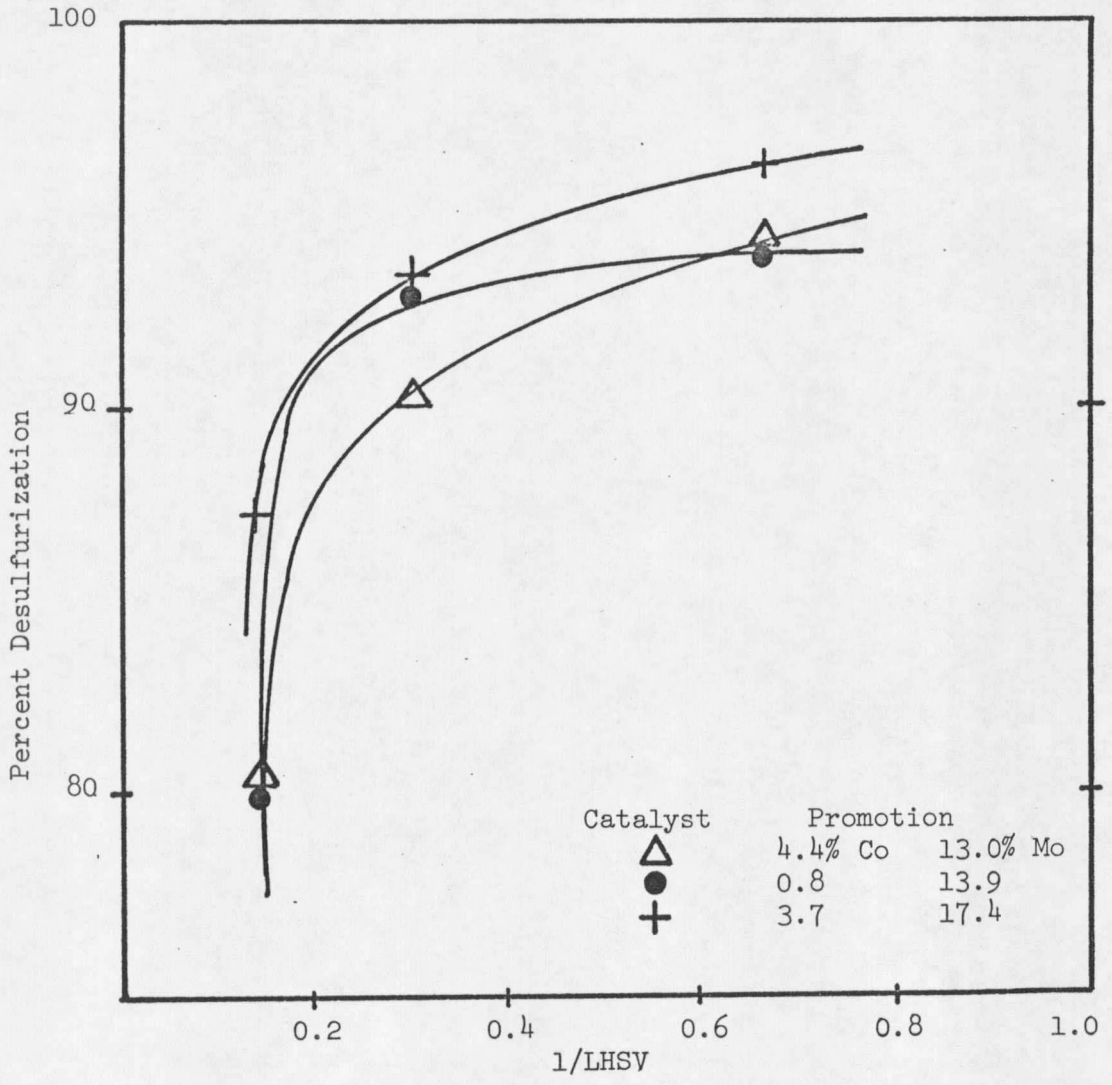


FIGURE 55
Percent Desulfurization vs. 1/LHSV at 650°F
for Promoted Nalcat 2910-B

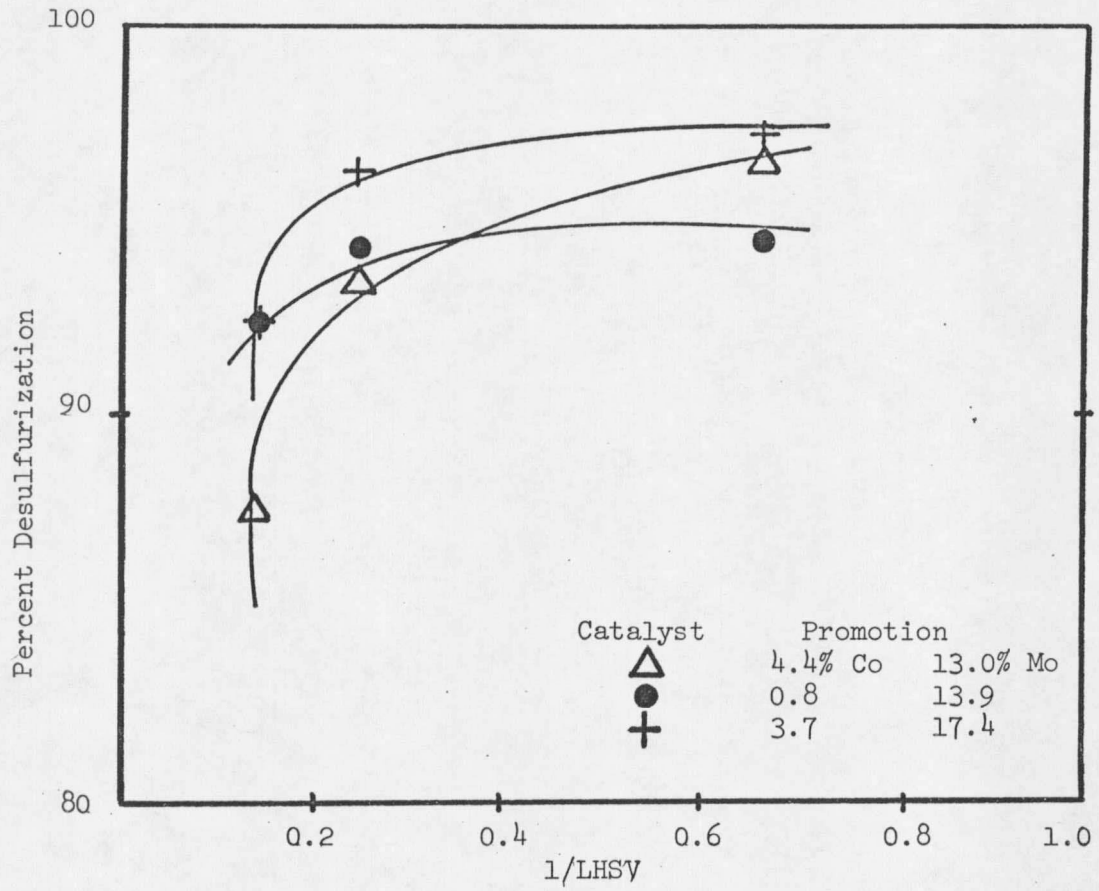


FIGURE 56
Percent Desulfurization vs. 1/LHSV at 725°F
for Promoted Nalcat 2910-B

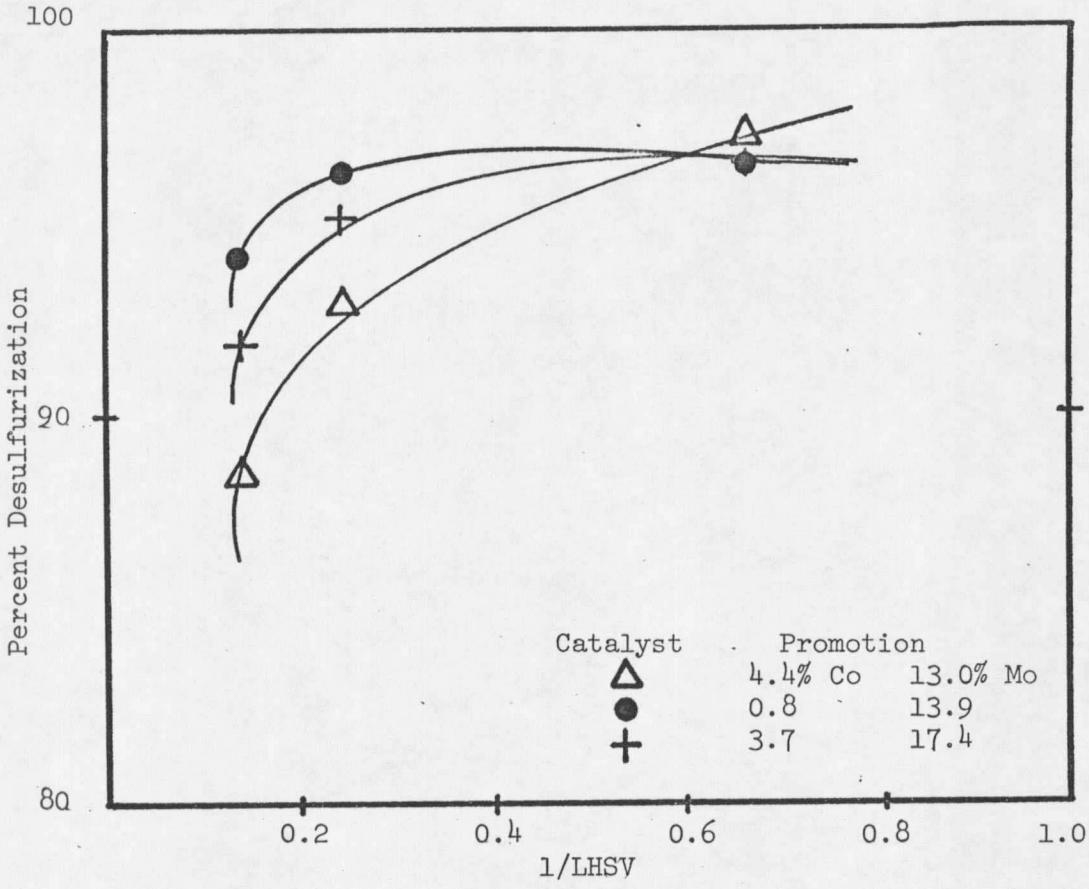


FIGURE 57
Percent Desulfurization vs. 1/LHSV at 800°F
for Promoted Nalcat 2910-B

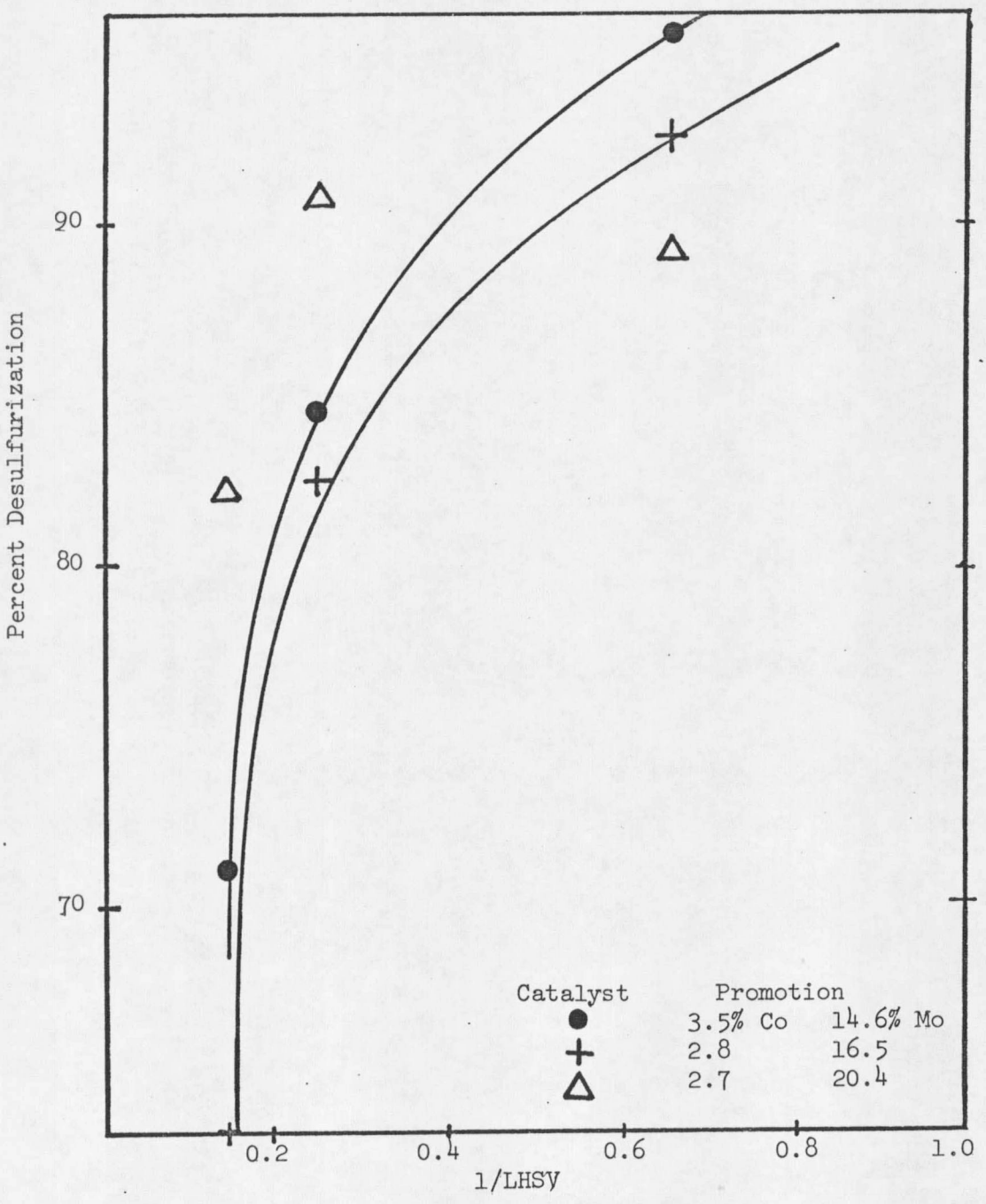


FIGURE 58
Percent Desulfurization vs. 1/LHSV at 650°F
for Harshaw 1802

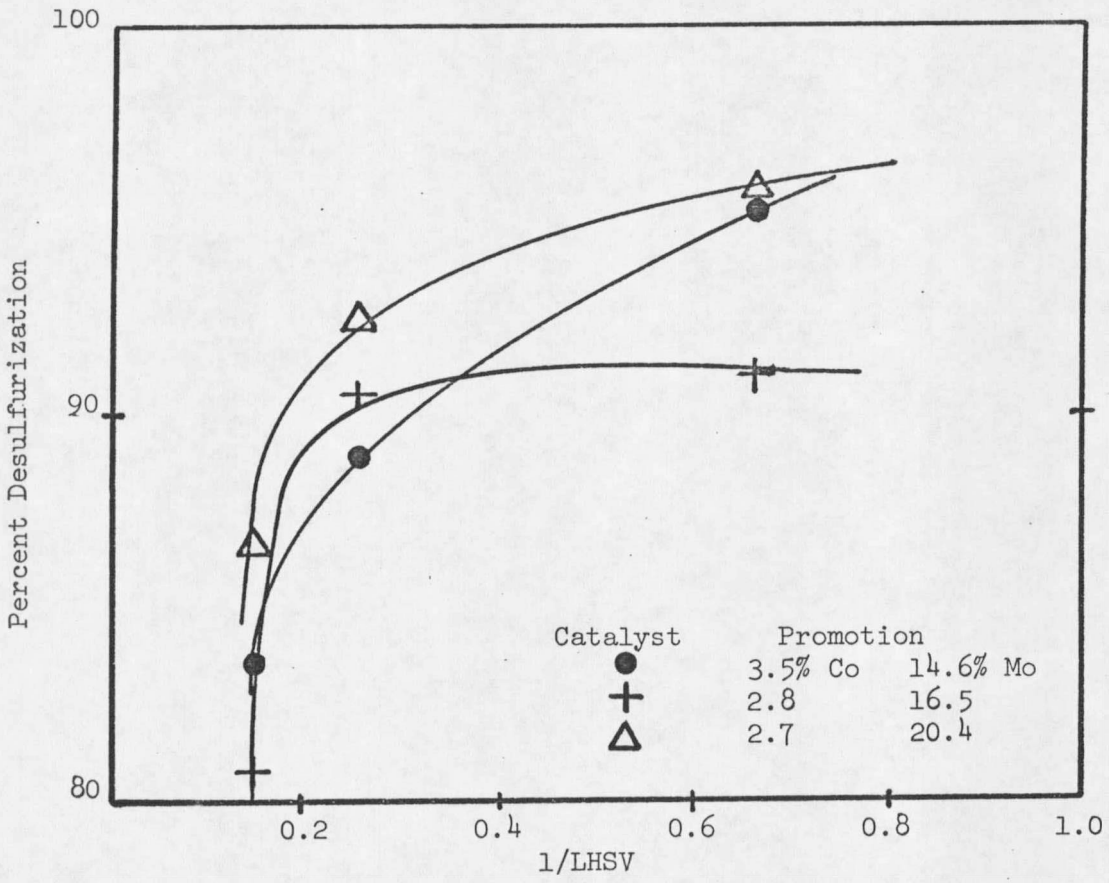


FIGURE 59
Percent Desulfurization vs. 1/LHSV at 725°F
for Harshaw 1802

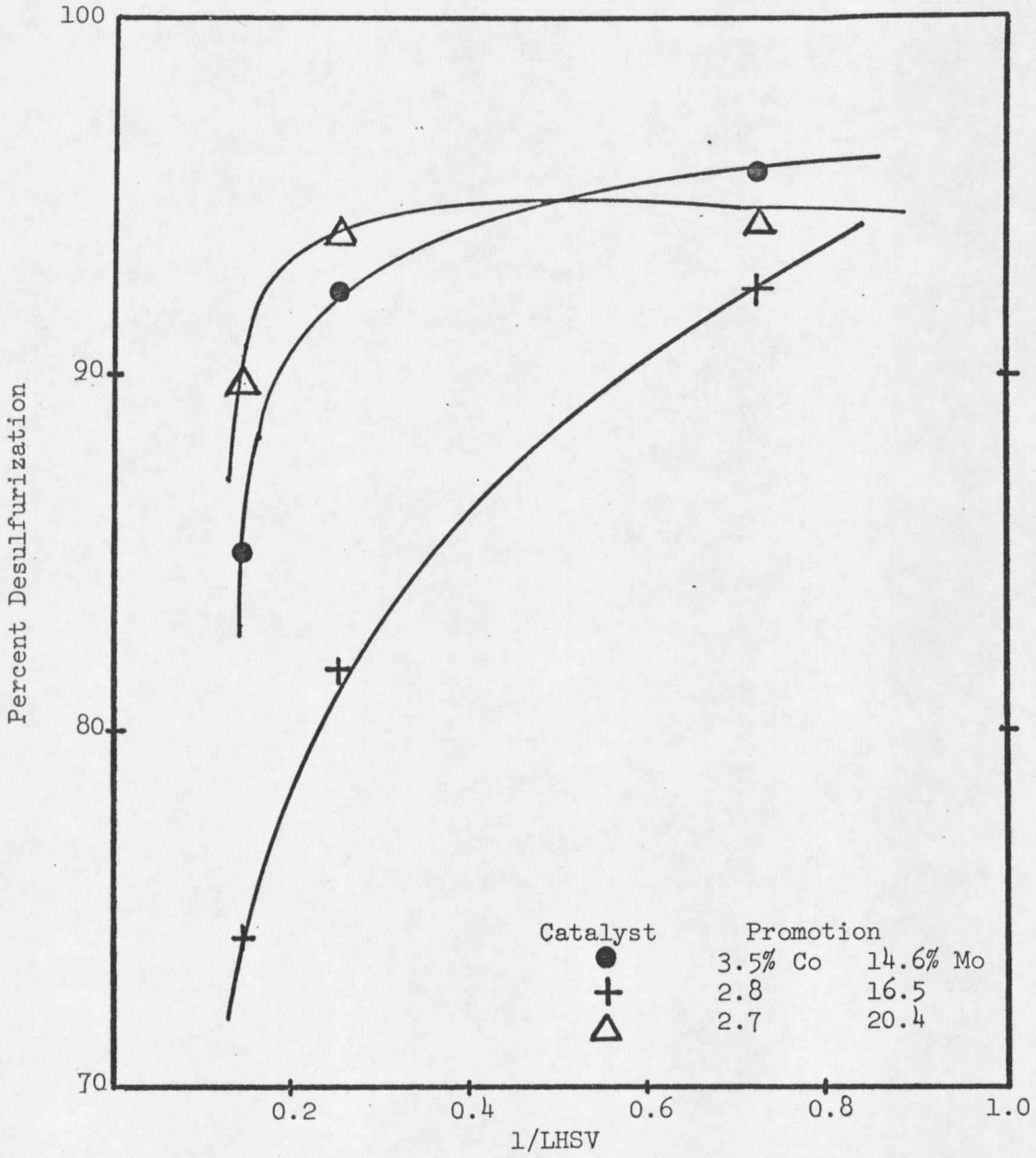


FIGURE 60
