



Evaluation of nickel tungsten catalysts for hydrodesulfurization
by Delmar Roy Henderson

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

Three catalysts of various compositions of nickel and tungsten on a silica-alumina support were prepared and tested to determine their effectiveness as desulfurization catalysts on Mo. 2 Diesel fuel. Comparisons were made with the commercial Houdry-C catalyst.

It was found that the three prepared catalysts and the Houdry-C were not significantly different. That is, sulfur removal was the same for all catalysts. It was also found that the catalyst life was the same for the prepared catalyst DR-3 as it was for Houdry-C.

Operating conditions were also evaluated and it was found that increasing temperature while operating at a LHSV of 1.0 or less would be of no value. It was also found that increasing hydrogen flow beyond 5000 SCF/bbl did not increase sulfur removal.

Unless the feed stock were high in nitrogen (4) as well as sulfur, there appears to be no advantage in using a nickel tungsten catalyst over the commercial Houdry-C.

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CATALYSTS FOR HYDRODESULFURIZATION

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DELMAR ROY HENDERSON

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Bozeman, Montana

August, 1968

ACKNOWLEDGMENT

The author wishes to thank the entire staff of the Chemical Engineering Department of Montana State University, particularly Dr. Lloyd Berg, who directed the research.

The author also wishes to acknowledge the Engineering Experiment Station of Montana State University for their financial support and to thank Husky Oil Company for supplying the oil used during most of the testing.

ABSTRACT

Three catalysts of various compositions of nickel and tungsten on a silica-alumina support were prepared and tested to determine their effectiveness as desulfurization catalysts on No. 2 Diesel fuel. Comparisons were made with the commercial Houdry-C catalyst.

It was found that the three prepared catalysts and the Houdry-C were not significantly different. That is, sulfur removal was the same for all catalysts. It was also found that the catalyst life was the same for the prepared catalyst DR-3 as it was for Houdry-C.

Operating conditions were also evaluated and it was found that increasing temperature while operating at a LHSV of 1.0 or less would be of no value. It was also found that increasing hydrogen flow beyond 5000 SCF/bbl did not increase sulfur removal.

Unless the feed stock were high in nitrogen (4) as well as sulfur, there appears to be no advantage in using a nickel tungsten catalyst over the commercial Houdry-C.

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I INTRODUCTION

Hydrodesulfurization of diesel fuel and other fossil fuels has been of considerable interest to the refiner since the early 1950's. The purpose of desulfurizing was prompted initially by bad odors in the fuel (customer dissatisfaction) and corrosion problems associated with equipment that refined and burned the fuels. However, the reduction of sulfur in fossil fuels has gained interest more recently because of two added factors: a) shortage of elemental sulfur available resulting in inflationary prices of the sulfur, and b) the increasing emphasis on air pollution and resulting laws that are being legislated and/or enforced by state bodies. Legislation is limiting the amount of sulfur permissible in the burned fuels by setting controls on the amounts of sulfur dioxide allowable to be emitted to the atmosphere. By October 1, 1969 (2), the New York State Air Pollution Board has set limits on industries, residences, hospitals, and schools which allow 0.2 pounds of sulfur per million Btu gross heat content. This amounts to about 0.26 weight percent sulfur allowable in fuel oil.

Using hydrogen to treat refinery products is not new. During the early part of the century, I. G. Farbenindustrie (1) pioneered solid fuel hydrogenation, later the basis of Hitler's oil-from-coal program. Esso-Standard Oil Company had high pressure (3000 psig) hydrogenation and hydrocracking in operation at Baton Rouge, Louisiana and Bayway, New Jersey during the 1930's. Following World War II, (predominately in the early 1950's), hydro-treaters were installed to

pretreat the feed to reformers. Excess sulfur, nitrogen, and/or metals in catalytic reformer feed stock suppressed or poisoned the platinum catalyst. Also, the sulfur in the feedstock would form iron sulfide scale that not only plugged the reactors but caused severe metal loss. The hydrogen source for these pretreating units was obtained from the reforming by-products. A typical reformer reaction dehydrogenates cyclohexane to benzene and hydrogen. The hydrogen is normally burned or used in hydrogen processing units.

Other reasons that prompted refiners to turn to hydrogen treating was that the conventional treating processes didn't do the job. Processes such as Doctor treating and copper chloride sweetening only convert mercaptan sulfur to a non-odorous disulfide with the total sulfur content of the feed remaining the same. Improvements can be made by hydro-treating thermally cracked distillates (1) which are difficult to market because of poor color and stability. The hydrogen process will reduce sulfur, carbon residue, and improve the color, odor, phenol, and neutralization numbers. The diesel oils can be made from the catalytic cracked gas oils by hydro-treating. The product results in better cetane and bromine numbers, higher gravity, improved stability and color, as well as reduced sulfur content, olefin content, and carbon-to-hydrogen ratio.

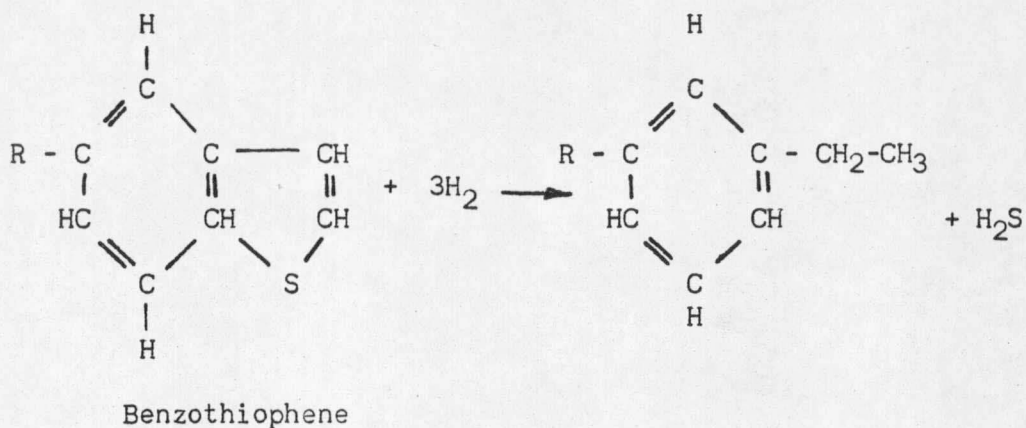
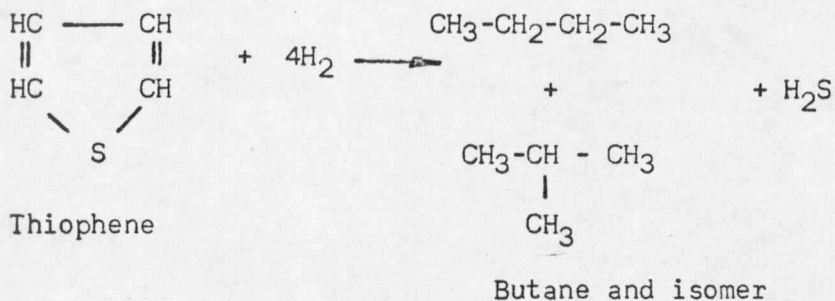
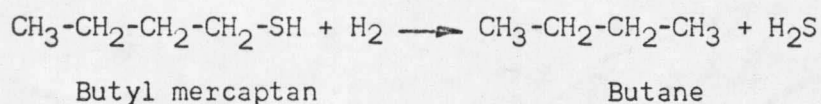
Not only diesel and middle distillates benefit from hydrotreating. Catalytic cracking also benefits by converting refractory sulfur com-

pounds and conjugated aromatics. Most of the cyclic sulfurs concentrate in the heavy gas oil. Refractory conjugated aromatics (multi-ring compounds) in heavy cycle oil crack to coke when the material is recycled in the reactor. A selective partial hydrogenation of these conjugated compounds reduces the refractoriness, resulting in less coke. Because the capacity of most catalytic cracking units is limited by the ability to burn coke from catalyst during regeneration, hydrogenation of heavy cycle oil allows several percent more catalytic gasoline yield at the maximum allowable coke rate.