Percent Desulfurization vs. 1/LHSV at 800°F
for Harshaw 1802

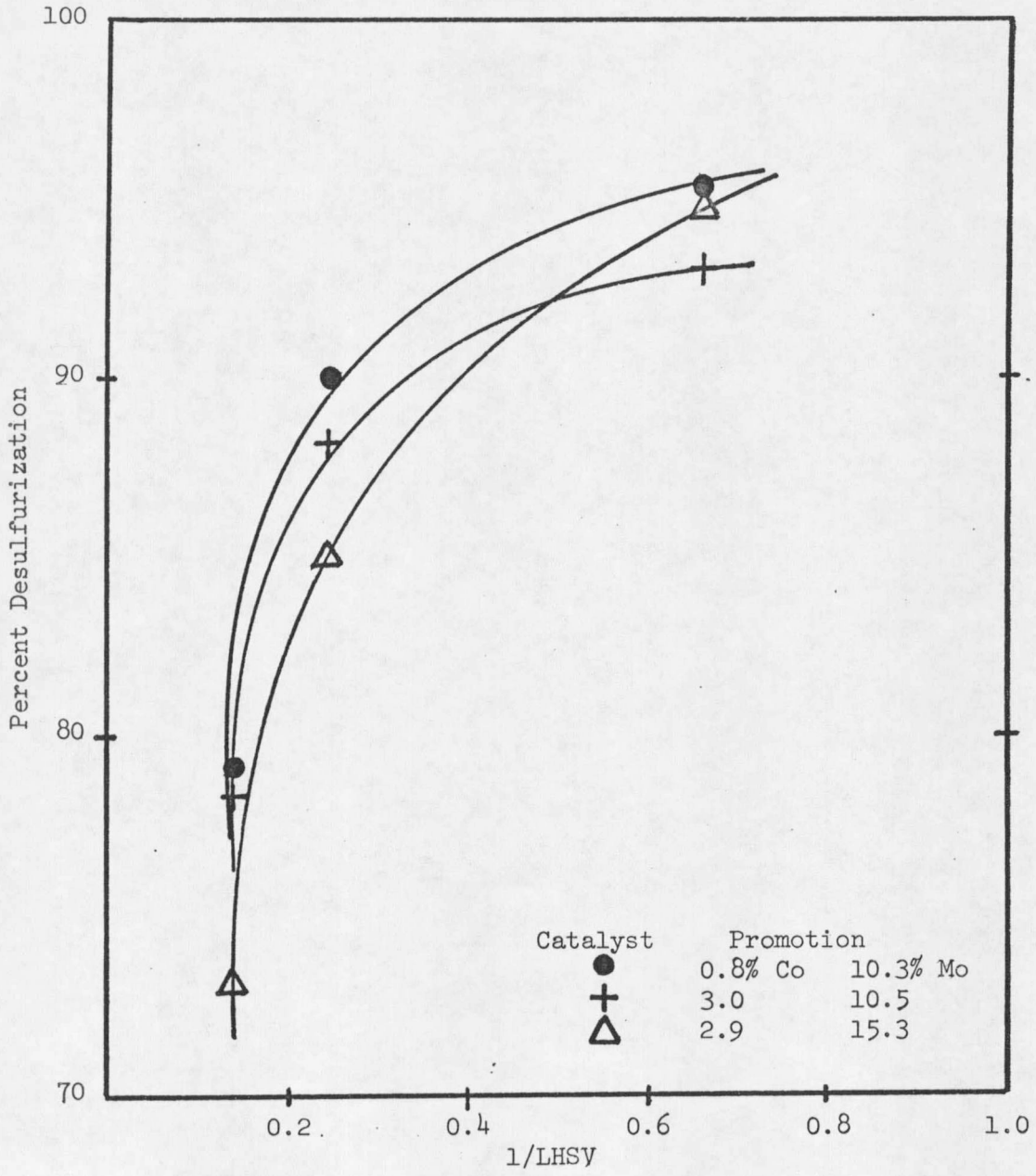


FIGURE 61
Percent Desulfurization vs. 1/LHSV at 650°F
for Harshaw 1602

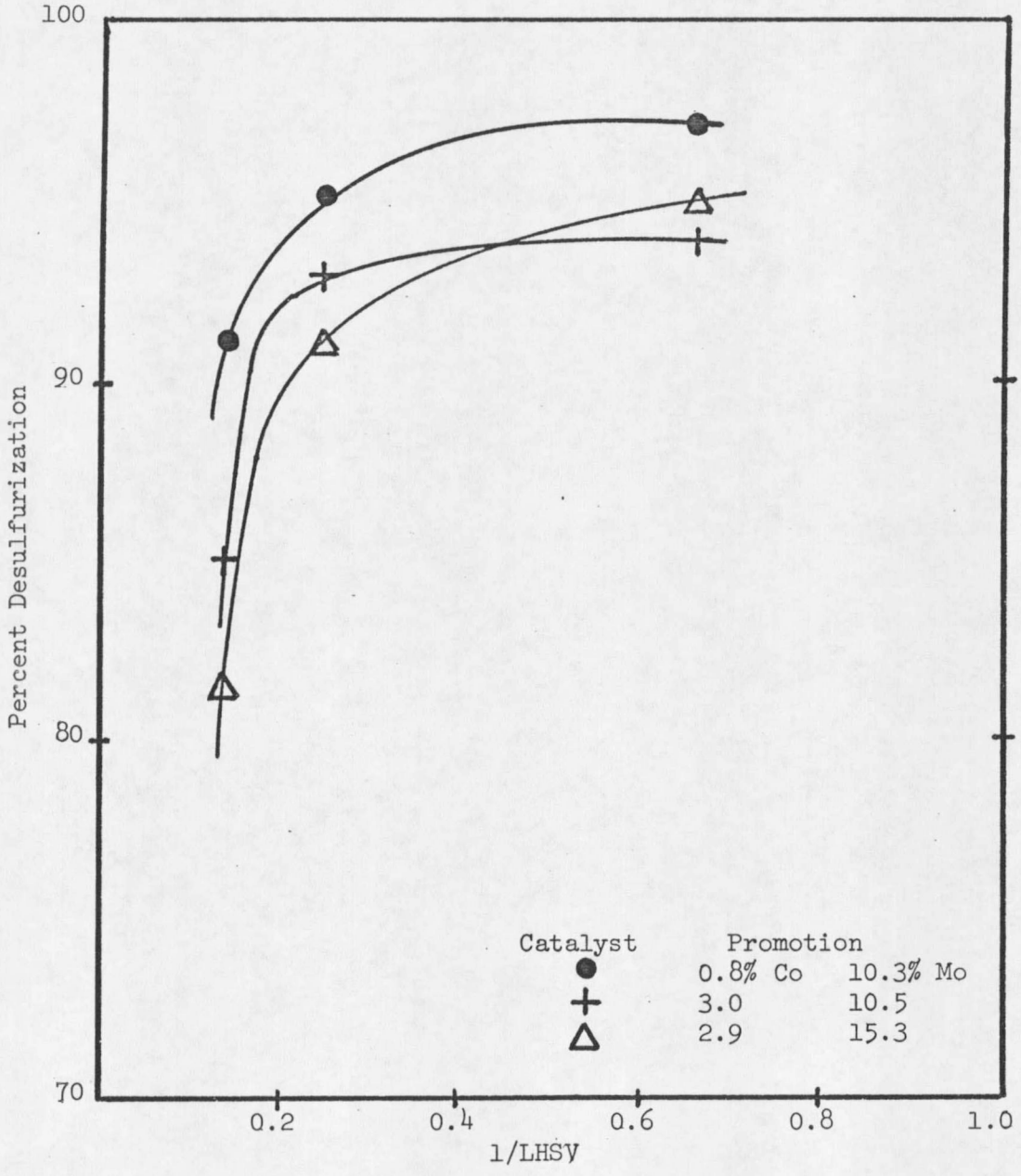


FIGURE 62
Percent Desulfurization vs. 1/LHSV at 725°F
for Harshaw 1602

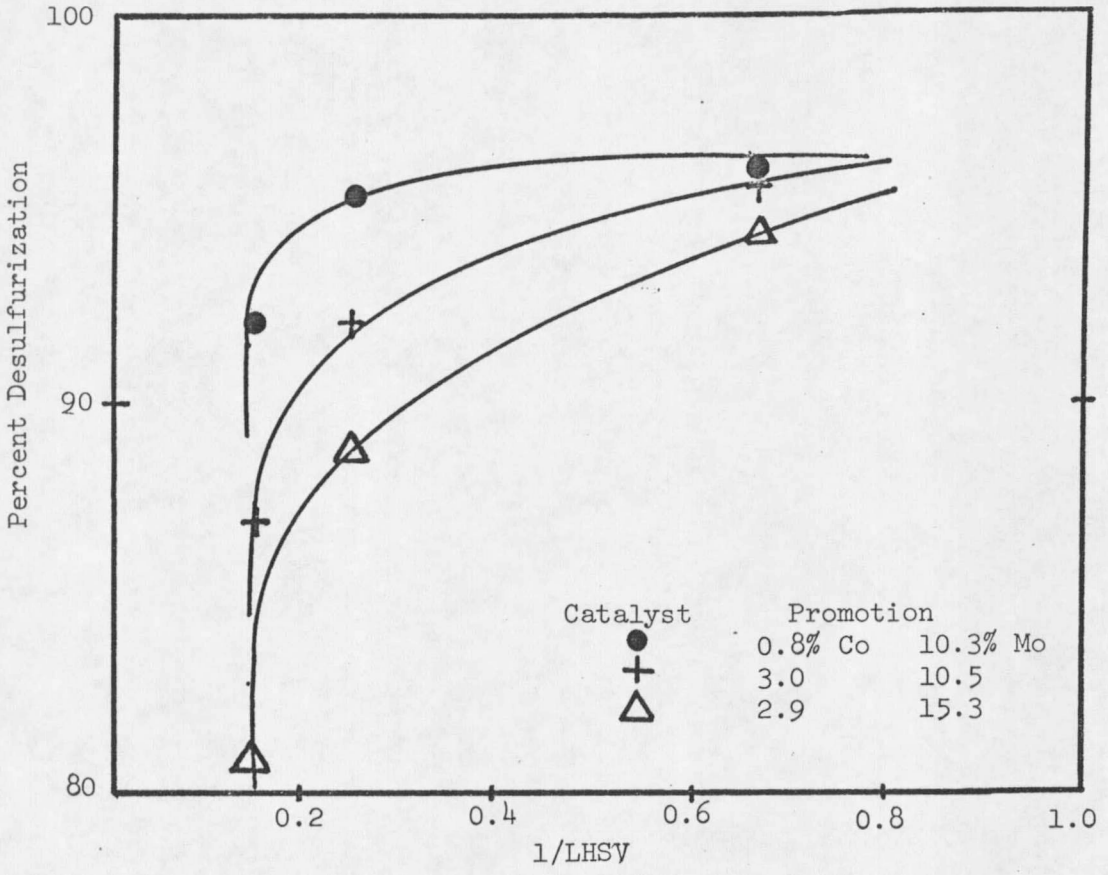


FIGURE 63
Percent Desulfurization vs. 1/LHSV at 800°F
for Harshaw 1602

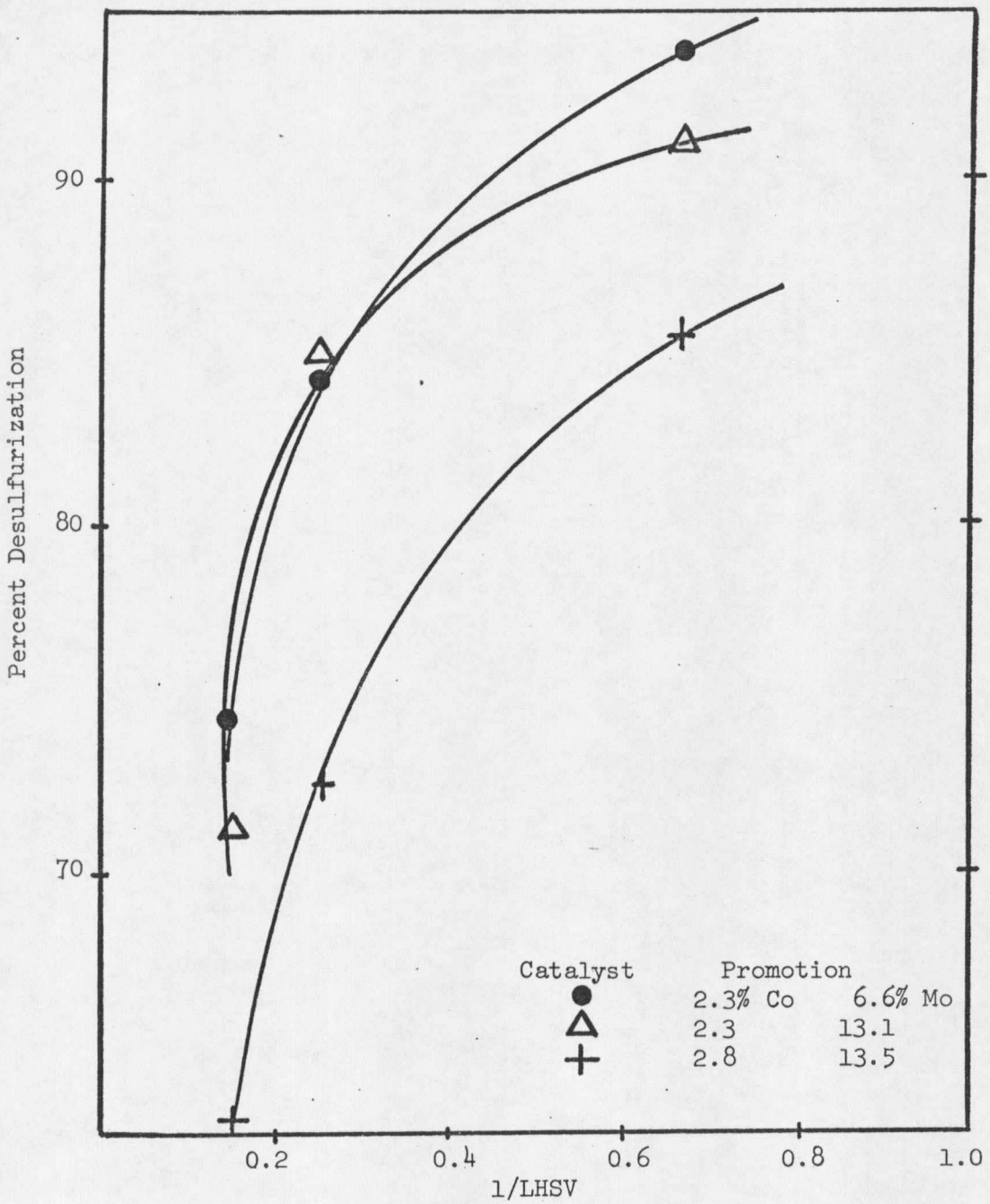


FIGURE 64
Percent Desulfurization vs. 1/LHSV at 650°F
for ALCOA H-151

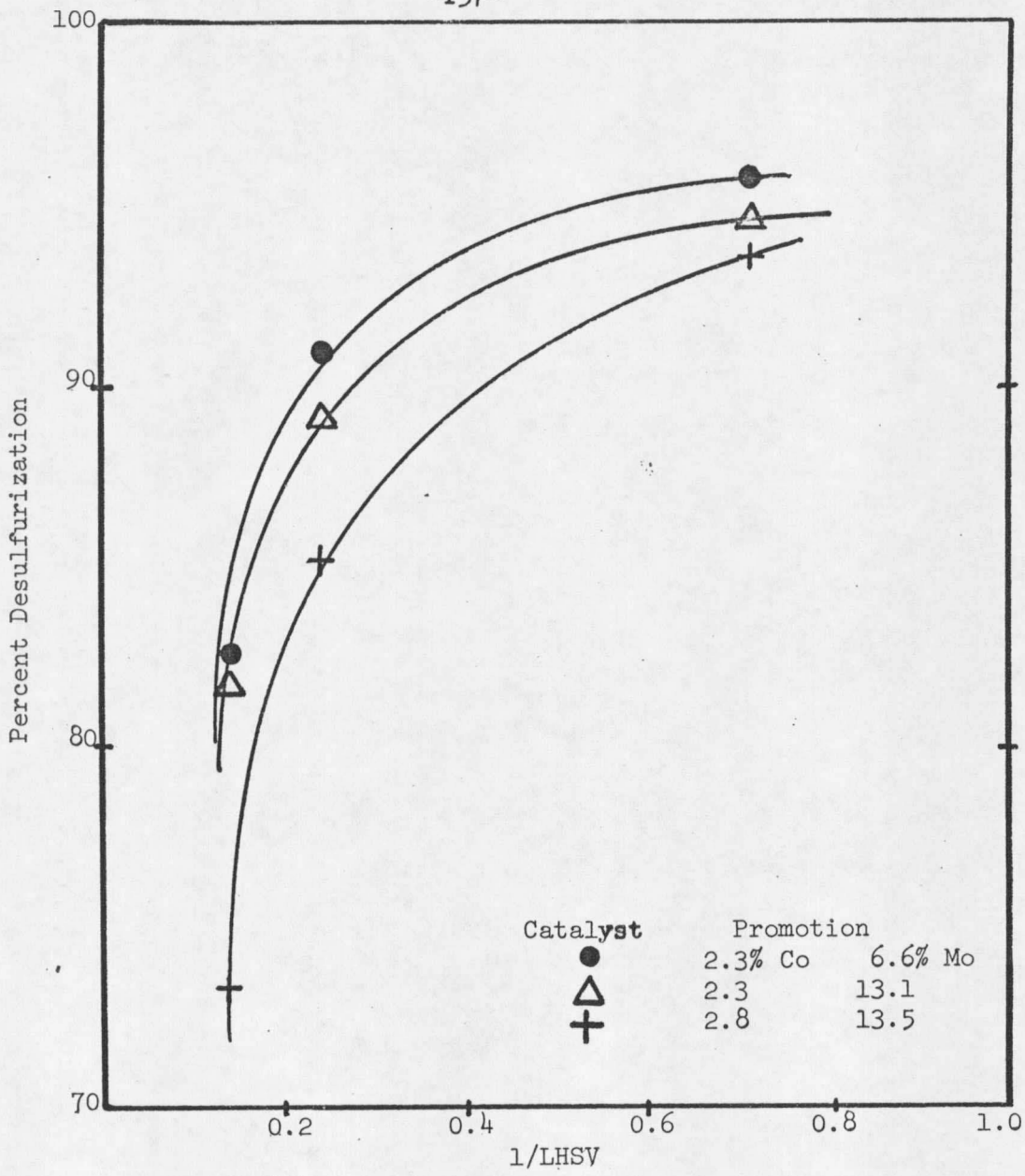


FIGURE 65
Percent Desulfurization vs. 1/LHSV at 725°F
for Alcoa H-151

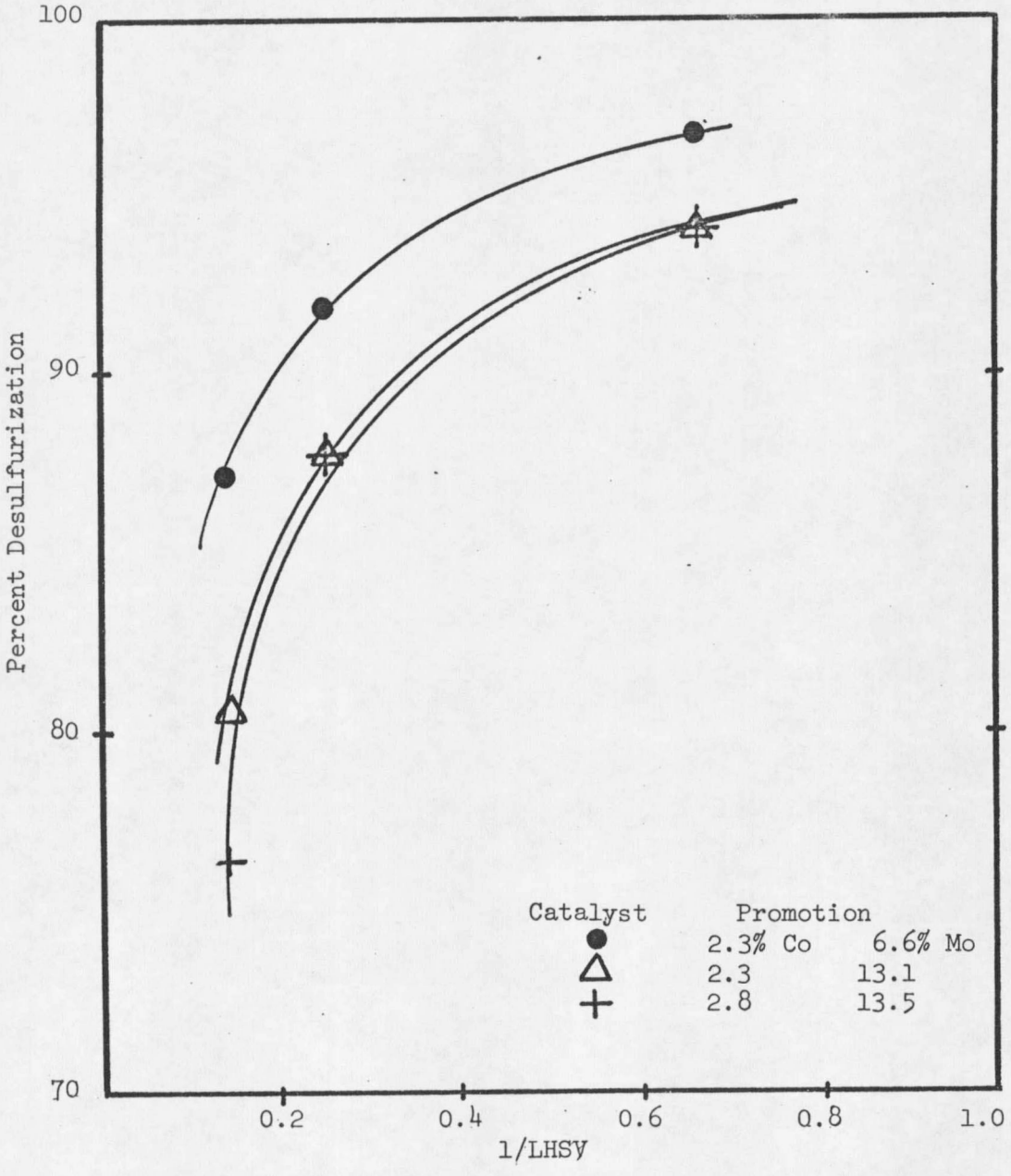


FIGURE 66