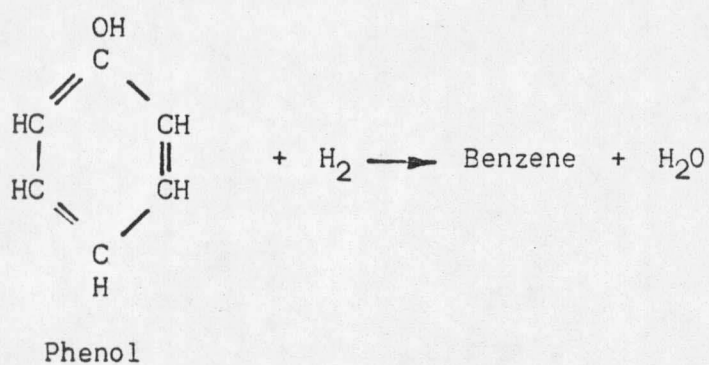
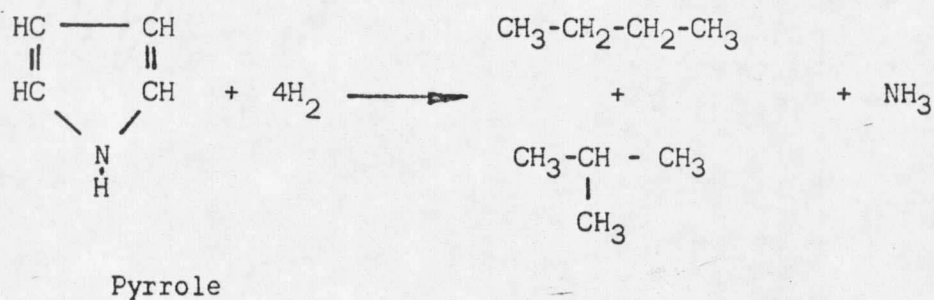
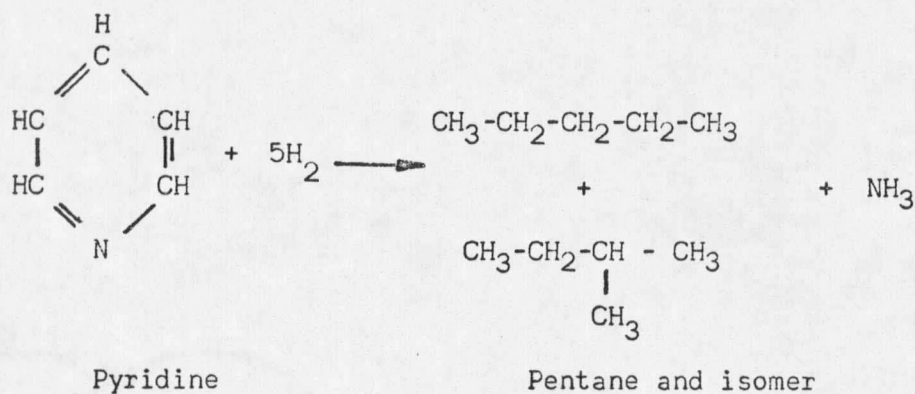
II PROCESS REACTIONS

Not only desulfurization takes place during hydro-treating. Some of the other processing reactions are denitrification, deoxygenation, olefin and diolefin saturation, and hydrocracking. Typical reactions of these compounds are:

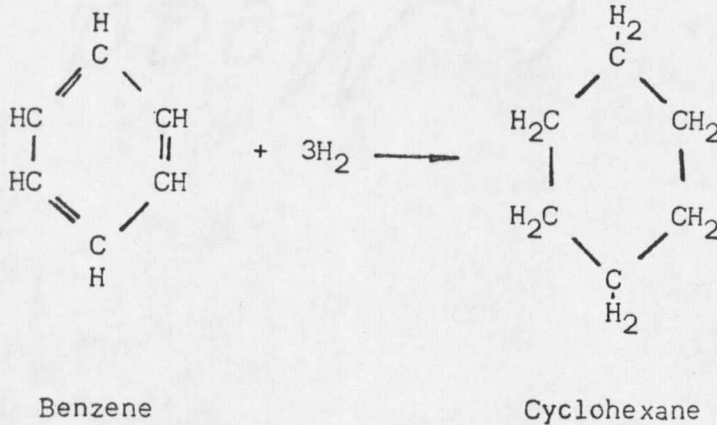
Desulfurization



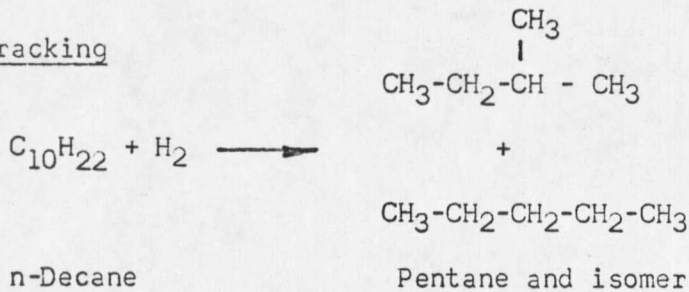
Denitrification



Saturation

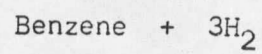
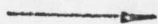
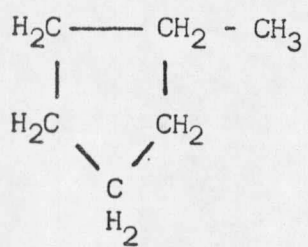


Hydrocracking



The most common impurities in the fossil fuels from refinery streams are sulfur compounds followed by nitrogen and oxygen. Mercaptans are more easily reacted than the refractory cyclic sulfur compounds. Metals such as vanadium, arsenic, and sodium are removed, apparently by the formation of metal hydrides.

Hydrogen required for treating distillates, gasoline etc., is usually obtained from the catalytic reformer off-gas. A typical reaction of reformer system is:



III OBJECTIVES OF THE THESIS

The purpose of this thesis was to apply nickel and tungsten to a support material (silica-alumina), thereby preparing a catalyst for hydrodesulfurization of diesel fuel.

Nickel tungsten catalysts have been used previously by Shell Development Company (3) for their vapor phase desulfurization process. The catalyst used by Shell contained approximately 70% nickel and 30% tungsten. Shell discontinued the use of this catalyst in favor of a cobalt molybdenum catalyst.

In 1965, Falk (4) completed a thesis on denitrification of gas oils using a nickel tungsten catalyst on a silica-alumina support. Falk's thesis indicated that a catalyst containing 7.5% nickel and 15.1% tungsten was an effective denitrification catalyst, being more active than existing commercial catalysts. Falk also inspected the effects of desulfurization in the same report. Falk's work centered around gas oils from California crudes that were relatively high in nitrogen and low in sulfur.

As an extension of Falk's investigation, it was proposed that a study be made using nickel tungsten catalysts on a medium boiling range diesel fuel of high sulfur content.

Primary objectives were established as follows:

- 1) Prepare a catalyst that contained an optimum amount of

nickel and tungsten; that is, obtain maximum sulfur conversion with the optimum amounts of nickel and tungsten on an aluminum-silicon oxide catalyst support.

2) Compare the optimum catalyst with a commercially used hydro-treating catalyst.

3) Select optimum operating conditions for maximum desulfurization with previously set pressure limitation.

4) Get a 98% removal of sulfur from diesel fuels.

5) Determine deactivation rate of the developed catalyst compared with the commercial catalyst by making extended runs on both catalysts of approximately 700 hours.

6) Evaluate the developed catalyst on diesel fuels of various sulfur concentrations.

7) Determine the order and reaction rate constant for the desulfurization system.

IV EQUIPMENT AND PROCEDURES

A. Reactor

Figure 2 shows a schematic diagram of the equipment used in the project. The reactor construction is shown in more detail in Figure 3. The reactor consisted of a piece of 1-inch schedule 80, 304 stainless steel pipe approximately 34 inches long with a threaded removable plug on the bottom for catalyst loading. The top 10-12 inches were filled with alundum pellets of 1/4-inch size. Above the catalyst a few inches of 1/8-inch alundum pellets were placed. The catalyst was mixed (60 cc of catalyst with 60 cc of 1/8-inch alundum pellets) with the 1/8-inch pellets to make up a volume of 120 cc. Below the catalyst bed, 1/4-inch alundum pellets were placed and a screen was inserted to prevent the catalyst from falling into the outlet line.