Percent Desulfurization vs. 1/LHSV at 800°F
for Alcoa H-151

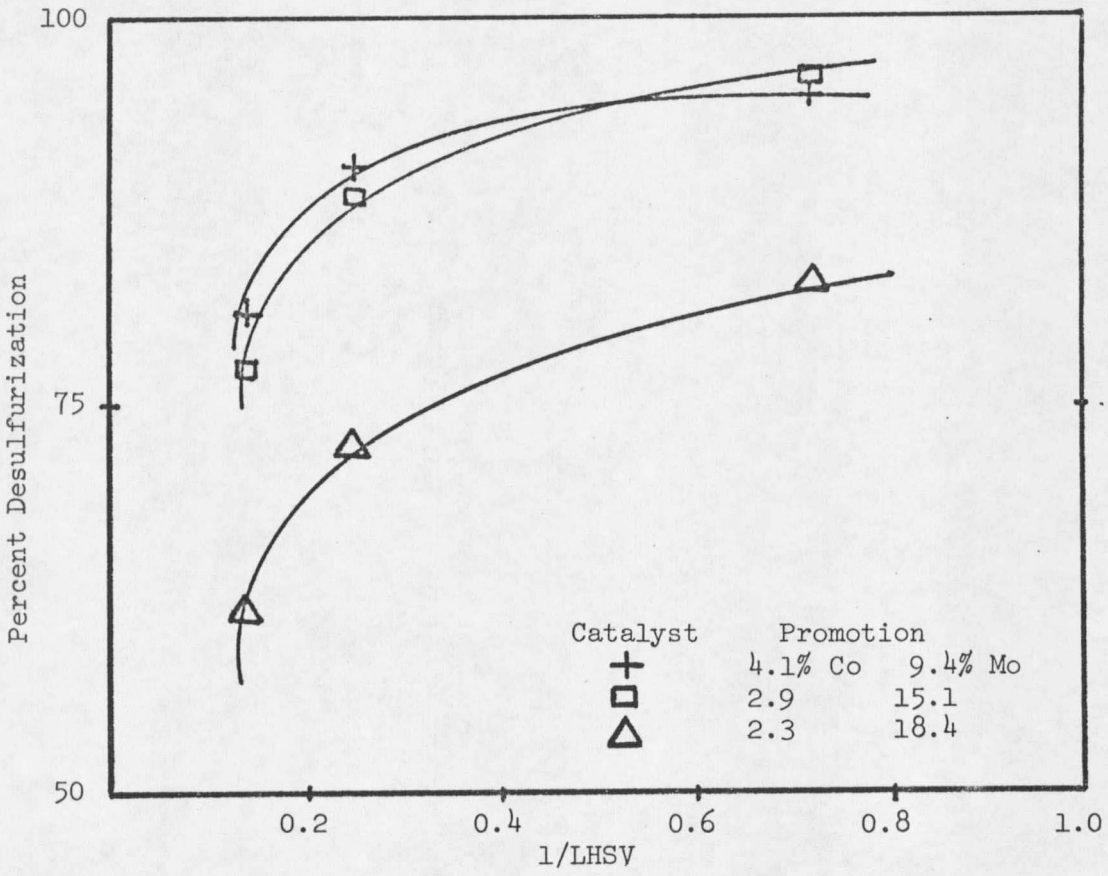


FIGURE 67
Percent Desulfurization vs. 1/LHSV at 650°F
for Norton 6473

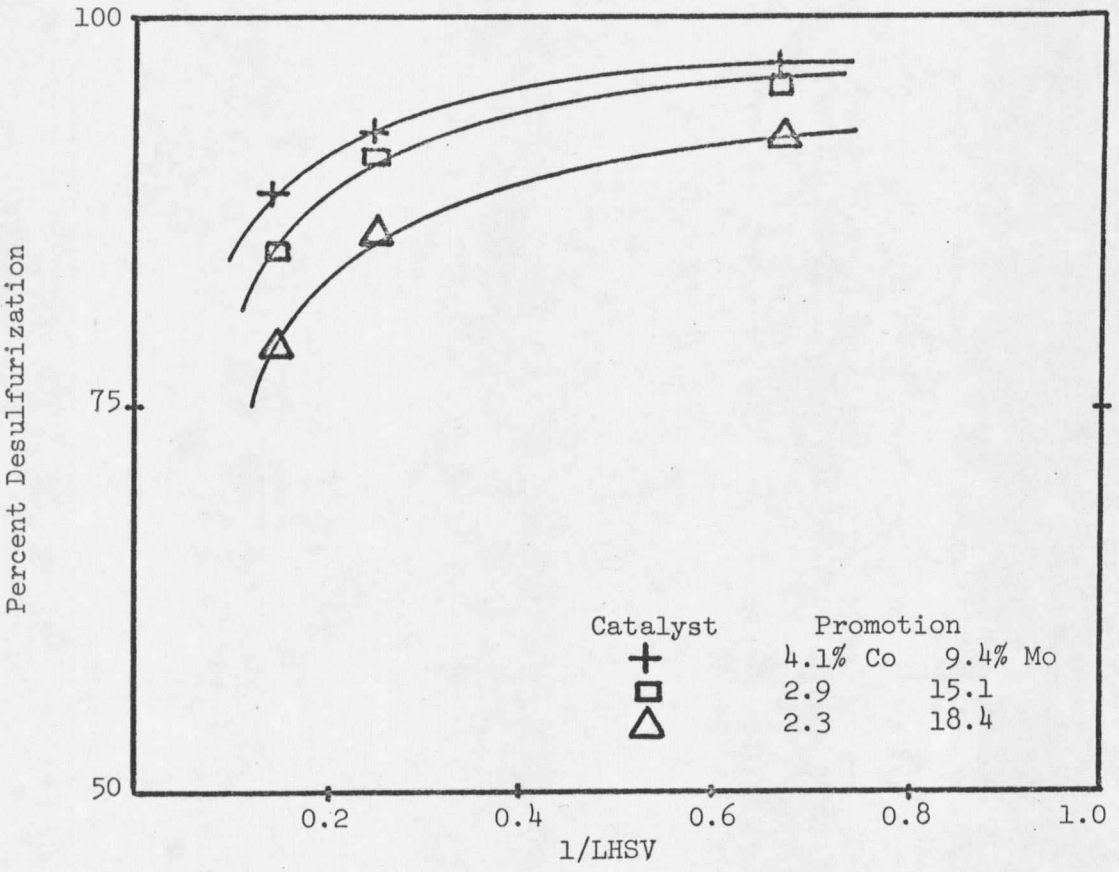


FIGURE 68
Percent Desulfurization vs. 1/LHSV at 725°F
for Norton 6473

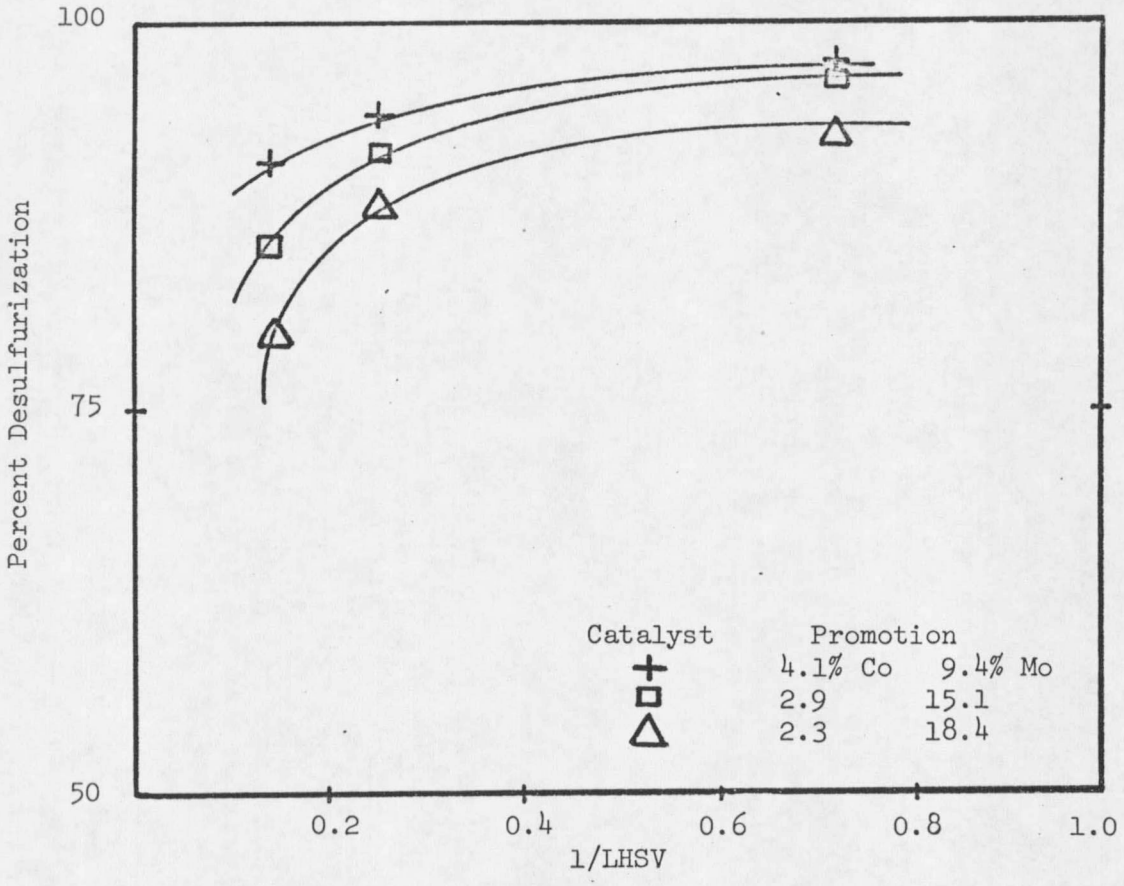


FIGURE 69
Percent Desulfurization vs. 1/LHSV at 800°F
for Norton 6473

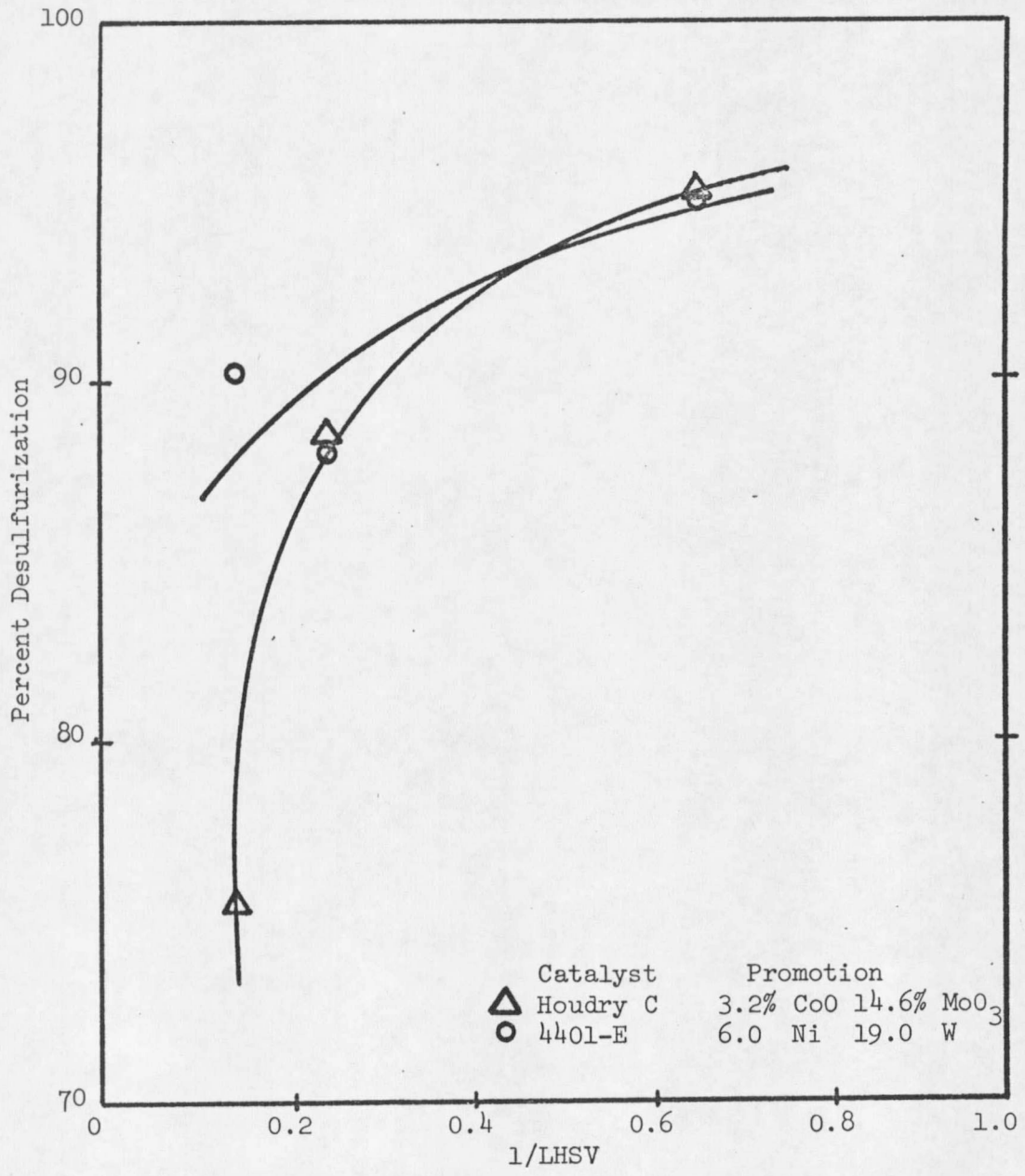


FIGURE 70
Percent Desulfurization vs. 1/LHSV at 650°F
for Houdry C and Harshaw Commercial Catalysts

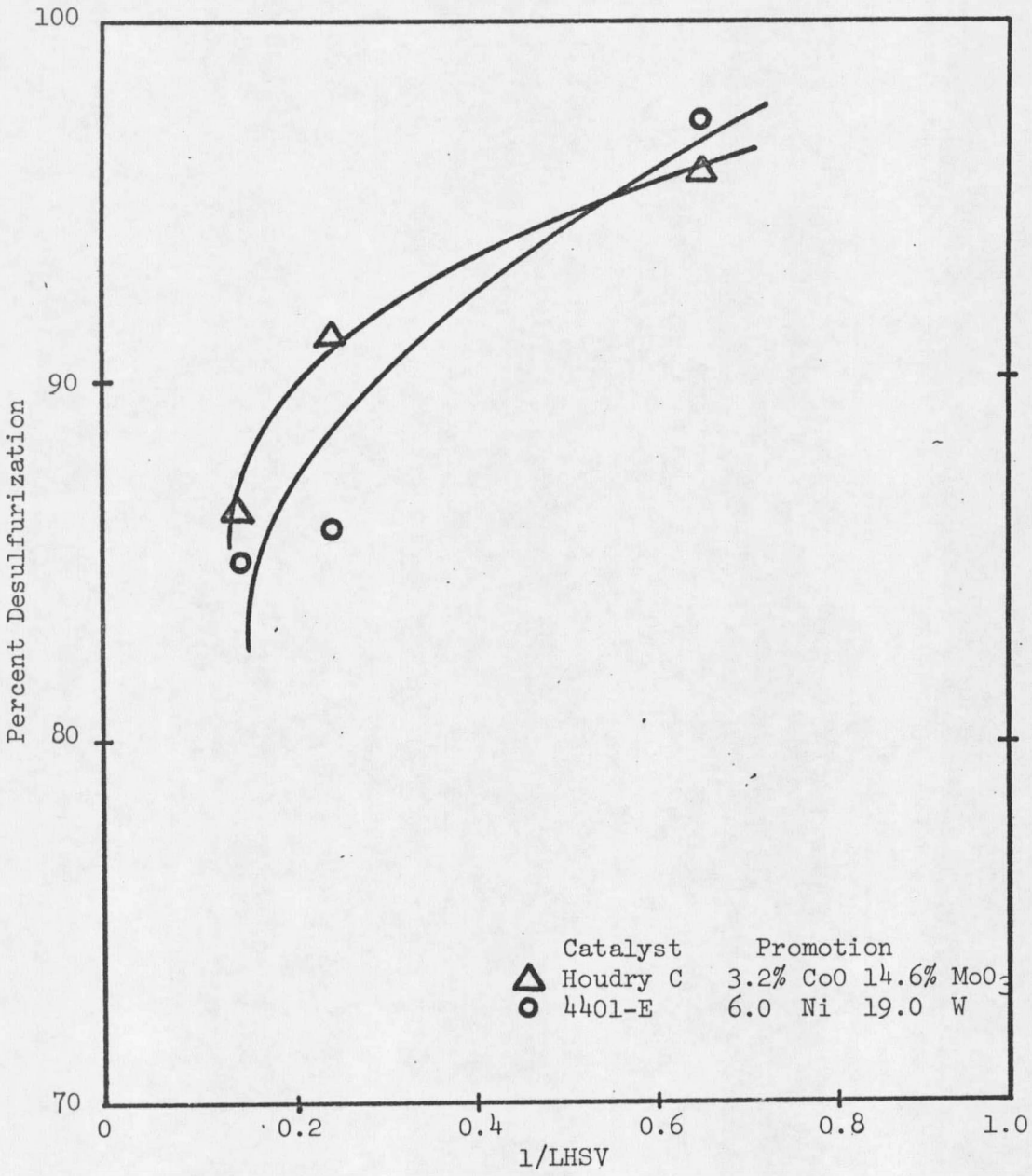


FIGURE 71
Percent Desulfurization vs. 1/LHSV at 725°F
for Houdry C and Harshaw Commercial Catalysts

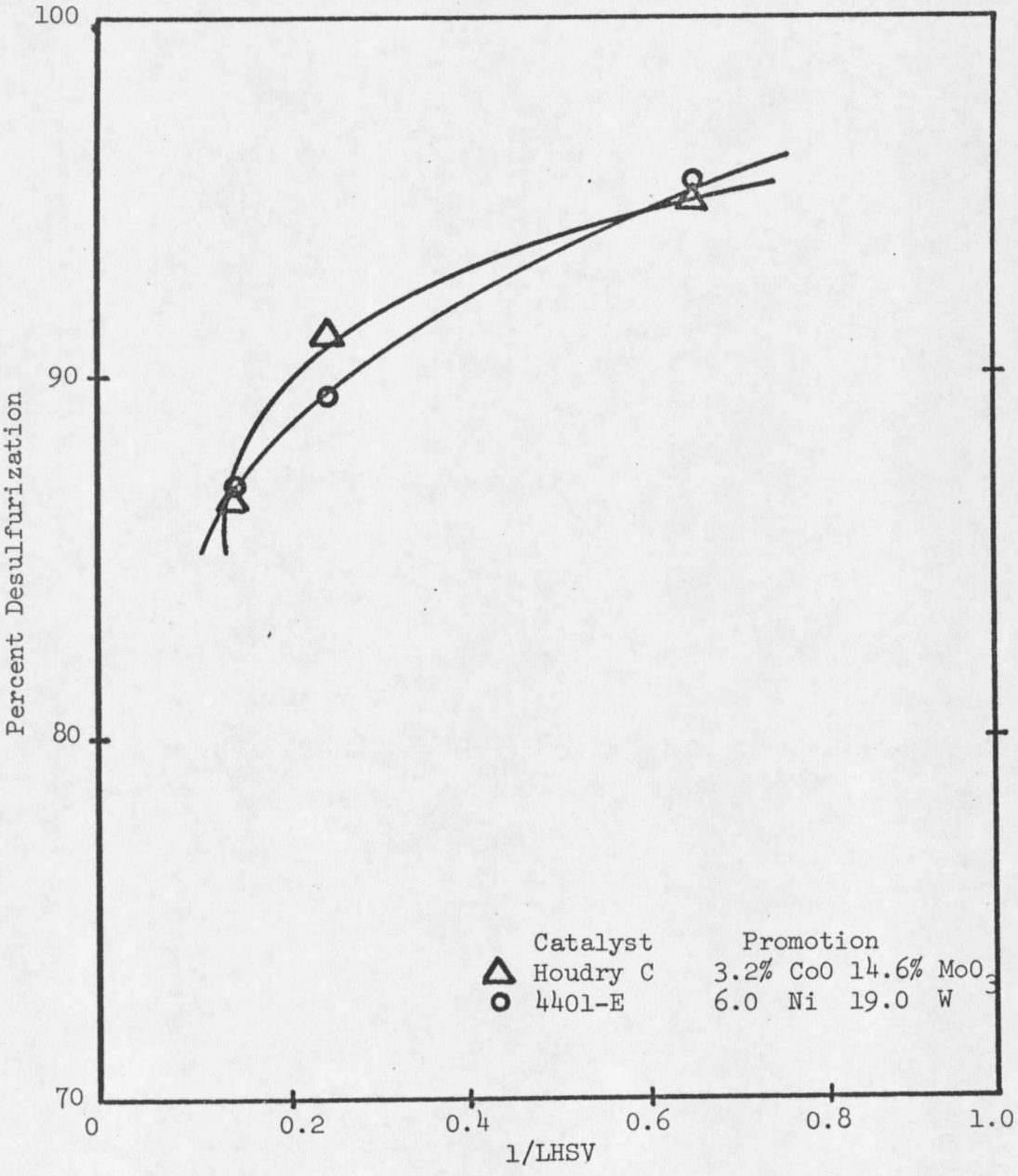


FIGURE 72
Percent Desulfurization vs. 1/LHSV at 800°F
for Houdry C and Harshaw Commercial Catalysts

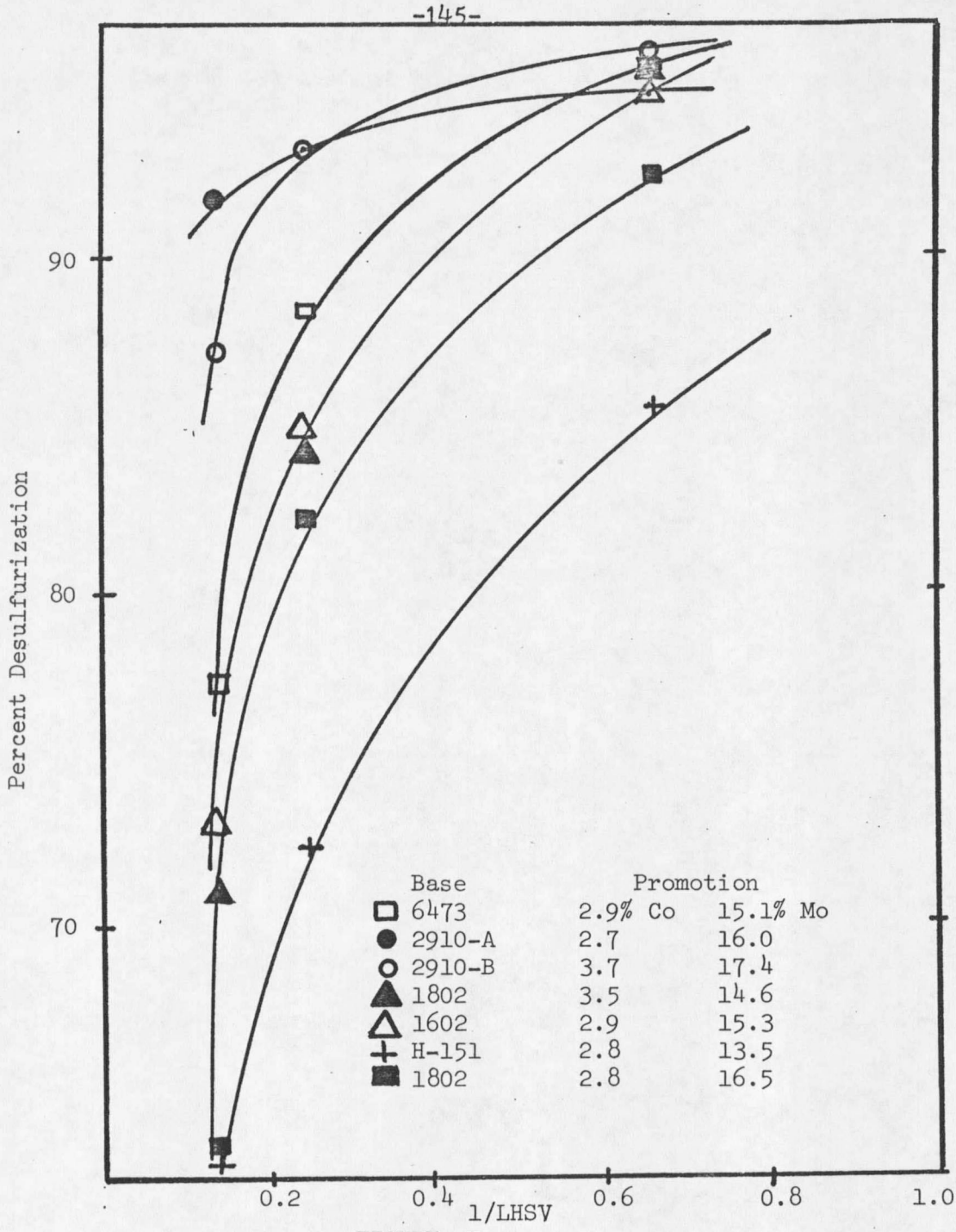


FIGURE 73

Percent Desulfurization vs. 1/LHSV at 650°F Noncrystalline Bases with Co Mo Promotion in 3% Co 15% Mo Range

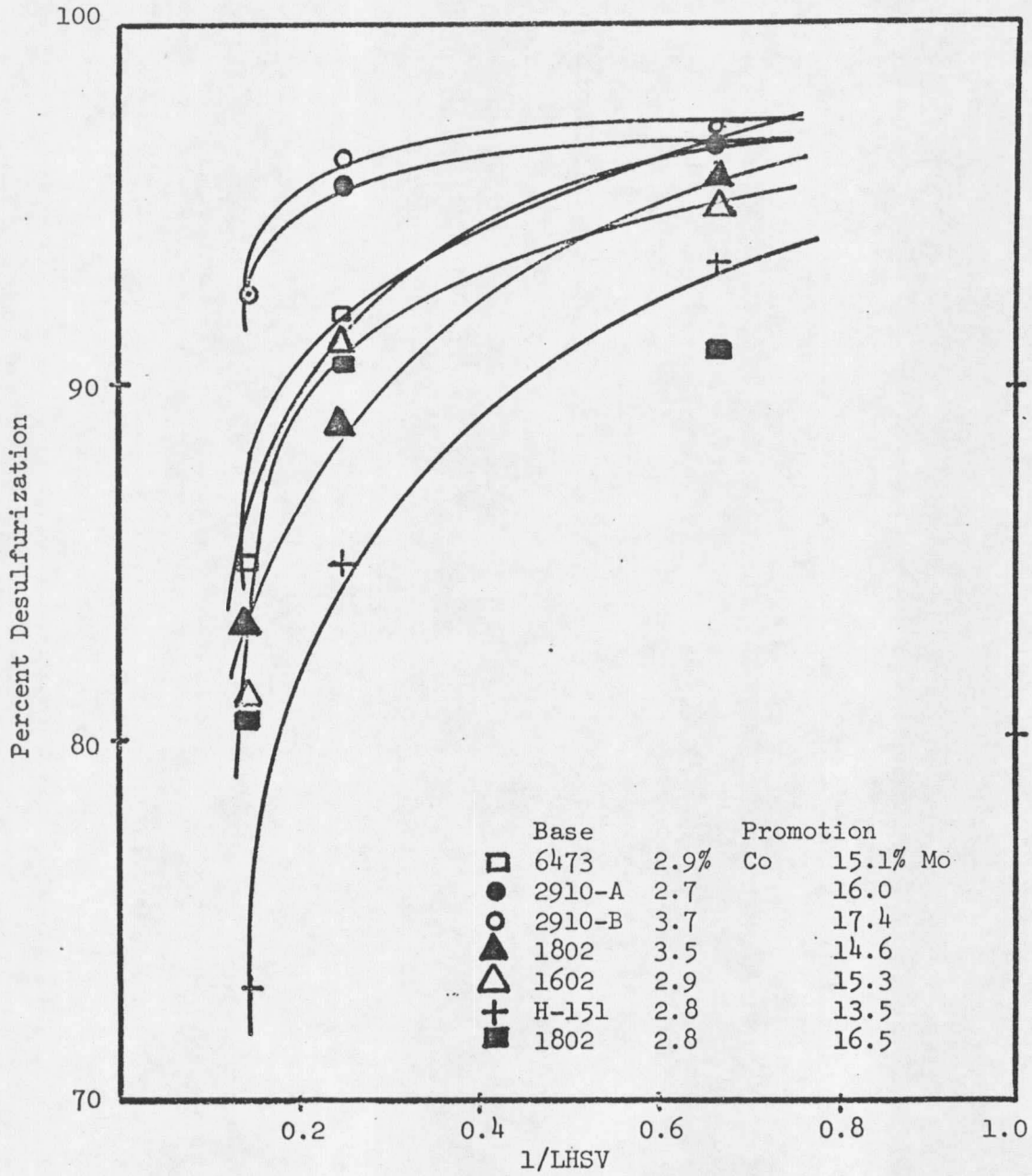


FIGURE 74
Percent Desulfurization vs. 1/LHSV at 725°F Noncrystalline Bases with Co Mo Promotion in 3% Co 15% Mo Range

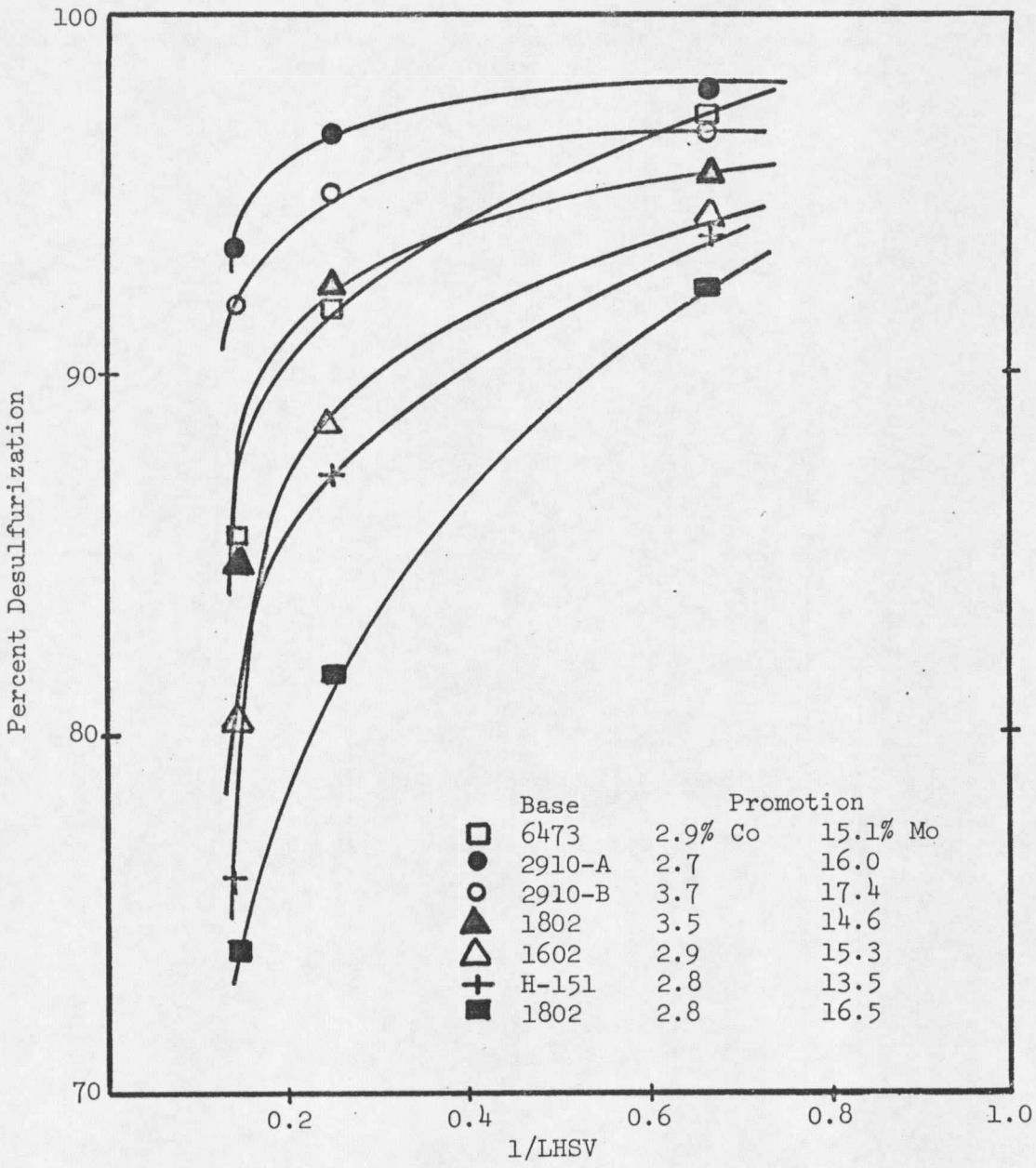


FIGURE 75
Percent Desulfurization vs. 1/LHSV at 800°F Noncrystalline Bases with Co Mo Promotion in 3% Co 15% Mo Range

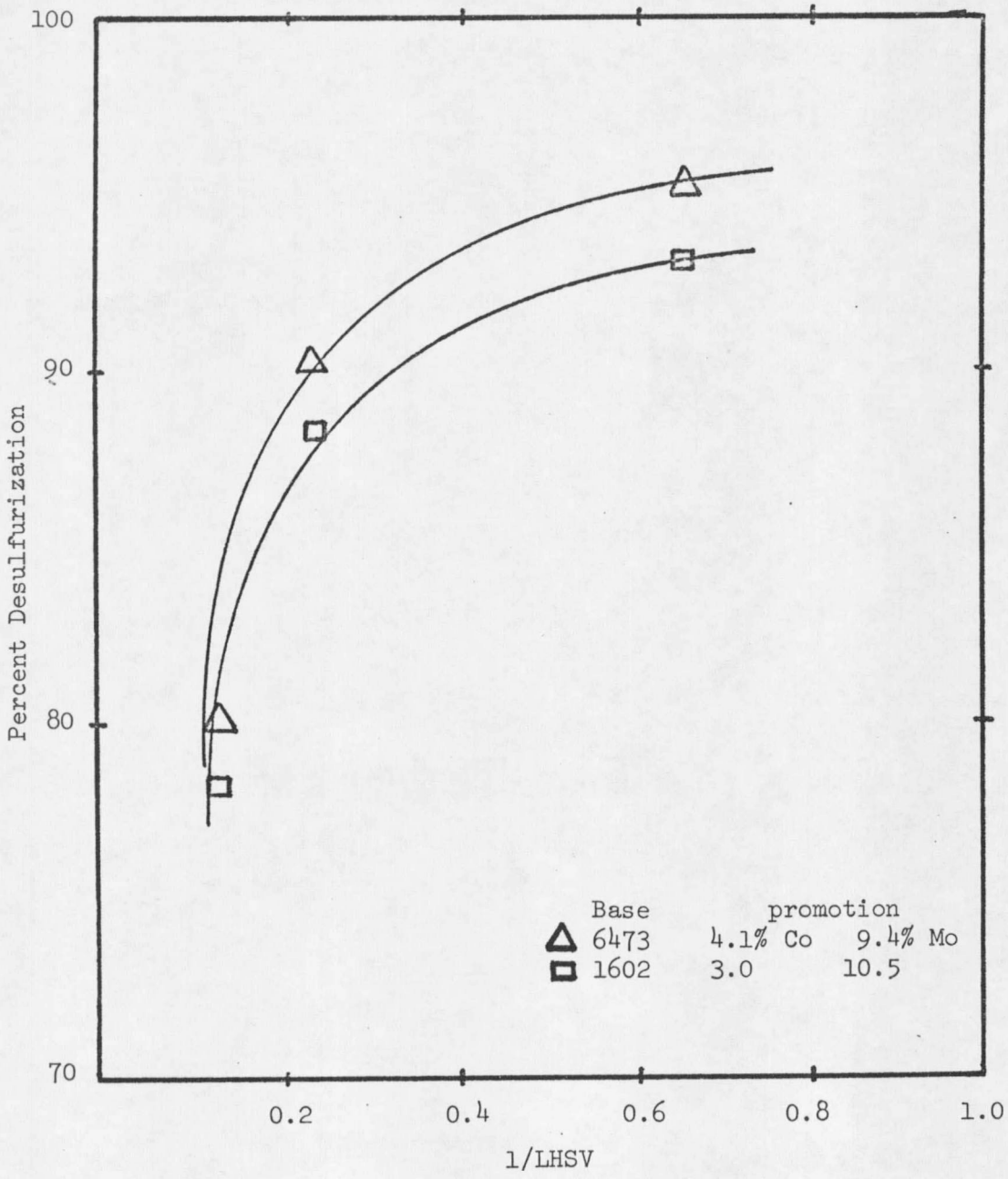


FIGURE 76
Percent Desulfurization vs. 1/LHSV at 650°F
for Noncrystalline Bases 5% Co 10% Mo Range

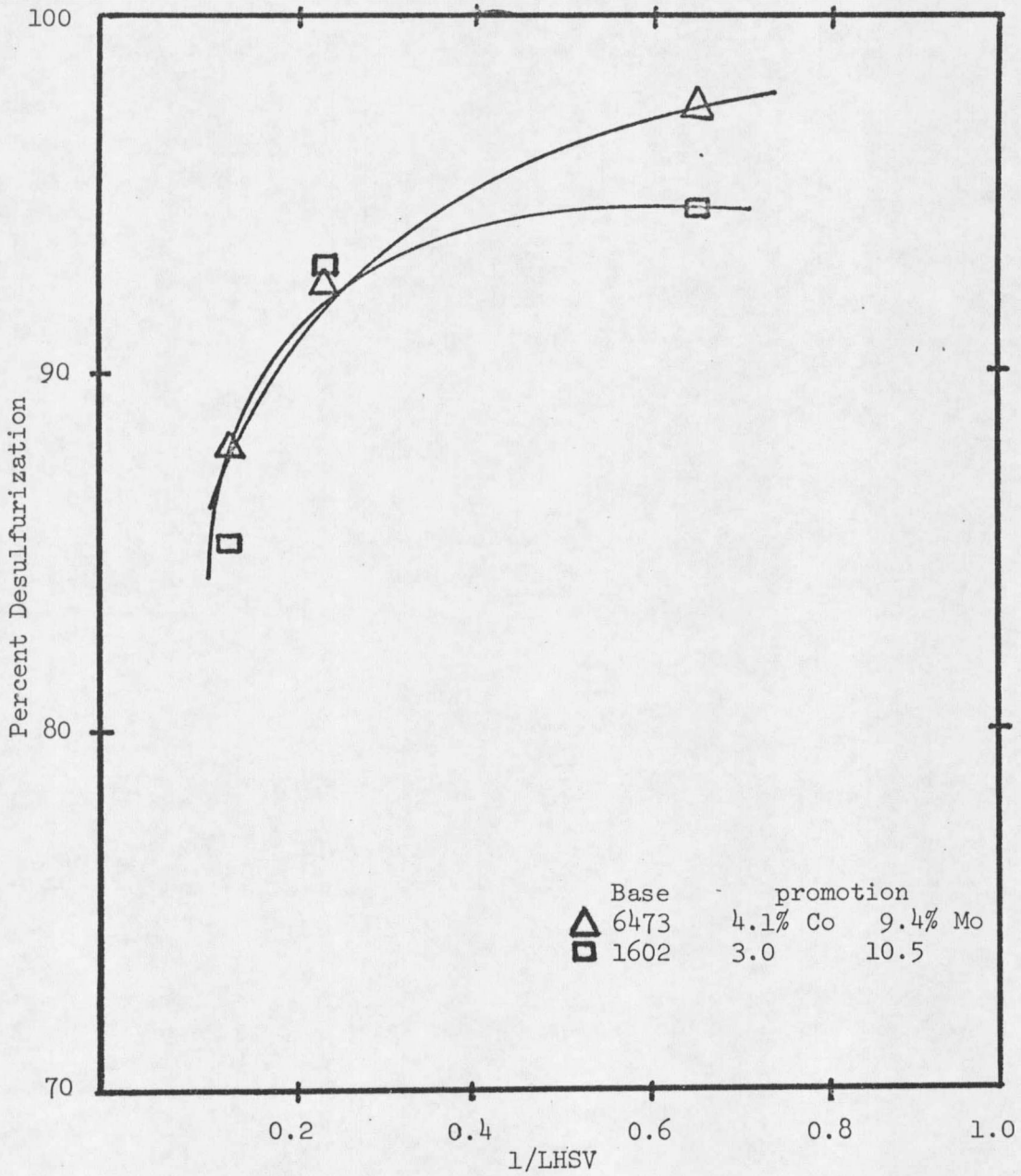


FIGURE 77
Percent Desulfurization vs. 1/LHSV at 725°F
for Noncrystalline Bases 5% Co 10% Mo Range