B. Temperature Measurement

A 1/4-inch stainless steel thermowell was inserted into the top and extended most of the way through the reactor. Three chromel-alumel thermocouples were placed at various distances (Figure 3) through the catalyst bed. The three chromel-alumel thermocouple readings were recorded on a Leeds and Northrup Micromax continuous recorder. An iron-constantan thermocouple was also installed and the temperature was checked on a portable potentiometer as a cross-check against the continuous recorder. Temperatures in the reactor were maintained by three separate Variacs. Ammeters were provided on each

circuit to prevent overloading of the Variac and also to indicate that the element was heating.

C. Hydrogen Flow

A Nupro micro control valve was used to adjust hydrogen flow rate. A pressure drop of 50 psig was maintained across the valve by setting a pressure regulator on the hydrogen cylinder. A sight-through rotameter was used as a flow indicator. The rotameter was calibrated with a wet test meter on hydrogen flow with no oil in the system. Also, hydrogen flow was checked periodically during the run with the wet test meter on the effluent gas. Within the accuracy of the rotameter the difference in inlet and effluent gas could not be detected.

D. Pressure

Pressure was maintained on the system by a Grove Mity-Mite back-pressure regulator. Pressure was recorded on a Foxboro two-pen recorder and charts were changed daily.

E. Pumping Rate

A Lapp Pulsafeeder diaphragm pump was used to maintain pumping rate of oil. The feed rate was checked by measuring the rate from a 1000 cc calibrated reservoir and instantaneous checks were made using a stopwatch and a 50cc calibrated column. Also, weight balances were made periodically during extended runs to obtain a yield balance.

F. Sampling

Samples were taken periodically during the run. Usually, after the unit was lined out, samples were taken at four- or eight-hour intervals. On the extended run, samples were reduced to 12 and 24 hour periods. To facilitate sampling, a sampling device was installed on the outlet of the back pressure valve (Figure 2). The system consisted of two solenoid valves actuated by an on-off timer. The timer was set to take a sample of approximately 60 to 80 cc of oil. The time for samples was approximately one hour during most of the runs since the space velocity was set at approximately 60 cc per hour.

G. Catalyst Preparation

The catalyst used in this case was a nickel tungsten catalyst prepared by applying the tungsten and nickel to the surface of an aluminum oxide-silicon oxide base. The base material was Harshaw 1602-T 1/8-inch extruded pellets containing approximately 6% silicon oxide and 94% aluminum oxide. Surface area, bulk density, and other pertinent data concerning the support are shown in Table VI of the appendix.

The general procedure for catalyst preparation was:

- 1) Dry and calcine the support material for 24 to 48 hours at 900°F.

- 2) Make up a saturated solution of tungstic acid dissolved in 14-16% aqueous ammonia. It was found that the saturated solution was approximately 0.016 gms tungstic acid per cc of aqueous ammonia solution.

The tungstic acid is relatively insoluble in most solvents. Addition of the acid was made slowly and the mixture was stirred constantly with a magnetic stirrer. Care was exercised to insure a pressure-tight seal to prevent loss of ammonia. The solution was also cooled periodically while dissolving the tungstic acid.

3) The calcined support was then covered with the ammonia-tungstic acid solution and placed in a cold water bath to prevent ammonia break-out and precipitation of the tungstic acid on the surface of the catalyst. During the adsorption, considerable heat is released. After a period of two to four hours a slight vacuum was pulled on the system to draw air out of the porous surface of the support material and allow further adsorption of the tungstic acid. This was continued for 24 hours. The remaining solution was filtered off and the support and adsorbed tungstic acid was calcined again for 24-48 hours at 900°F. The literature indicated that tungstic acid will be oxidized to WO_3 at 900°F. The weight gain (assumed as WO_3) is determined. The procedure had to be repeated three to four times to obtain 16 to 17% tungsten on the catalyst.

4) A solution of nickelous nitrate was used to apply the nickel to the catalyst support. The catalyst support was covered with a water solution of nickelous nitrate and a slight vacuum was pulled on the container to withdraw air from the support. The "soaking" was maintained for 24 hours. Calcining was repeated at 900°F, as outlined in Step 3.

The procedure was to apply tungsten first, followed by nickel. It was found that the ammonia solution used to dissolve the tungstic acid would leach part of the nickel off the support if the nickel was applied first. This was evident from the familiar blue solution formed with a nickel-ammonia complex. Since the promoter amount is established by subsequent weight increases, the amount of nickel leached off would not be known.