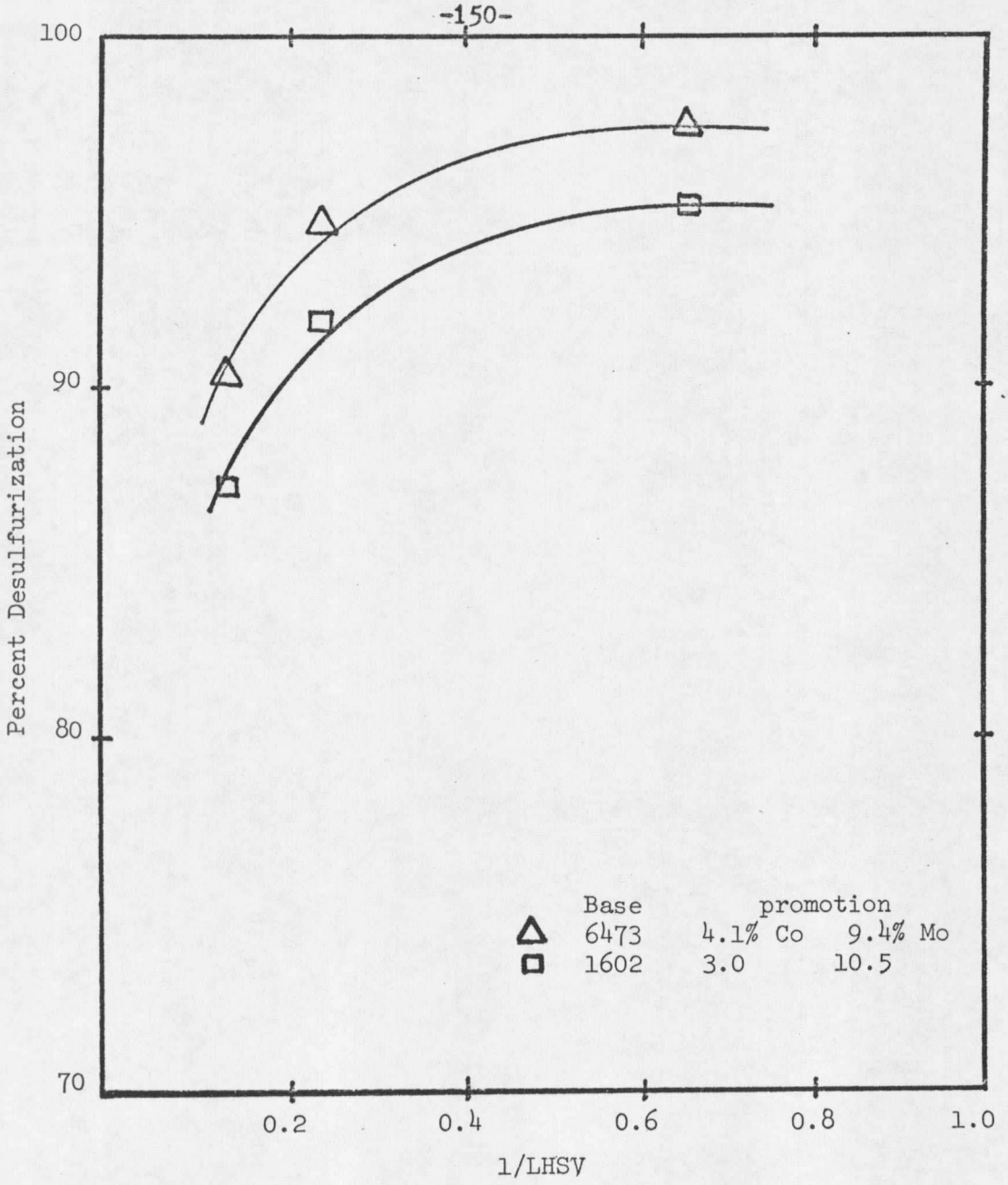


FIGURE 78
Percent Desulfurization vs. 1/LHSV at 800°F
for Noncrystalline Bases 5% Co 10% Mo Range

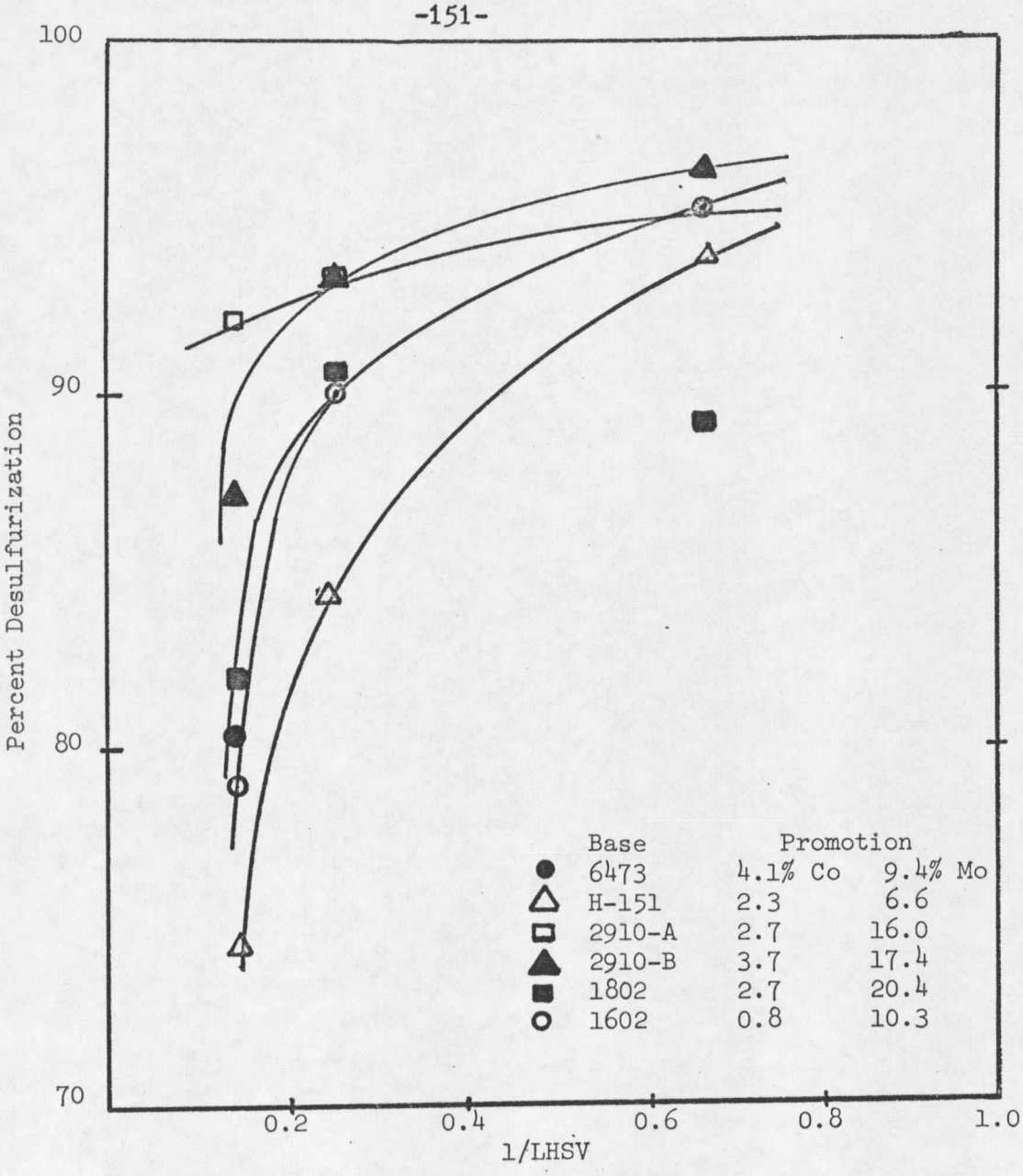


FIGURE 79
Percent Desulfurization vs. 1/LHSV at 650°F
for Best Catalyst Promotions
Noncrystalline Materials

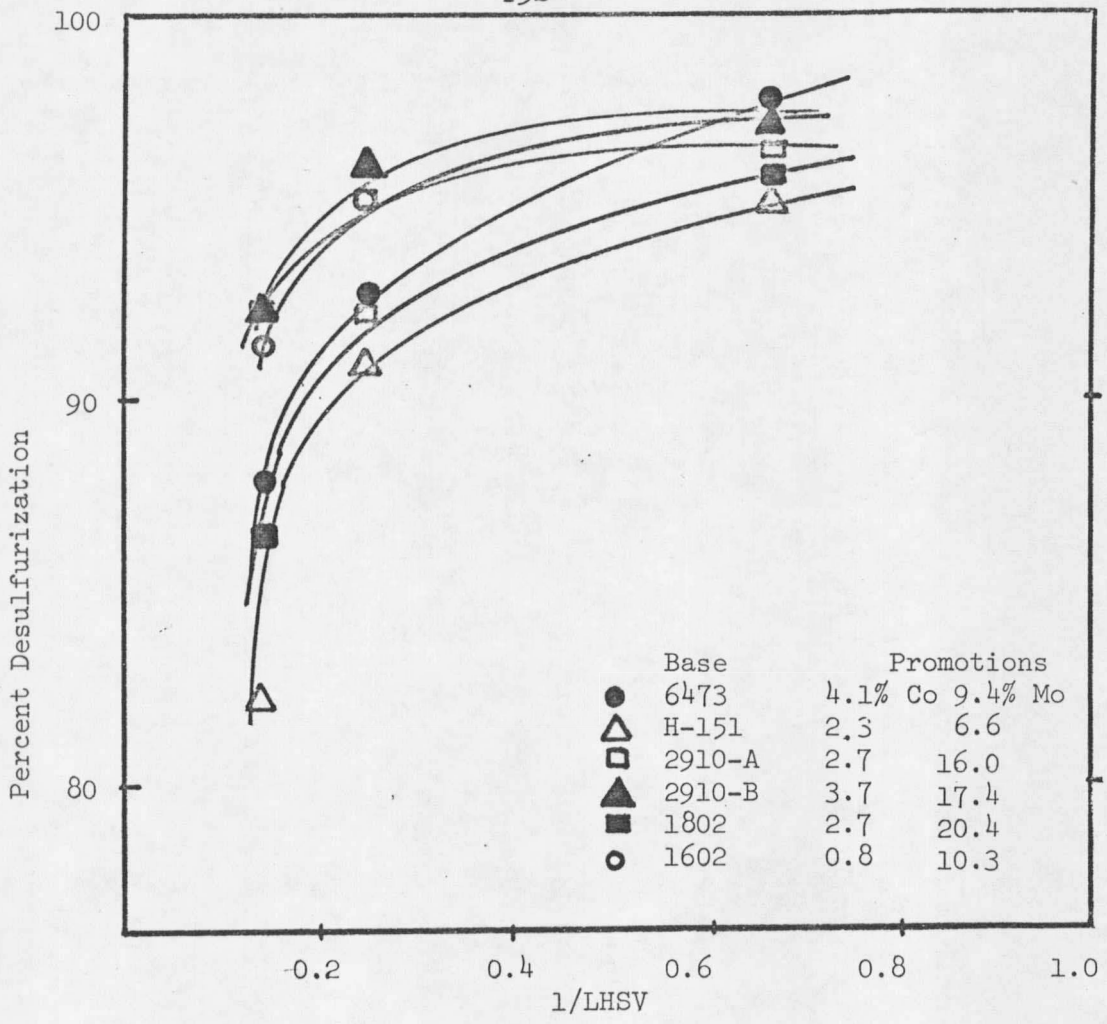


FIGURE 80
Percent Desulfurization vs. 1/LHSV at 725°F
for Best Catalyst Promotions
Noncrystalline Materials

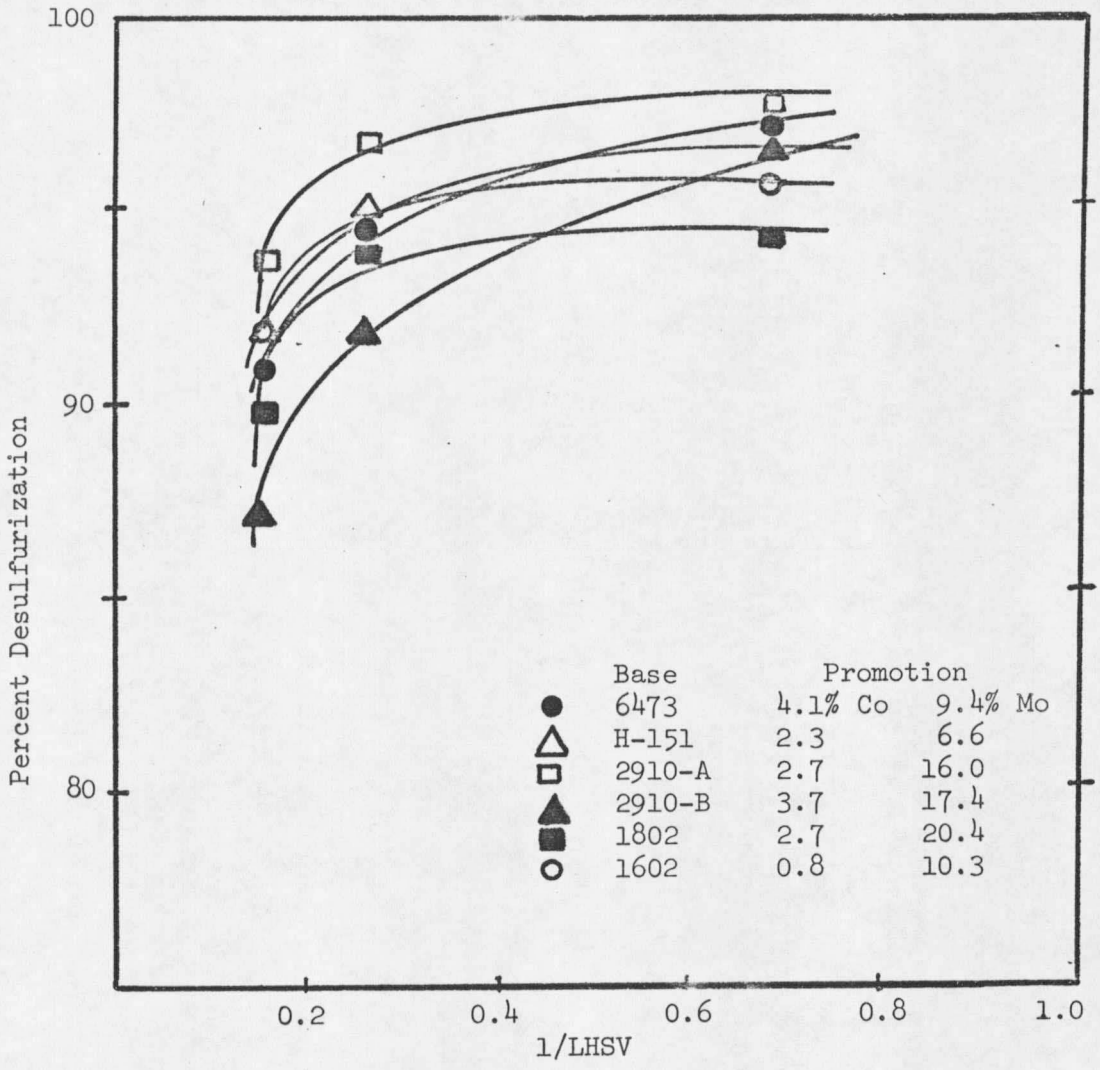


FIGURE 81
Percent Desulfurization vs. 1/LHSV at 800°F
for Best Catalyst Promotions
Noncrystalline Materials

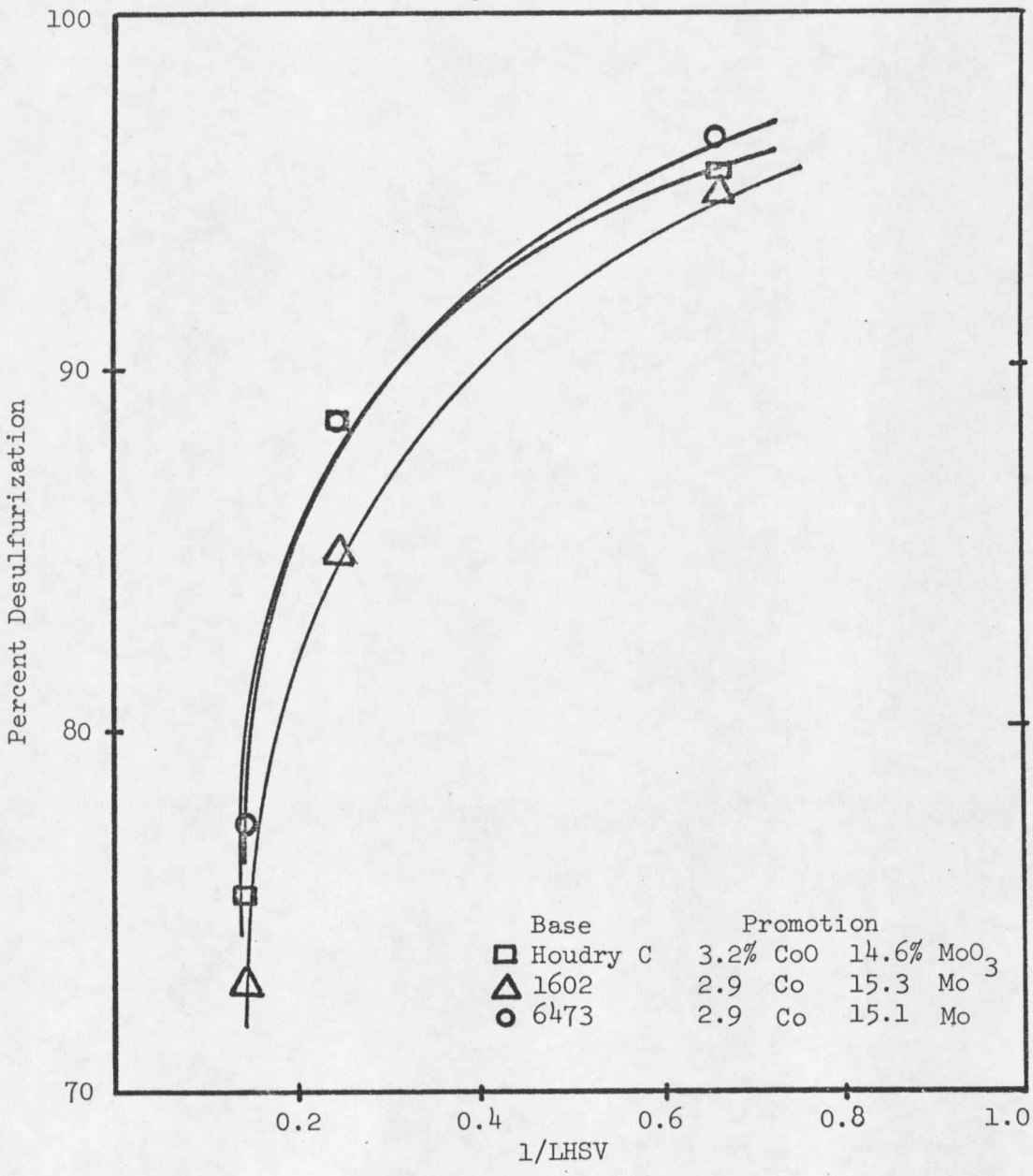


FIGURE 82
Percent Desulfurization vs. 1/LHSV at 650°F
Pore Volume 0.45-0.48 cc./gm.