H. Chemical Analysis

Sulfur analysis was performed using the lamp method (ASTM D 157) (10). A single sulfur analysis was made on each sample. Sufficient samples (may be considered replications) were taken to insure repeatability of the testing procedure. Nitrogen was determined by the modified Kjeldahl method.

I. Start-up Procedure

The reactor and system were purged with hydrogen for approximately 30 minutes. During this same period the temperature of the reactor was brought up to 200-300°F. After purging at atmospheric pressure, the system was pressured up to 300 psig by setting the Grove back pressure control valve. Hydrogen flow was continued at the rate of 1.5 - 2.0 SCH and the temperature of the reactor brought up to 650°F at the rate of 100-150°F per hour. Upon reaching 650°F, the system was checked thoroughly for leaks. With the system at 300 psig and 650°F, the unit was ready for catalyst sulfiding.

Catalyst sulfiding information in the literature (5) indicates that the sulfide form is the catalyst-active form. Falk (4) also indicated that the sulfide is the active form of the nickel and tungsten catalyst. The sulfiding is accomplished by passing a gas mixture containing 20% hydrogen sulfide and 80% hydrogen over the catalyst bed. The sulfiding was maintained at a rate of a SCF/hr for a period of 4-5 hours. The temperature was held at 650°F while sulfiding. This procedure was used on all runs except No. 8 and on the Harshaw catalyst 4401E which was the presulfided form. Sulfiding was carried out at 300 psig in all cases.

J. Feedstock

For the greater part of this desulfurization study, the feedstock was Number 2 diesel fuel containing 1.66 weight percent sulfur. The fuel was obtained from the Husky Oil Company refinery at Cody, Wyoming. Inspection data on the fuels are shown in Table VII of the appendix. Other fuels tested were Number 2 diesel from Continental Oil Company at Billings, Montana and Number 2 diesel from Caribou Refining Company at Cowley, Wyoming.

V DISCUSSION AND INTERPRETATION OF RESULTS

A. Introduction

A total of ten runs was made during the period of the research. Preliminary runs were made on Houdry-C and Harshaw 4401E catalysts to become familiar with the equipment, establish operating techniques, and perfect the analytical procedures.

B. Preliminary Runs

The initial run was made using Houdry-C catalyst. This run was continued for 30 hours and then stopped because of pump problems. Pumping rates varied drastically and the results were deemed useless.

The second run was again made with Houdry-C catalyst. The purpose of this run was to collect data on the various operating effects such as temperature and space velocity. Data were also collected on Harshaw 4401E presulfided nickel tungsten catalyst. Pressure was also observed as a variable.

C. Operating Variables

1) LHSV (liquid hourly space velocity). Figure 4 shows the effect of LHSV on sulfur conversion at two different temperature levels. The results were as expected; that is, conversion increased with increased temperature and decreased with increased LHSV. The data indicate that little can be gained by increasing the temperature at LHSV of 1.0 or less. Should increased unit capacity be desired at constant sulfur conversion, an increase in LHSV accompanied by an increase in

temperature would accomplish the job. However, increasing the temperature also induces cracking, resulting in more gas make (less saleable product). This can be observed on the gas analysis data (Table XVII) and the ASTM distillation. The distillation of product obtained while operating at 770°F (Figure 5) shows a lower boiling point distillation curve and a higher API gravity.

From Figure 4 the LHSV conversion data indicate that the Harshaw 4401E catalyst would not be a very effective catalyst for desulfurization. This catalyst is a nickel tungsten type on a support material containing a high percentage of silica.

The Houdry-C data show a somewhat better conversion at LHSV greater than 1.0 than does the prepared DR-3 catalyst.

2) Temperature. Figure 6 shows the effect of temperature on sulfur conversion. As expected, the conversion increases with increased temperature. The data for determining the temperature effect were collected using a LHSV of 1.0, hydrogen flow of 3550 SCF/bbl, pressure of 300 psig, and prepared catalyst DR-3. (See Table XIII of appendix.) A first degree curve was fitted to the data by the method of least squares.

3) Hydrogen Flow. The effect of hydrogen flow is shown on Figure 7. Other variables were held constant at the following values: LHSV -- 1.0, temperature -- 700°F, and pressure -- 300 psig. Houdry-C

catalyst was used to make this evaluation. A second degree curve was fitted to the data. The results are in agreement with Falk (4) and Whitcomb (6). The conversion increases with increased hydrogen flow out to approximately 5000 SCF/bbl. Above 5000 SCF/bbl, the catalyst activity may be considered independent of hydrogen flow.

A hydrogen flow rate of 3500-4000 SCF/bbl was used for most of the investigations. The catalyst life studies were made using a flow of 7000 SCF/bbl.

4) Pressure. As expected, the sulfur conversion increased with increasing pressure (Figure 8). Harshaw 4401E catalyst was used during this test run. Pressures of 300, 650, and 1000 psig were selected to collect data.

The pressure for all remaining runs was set at 300 psig. Selection of 300 psig was based on the availability of hydrogen at this pressure from reformer units in most refineries.

D. Catalyst Evaluations

Three catalysts were prepared using varying amounts of nickel and tungsten applied to Harshaw's 1602-T support material. The catalyst compositions are shown in the following Table:

TABLE I. Prepared Catalyst Compositions

<u>Catalyst No.</u>	<u>% Nickel</u>	<u>% Tungsten</u>
DR-1	1.57	16.65
DR-2	10.20	16.65
DR-3	7.30	5.85

Runs Numbers 5, 6, and 8 (Tables XI, XII, and XIV of appendix) were evaluations of the three prepared catalysts. The results of conversion versus time are shown on Figures 9, 10, and 11. Run No. 8 was presulfided for one-half the normal sulfiding period. The results are quite evident; the conversion starts at 95.65% and increases to about 97.0% during the first 40 hours. The period of 40 hours to 103 hours gives a mean conversion of 97.223% with very little change in the slope of the line. This portion of the run was used to compare with Runs 5 and 6.

Conversion has been corrected for temperature and hydrogen flow to the base conditions of 700°F and 4000 SCF/bbl. Data shown on Figures 6 and 7 were used to establish a correction factor for the temperature and hydrogen flow.

Table II (below) shows the comparisons of the three catalysts. Table III (below) gives an analysis of variance for the weight percent sulfur in the product oil for the three different catalysts.

TABLE II. Sulfur Conversion for Prepared Catalysts

<u>Catalyst No.</u>	<u>Mean Conversion</u>		<u>H₂ Flow</u>	<u>Temperature</u>
	<u>Uncorrected</u>	<u>Corrected</u>		
DR-1	97.541	97.462	3878	706
DR-2	96.869	96.675	4103	710
DR-3	97.226	97.194	3897	703

TABLE III. Analysis of Variance on Prepared Catalysts

Source of Variation	df	Sums of Squares	Mean Sums of Squares	F	Decision
Different Catalysts	2	** 7.0095	3.50047	3.5	Accept*
within (error)	41	41.3063	1.00747		
Total	43	48.3158			

*Tested at 1.0% level F 2/41 df = 5.18

**Sums of squares x 0.001

It is hypothesized that the weight percent from all three prepared catalysts is the same. From the Analysis of Variance (Table III), we accept the hypothesis since the experimental F was found to be less than the F arrived at from statistical tables (12). The test (F) can be interpreted to mean that a value of F as large or larger than 5.18 will occur only one time out of 100 as a result of chance sampling errors if the hypothesis is true. In this case, the hypothesis is true; that is, all the sample weight percent sulfur may be considered the same.

E. Catalyst Life Comparisons

Since catalyst deactivation is very important when making a catalyst selection, it was desirable to obtain some type of comparable results with the commercial catalyst. A literature study was made to determine if there were any published data available on the life of Houdry-C catalyst. The search revealed some data on cobalt molybdenum (similar to Houdry-C) in terms of bbl/lb, but gave no indication of the conversion at the beginning and the end.

It was decided that 700-hour runs would be made on the Houdry-C and the prepared DR-3 catalysts. Figures 12 and 13 show the results of the two runs. During the run on DR-3, data were collected (interval between 400-500 hours) on the effects of LHSV and temperature. These data were used in Figure 4 and in the determination of the reaction order and rate.