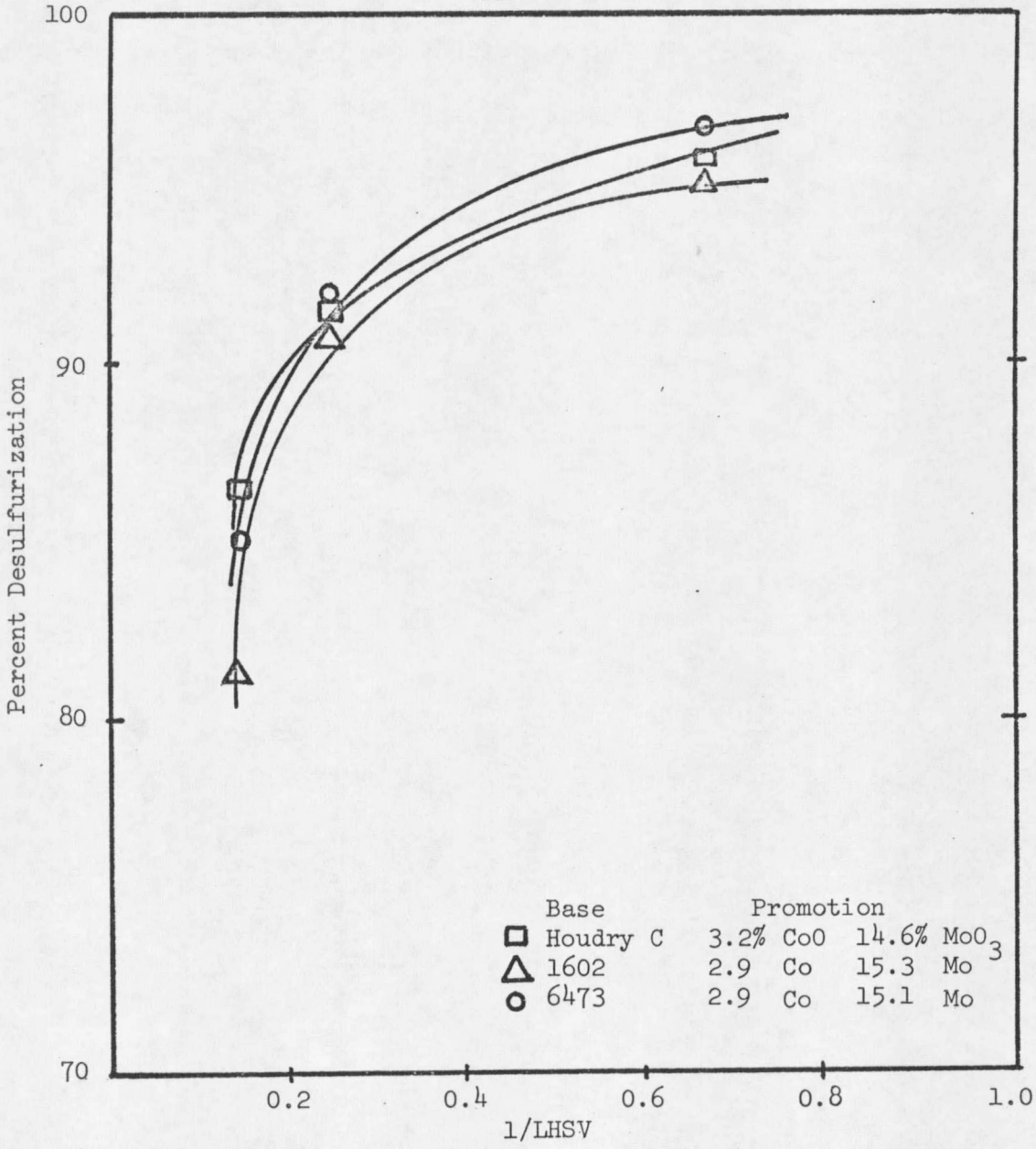


FIGURE 83
Percent Desulfurization vs. 1/LHSV at 725°F
Pore Volume 0.45-0.48 cc./gm.

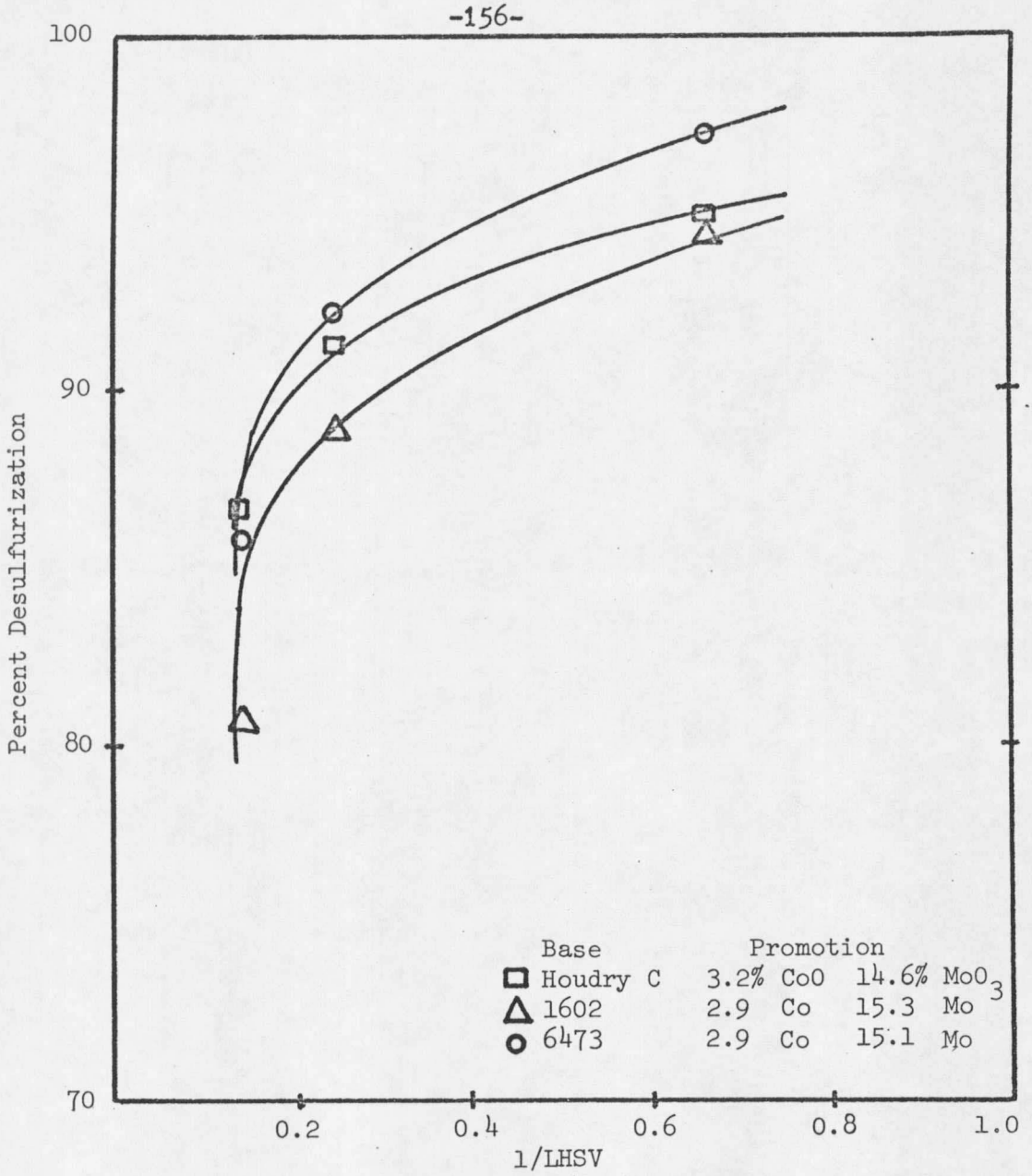


FIGURE 84
Percent Desulfurization vs. 1/LHSV at 800°F
Pore Volume 0.45-0.48 cc./gm.

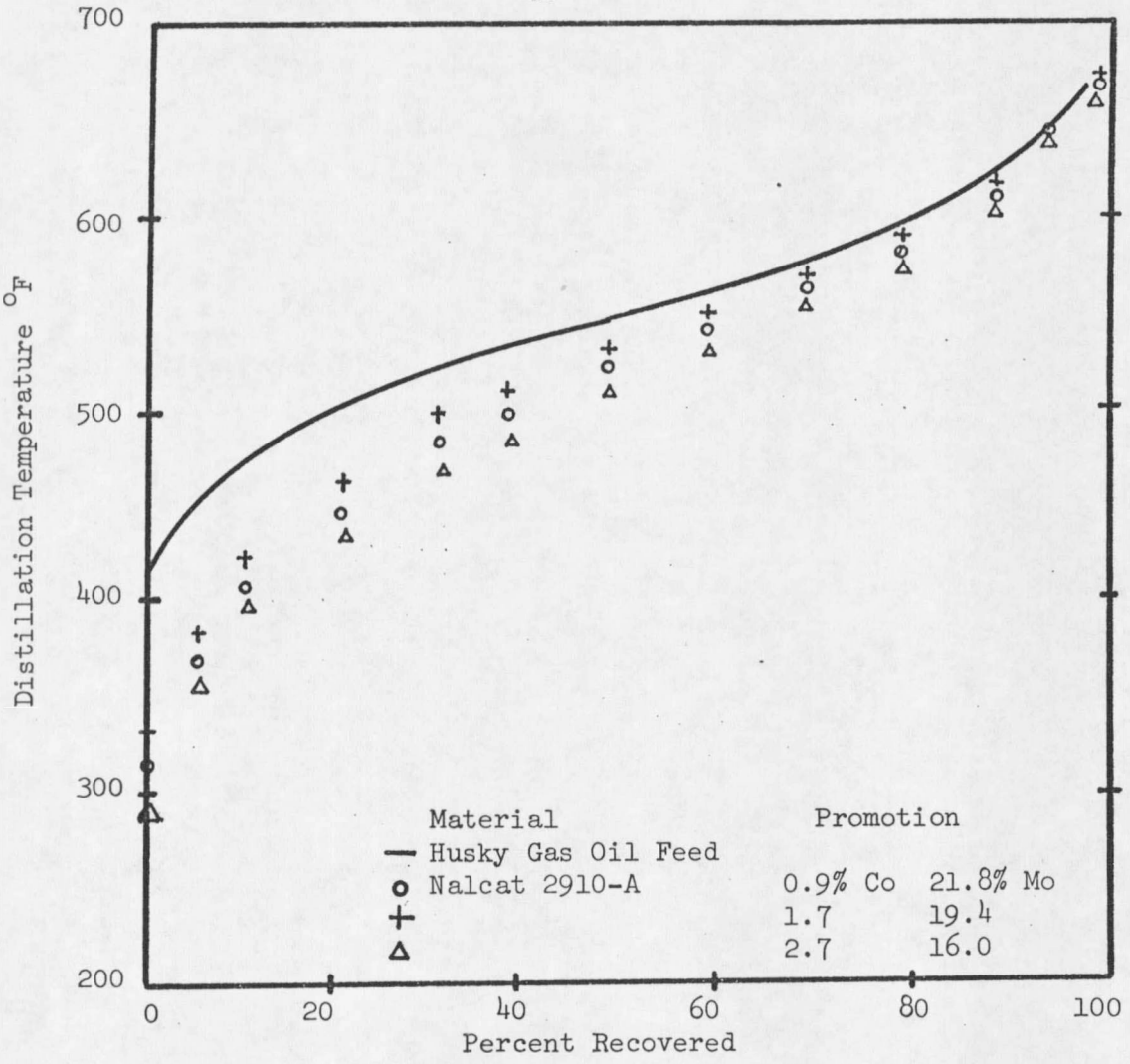


FIGURE 85
Percent Recovered vs. Distillation Temperature
for Nalcat 2910-A

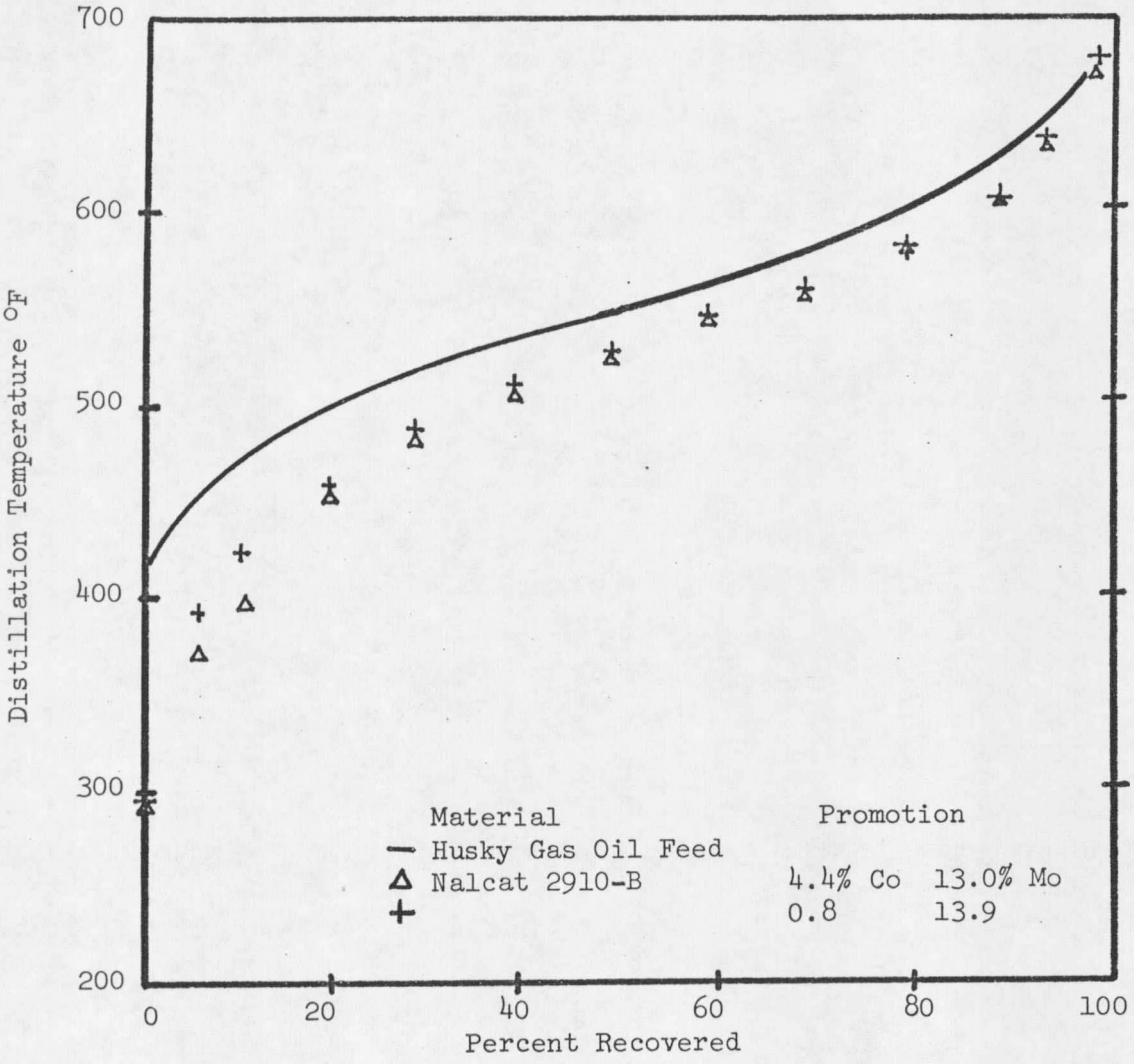


FIGURE 86
Distillation Temperature vs. Percent Recovered
for Nalcat 2910-B

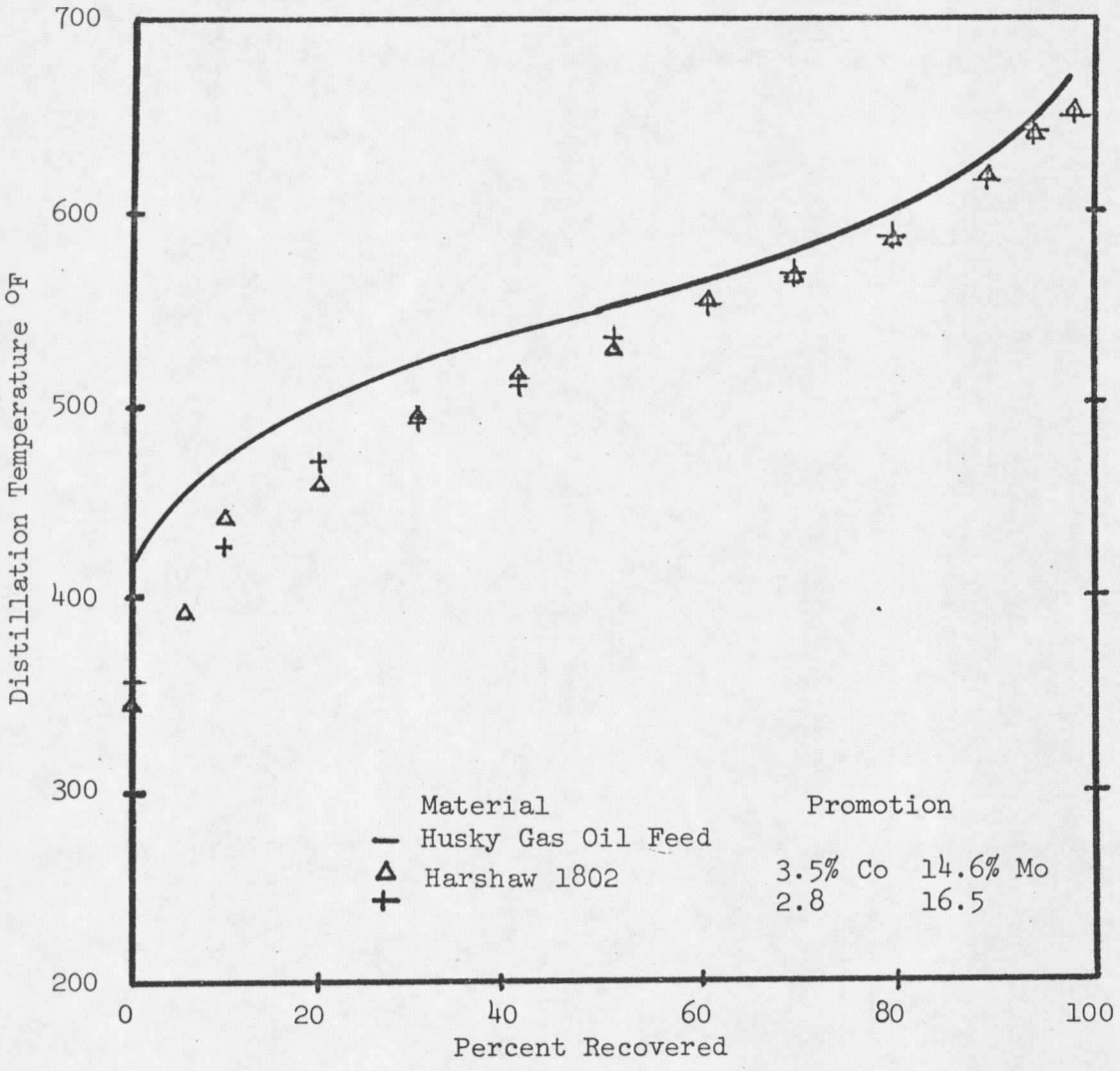


FIGURE 87
Distillation Temperature vs. Percent Recovered
for Harshaw 1802

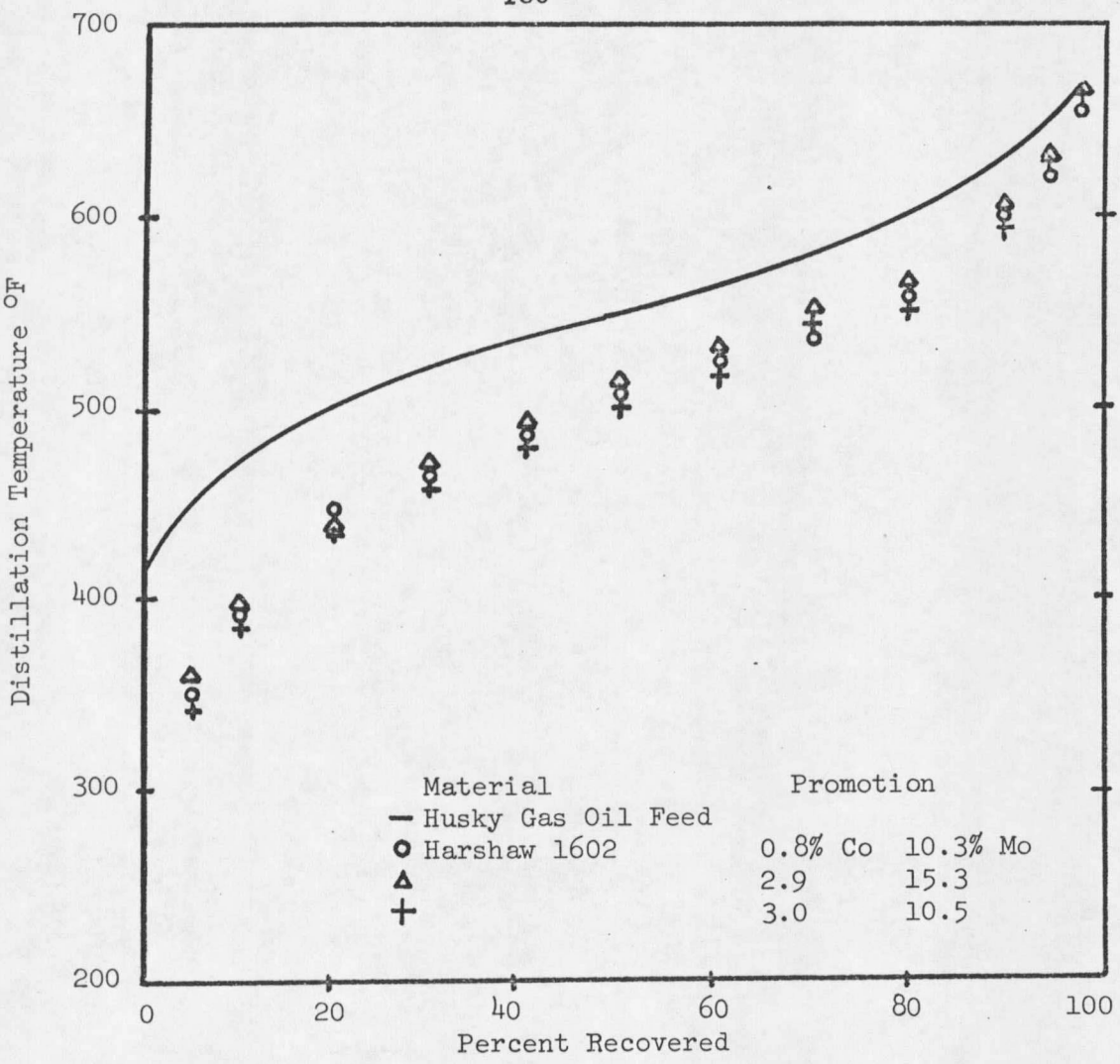


FIGURE 88
Distillation Temperature vs. Percent Recovered
for Harshaw 1602

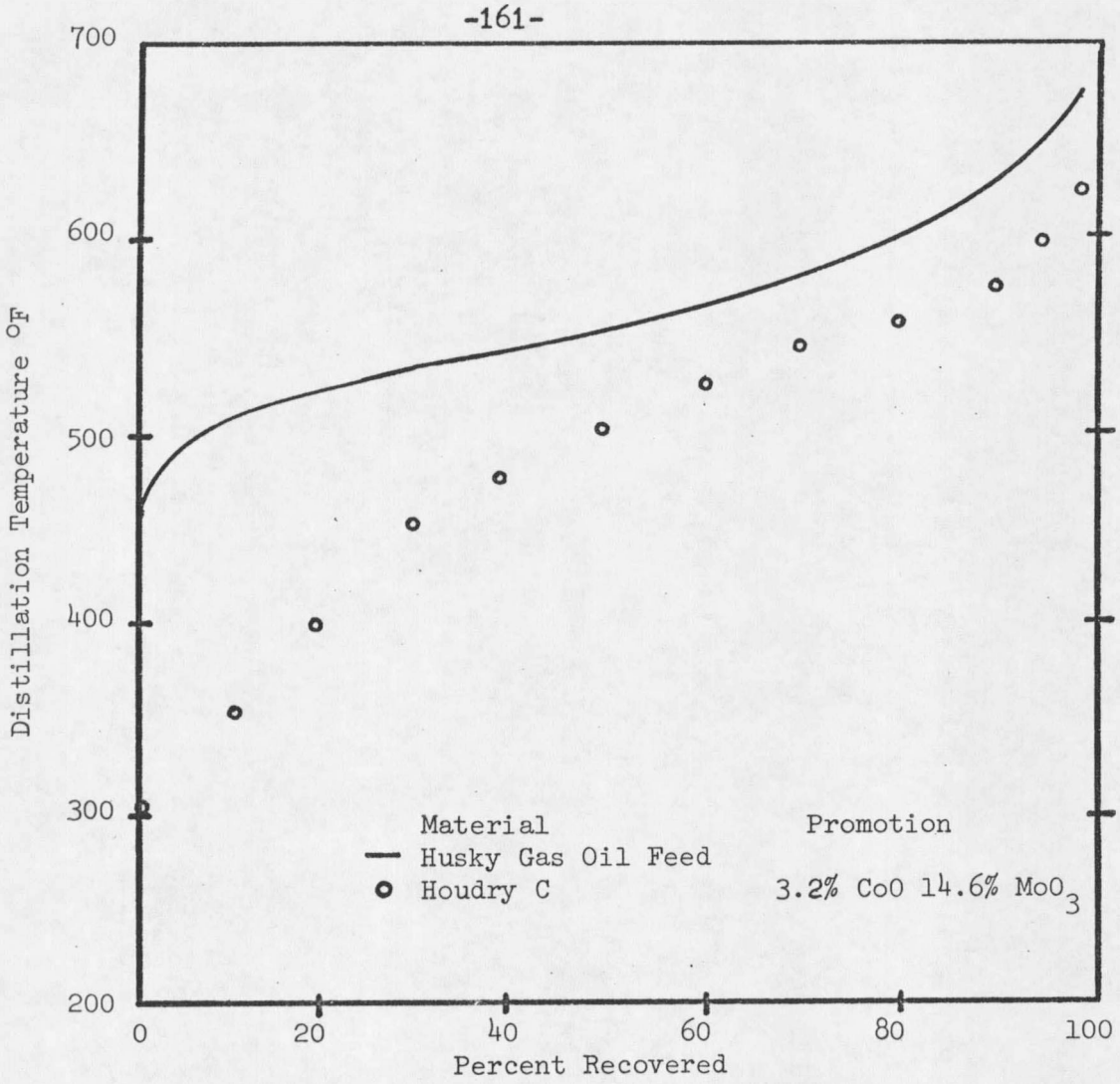


FIGURE 89
Distillation Temperature vs. Percent Recovered
for Houdry C

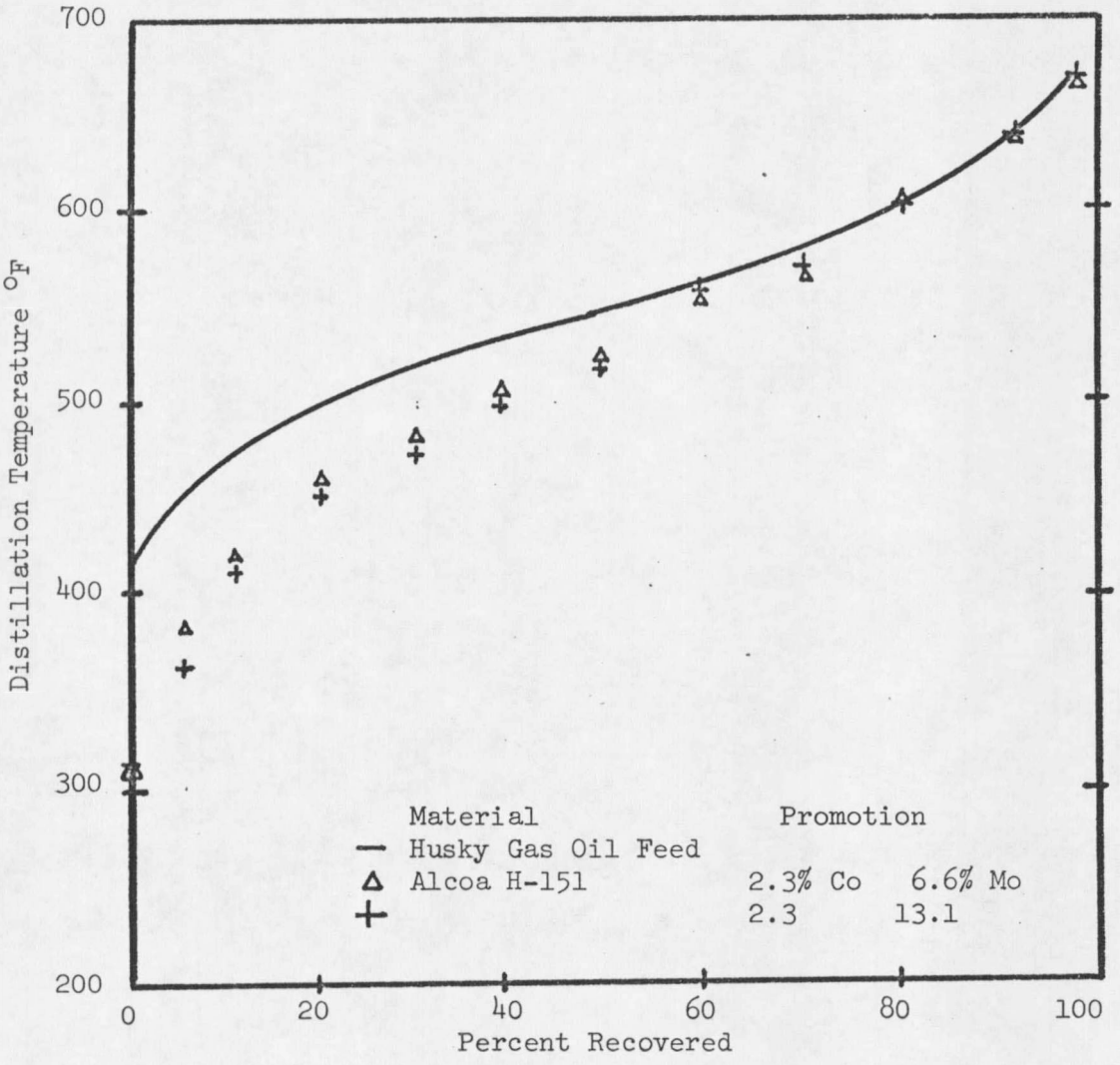


FIGURE 90
Distillation Temperature vs. Percent Recovered
for Alcoa H-151

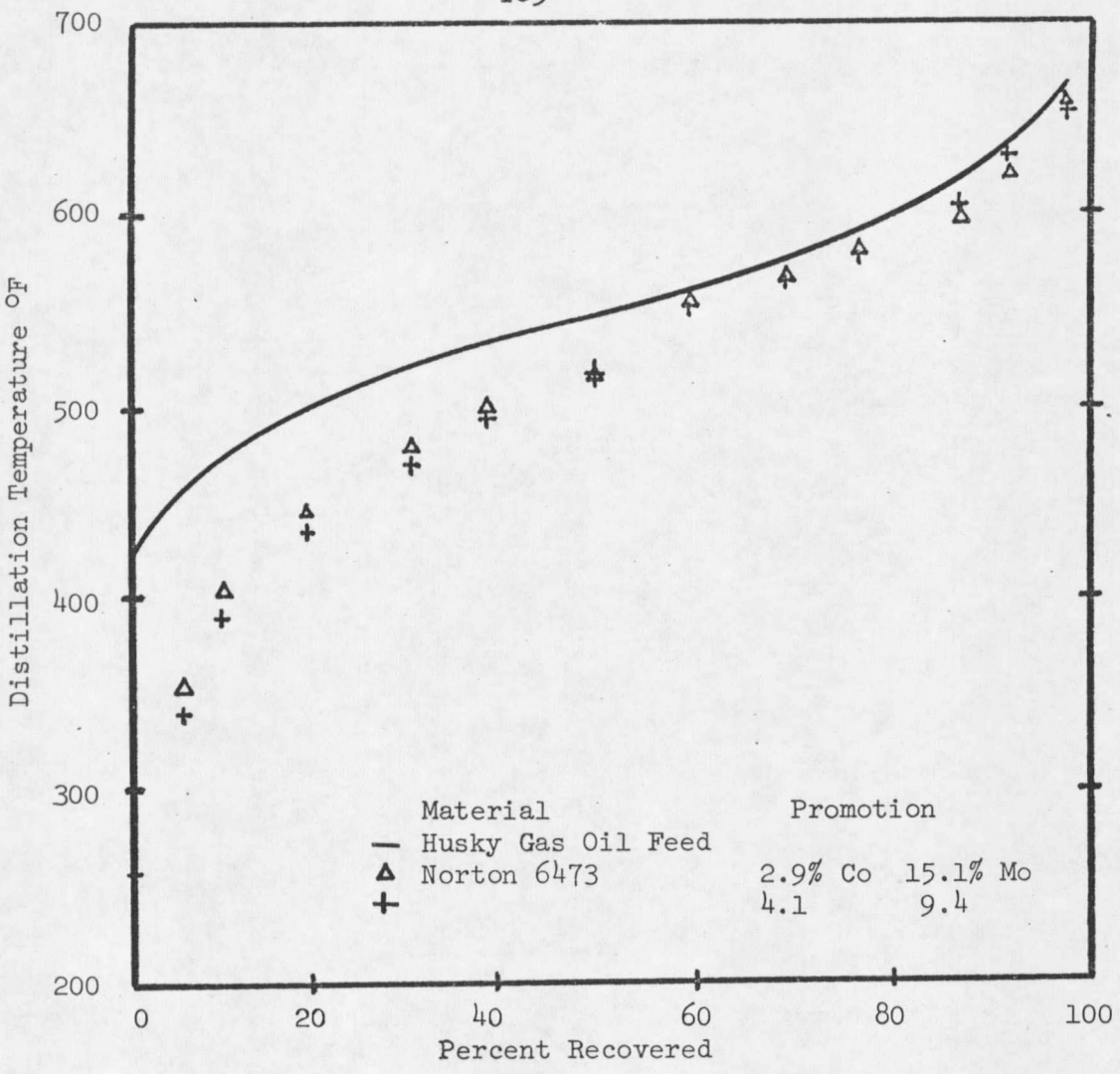


FIGURE 91
Distillation Temperature vs. Percent Recovered
for Norton 6473

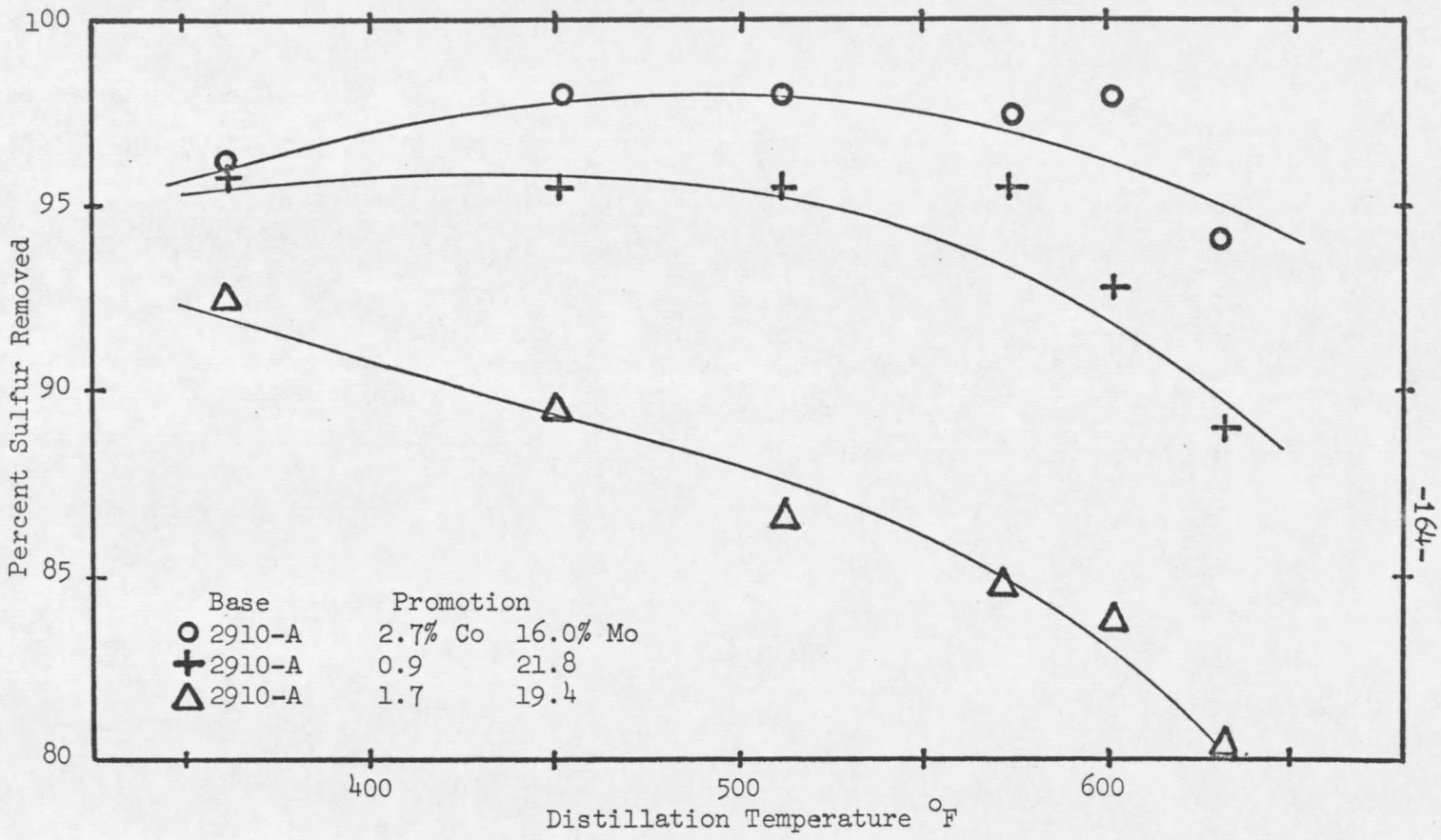


FIGURE 92
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

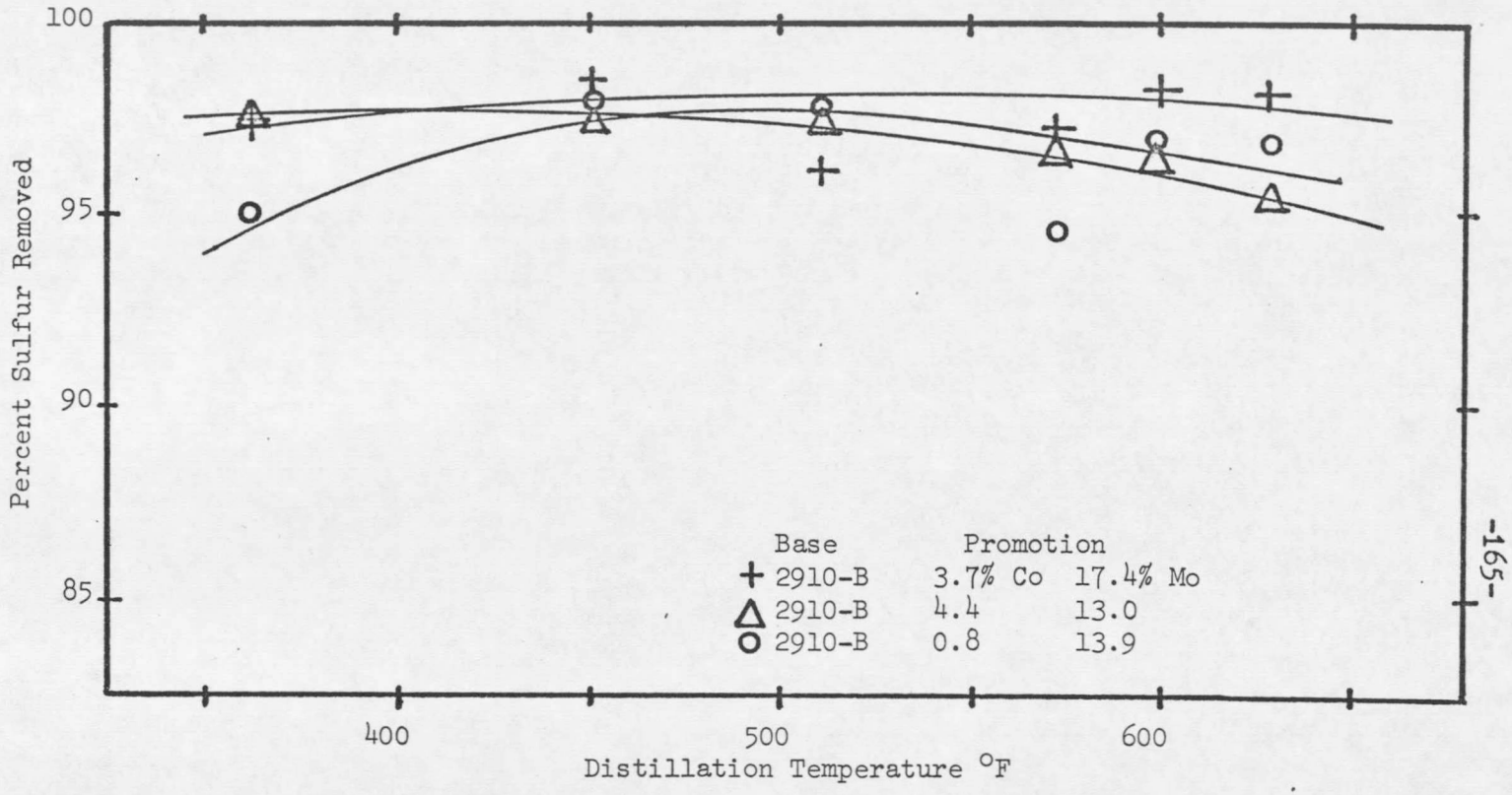


FIGURE 93
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

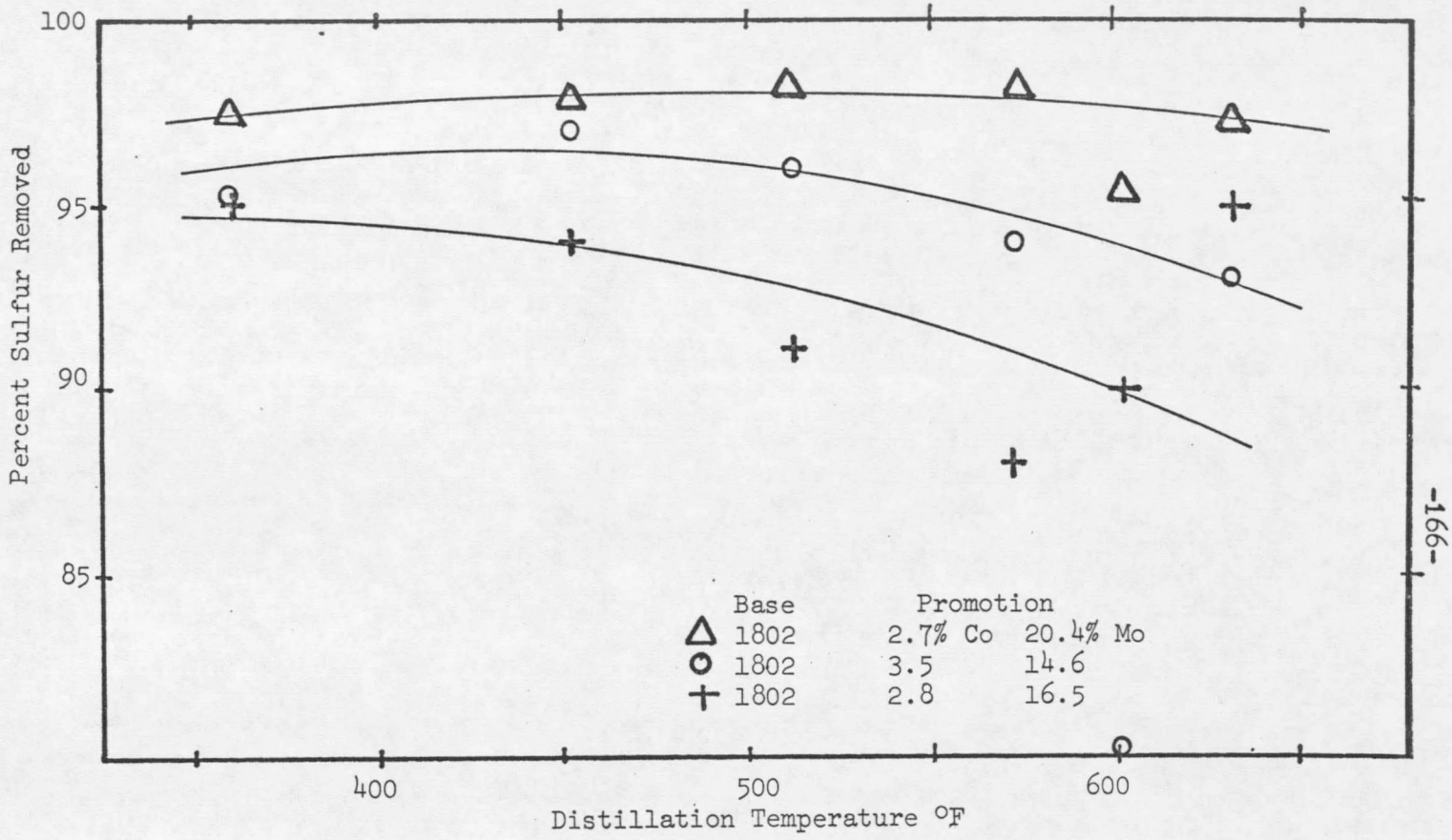


FIGURE 94
Percent Sulfur Removed vs. Distillation Temperature for Samples taken at LHSV 1.5 800°F

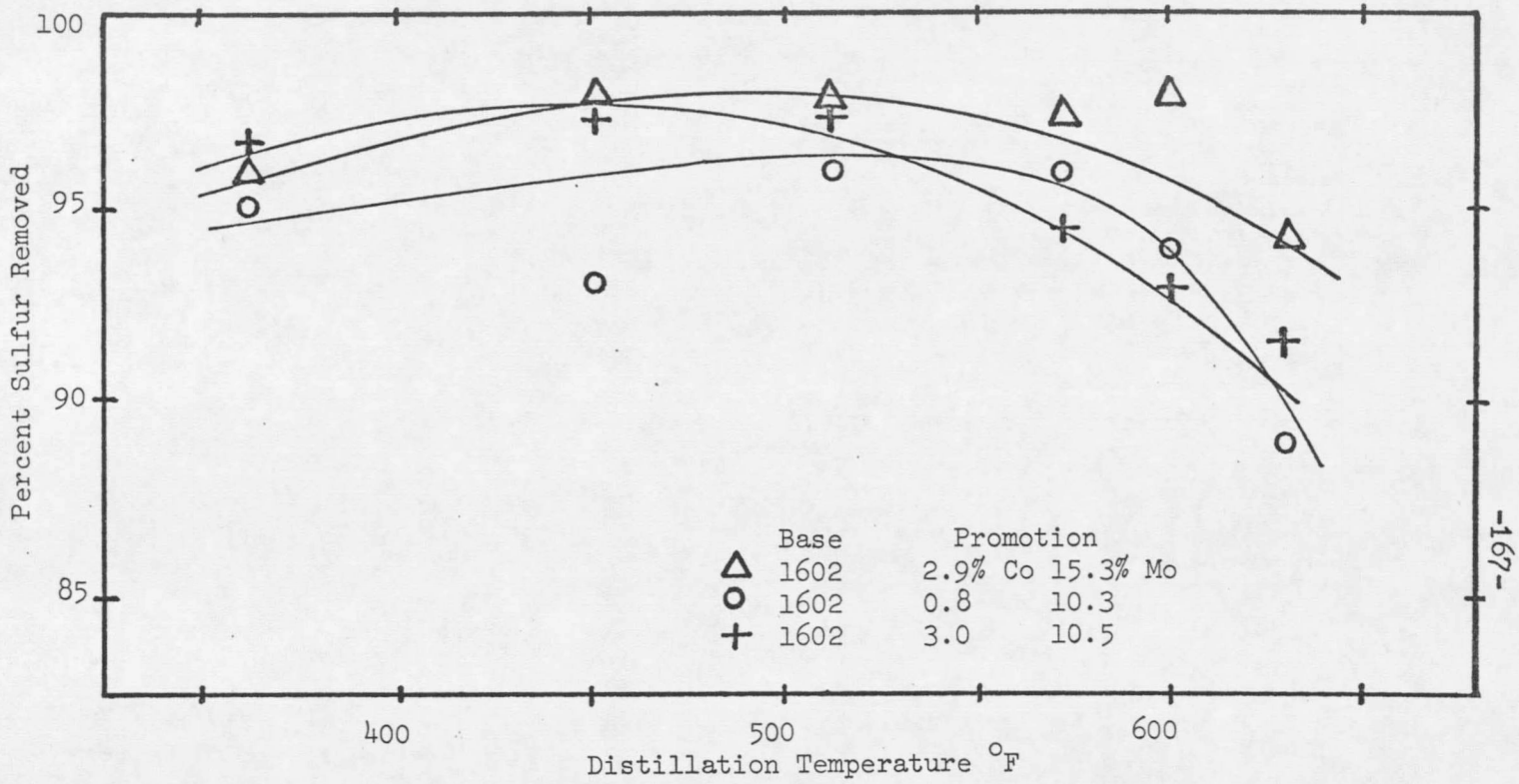


FIGURE 95
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

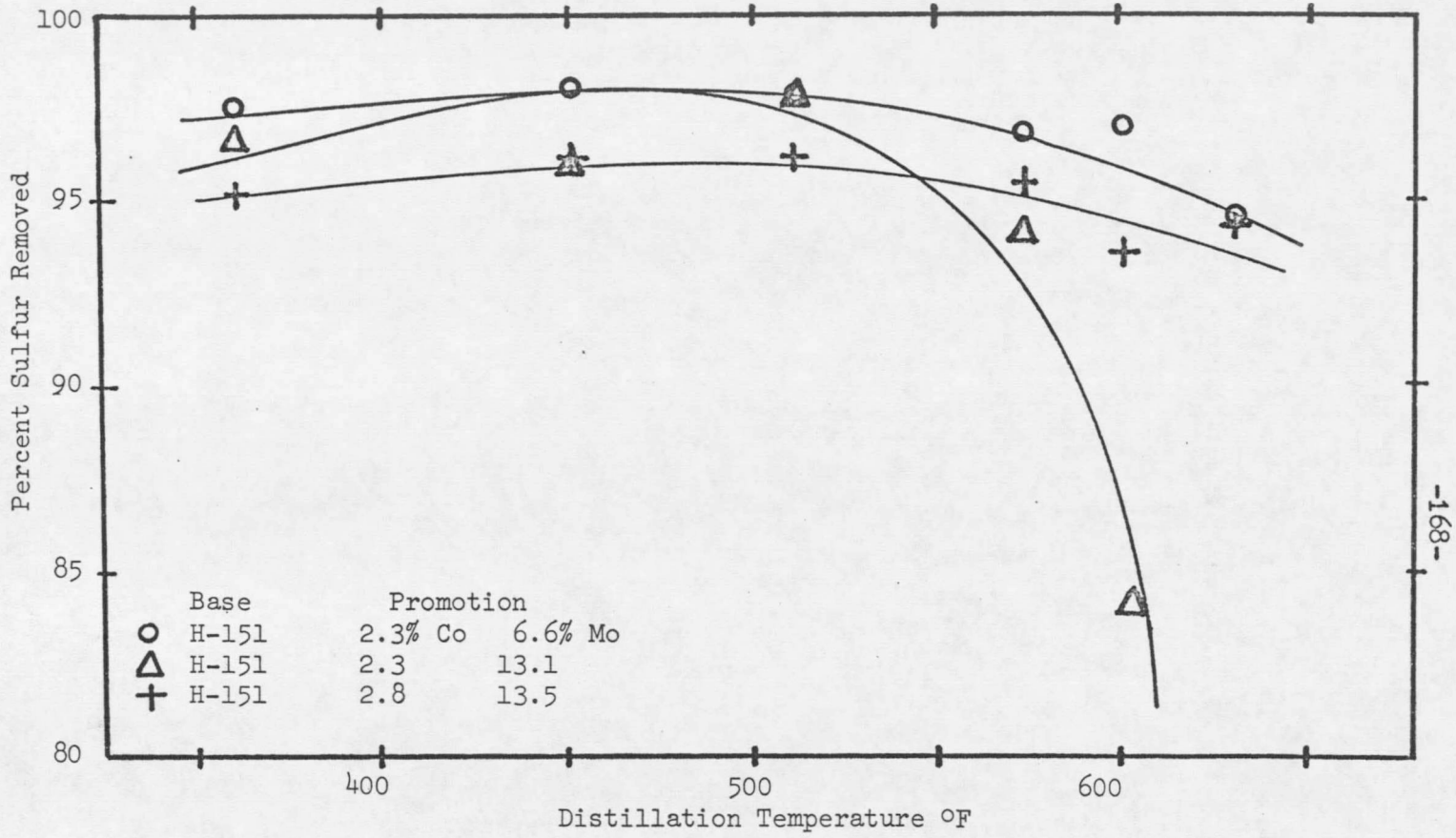


FIGURE 96
Percent Sulfur Removed vs. Distillation Temperature for
Samples taken at LHSV 1.5 800°F

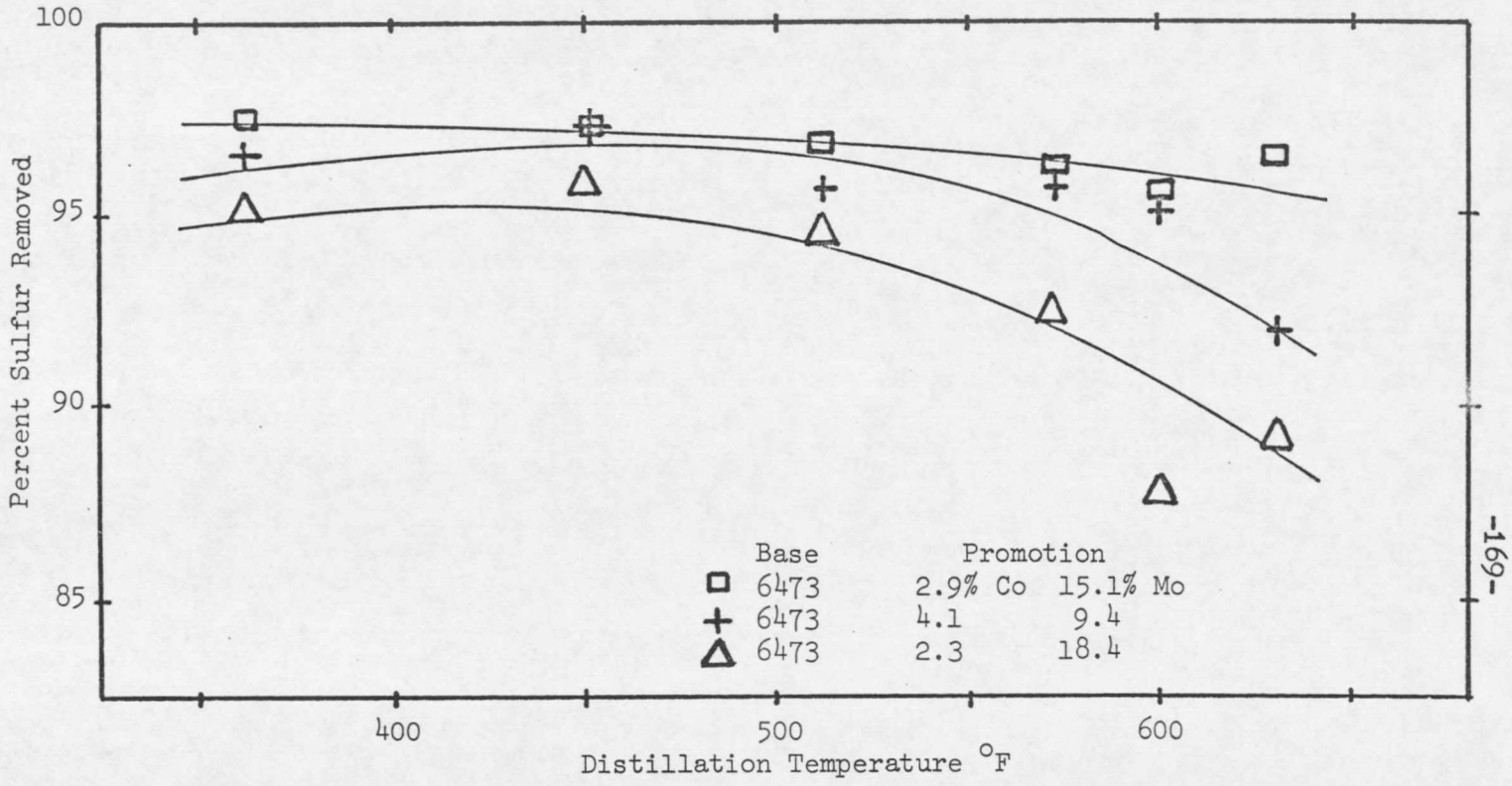


FIGURE 97
Percent Sulfur Removed vs. Distillation Temperature for Samples taken at LHSV 1.5 800°F

TABLE VIII

Noncrystalline Base Materials
°API Gravity Product

Base	Promotion		°API
2910-A	2.7% Co	16.0% Mo	33.1
	1.7	19.4	32.5
	0.9	21.8	32.7
2910-B	4.4% Co	13.0% Mo	33.2
	0.8	13.9	33.1
	3.7	17.4	33.3
H-151	2.3% Co	6.6% Mo	33.3
	2.3	13.1	33.5
	2.8	13.5	33.2
1602	0.8% Co	10.3% Mo	32.7
	3.0	10.5	32.7
	2.9	15.3	32.5
1802	3.5% Co	14.6% Mo	32.3
	2.8	16.5	32.2
	2.7	20.4	33.6
6473	None--Base Material		30.7
	4.1% Co	9.4% Mo	33.6
	2.9	15.1	33.4
	2.3	18.4	33.0

Feed 30.4 °API @ 60°F

Samples taken at LHSV 1.5 800°F

X. LITERATURE CITED

1. Sledjeski, E.W., and R.E. Maples, "Effect of Residual Sulfur Limits on U.S. Refining", Oil and Gas Journal, Vol. 66, No. 18 (April 29, 1968), pp. 55-63.

2. McKinley, J.B., "The Hydrodesulfurization of Liquid Petroleum Fractions", Editor P.H. Emmett, Catalysis, Vol. 5, New York, Reinhold, (1957), pp. 405-497.

3. Andrews, E.B., "Cobalt Molybdenum Desulfurization Catalysts", Chemistry and Industry, (Nov. 12, 1960), pp. 1396-1400.

4. Beuther, H., and O.A. Larson, "Role of Catalytic Metal in Hydrocracking", Industry and Engineering Chemistry Process Design, Vol. 4 (April 1965), pp. 177-181.

5. Ashley, J.H., and D.C.H. Mitchell, "Cobalt-Molybdenum-Alumina Hydrodesulfurization Catalysts", Journal of the Chemical Society, Section A, Part I (1968), pp. 2821-2827.

6. Ashley, J.H., and D.C.H. Mitchell, "Cobalt-Molybdenum-Alumina Hydrodesulfurization Catalysts", Journal of the Chemical Society, Section A, Part II (1969), pp. 2730-2735.

7. Beuther, H., R.A. Flynn, and J.B. McKinley, "For Better Hydrodesulfurization Activity of Promoted Molybdenum Oxide-Alumina Catalysts", Industry and Engineering Chemistry, Vol. 51 (Nov. 1959), pp. 1349-50.

8. Henderson, D.R., "Evaluation of Nickel Tungsten Catalysts for Hydrodesulfurization", M.S. Thesis in Chemical Engineering, Montana State University, Bozeman, Montana (1968).

9. Falk, A.Y., "Tungsten as a Hydrodenitrogenation Catalyst for Petroleum Oil Fractions", Ph.D. Thesis in Chemical Engineering, Montana State University, Bozeman, Montana (1966).

10. Whitcomb, D.C., "Cobaltous Chloride as a Hydrodenitrogenation Catalyst", Ph.D. Thesis in Chemical Engineering, Montana State University, Bozeman, Montana (1968).

11. Barmby, D.S., "The Chemistry of Catalytic Cracking with Molecular Sieve Catalysts", Journal of Catalysis, New York, Academic Press (1968).

12. Gabriel, S., "Silica Alumina Cracking Catalysts", Chemistry and Industry, (Nov. 12, 1960), pp. 1401-1408.

13. Breck, D.W., and J.V. Smith, "Molecular Sieves", Scientific American, Vol. 200 (Jan. 1959), pp. 85-94.

14. Lawrence, P.A., R.W. Aitken, and R.N. Bennett, British Patent No. 1,088,933, (Feb. 12, 1965).

15. Levenspiel, O., Chemical Reaction Engineering, New York, Wiley, (1967) pp. 338-474.

16. Van Zoonen, D., and C. Th. Douwes, "Effect of Pellet Pore Structure on Catalyst Performance", Journal of the Institute of Petroleum, Vol. 49, No. 480 (Dec. 1963), pp. 383-391.

17. Kiovsky, J.R., and L. Berg, "Factors Affecting the Activity of Cobalt Molybdenum Desulfurization Catalysts", Oil and Gas Journal, Vol. 62 (March 30, 1964), pp. 71-72.

18. Cortelyou, C.G., R.C. Malett, and H.H. Meredith, "A New Look at Desulfurization", Chemical Engineering Progress, Vol. 64 (Jan. 1968), pp. 53-59.

19. Hicks, C.L., U.S. Patent No. 3,183,182 (May 11, 1965).

20. Frye, C.G., and J.F. Mosby, "Kinetics of Hydrodesulfurization", Chemical Engineering Progress, Vol. 63 (Sept. 1967), pp. 66-70.

21. Gulf HDS, Hydrocarbon Processing, Vol. 47 (Sept. 1968), p. 197.

22. Harshaw HT-100 Product Information Pamphlet, Harshaw Chemical Company, Cleveland, Ohio.

23. Blume, J.H., D.R. Miller, and L.A. Nicolai, "Remove Sulfur from Fuel Oil at Lower Cost", Hydrocarbon Processing, Vol. 48 (Sept. 1969), pp. 131-136.

24. ASTM Standards on Petroleum Products and Lubricants, American Society for Testing Materials, Part 17, Philadelphia, (Jan. 1968), p. 455.

25. ASTM Standards on Petroleum Products and Lubricants, American Society for Testing Materials, Part 17, Philadelphia, (Jan. 1968), p. 8.

MONTANA STATE UNIVERSITY LIBRARIES
3 1762 10010797 6

D378
G883
cop.2

Grimm, Carlton D
The role of the support in catalytic hydrodesulfurization of diesel fuel

NAME AND ADDRESS
Gary R Hass Cobleigh 403 (S) BMJ
Gary R Hass (S) BMH Cobleigh 403
S. Kujawa 421 Cobl

D378
G883
cop.2