For the extended run the operating variables were set at: LHSV -- 1.0, temperature -- 700°F, pressure -- 300 psig, and hydrogen flow -- 7000 SCF/bbl. The comparative results of the two runs are shown in Table IV, below.

The slope of the regression line indicates that the deactivation rate is slightly higher on the DR-3 catalyst but the mean conversion is higher than the Houdry-C. In view of the small differences in conversion and regression line slope it is concluded that there is no difference in deactivation between the two catalysts.

TABLE IV. Catalyst Life Comparison: Houdry-C and DR-3.

Catalyst	DR-3	Houdry-C
Mean Conversion	97.532	97.347
Slope Regression Line	0.309×10^{-3}	0.152×10^{-3}
Product Yield Wt %	92.83	95.12
API Gravity	34.3	34.1
ASTM Distillation		
IBP	400	403
10%	474	475
30%	524	525
50%	554	553
70%	579	578
90%	615	612
EP	658	654

During the extended run, gas samples were collected and a weight balance was taken periodically. Also, product API gravity and ASTM distillations were observed. These data are also shown in Table IV. The ASTM distillation plots are shown in Figure 5.

The reduced yield on DR-3 catalyst and increased gas volumes indicated that the nickel tungsten catalyst may be causing more cracking than the Houdry-C. An alternate possibility is that the 6% silica in the support material (Harshaw 1602-T) induces cracking. The author's experience with catalytic cracking catalysts substantiates this belief. The use of silica-alumina mixtures in lieu of alumina only catalyst yields considerably more gasoline (less bottoms) from catalytic cracking units.

F. Results of Desulfurization on Other Feedstocks

a) Cowley, Wyoming Diesel Fuel. Number 2 diesel fuel was obtained from Caribou Refining Company at Cowley, Wyoming. The sulfur content was 1.97%. Other inspection data are shown in Table VII of the appendix.

This fuel was charged to the unit at the end of the 700-hour catalyst study on DR-3. The unit was operated approximately 50 hours on this fuel. The results are shown below in Table V.

b) Continental Oil Diesel Fuel from Billings, Montana. Following the run on Cowley fuel, Number 2 diesel fuel from Continental Oil Company was charged to the unit. This fuel contains 0.187% sulfur and has been previously hydro-treated by Continental. Other inspection data are shown in Table VII of the appendix. The results of this run are also shown in Table V below.

TABLE V. Results of Desulfurization of Other Feeds.

	<u>Cowley</u>	<u>Continental</u>
% Sulfur in Feed	1.97	0.187
% Sulfur in Product	0.0439	0.0313
Mean Conversion	97.77	83.3

Sulfur conversion on the Cowley fuel was satisfactory. However, desulfurization of the Continental fuel wasn't particularly successful. Possibly the reason for the poor results is that the fuel, having been previously treated, has most of the "easy to remove" compounds missing, leaving the more difficult cyclic compounds.

G. Thermodynamics and Kinetics of Desulfurization

The reaction of sulfur compounds to saturated hydrocarbons and hydrogen sulfide (see Section II) is discussed by Mitchell (5). The equilibrium constants are highly positive (negative ΔF) for the range of 25°C to 600°C. Green (7) also evaluated the thermodynamics for thiophene reacted with hydrogen to yield butane and hydrogen sulfide. He showed a ΔF of -14,560 at 375°C. For hydrodesulfurization of thiophene, $\log K_{eq}$ decreases rapidly with increasing temperature and becomes negative above 525°C. Since the reactions do not occur in the absence of a catalyst (5), (up to 500°C), they must be controlled by rate processes.

Whitcomb (6) has described the kinetics of denitrification and desulfurization in some detail. Also, Rosenheimer (8) reviewed the kinetics of denitrification, desulfurization, and olefin saturation. Based on information from Whitcomb's thesis (6), the desulfurization rate equation was written as:

$$-r_s = K'_s (S)^{a'} (H)^{b'}$$

Since the hydrogen flow was maintained at 4000 SCF/bbl or above for this study, the (H) would be in excess and would not effect the rate of reaction. The modified rate equation can then be written:

$$-r_s = K_s (S)^a$$

where

$$K_s = K'_s (H)^b$$

The pseudo order of the reaction was found by plotting the $\log(r_s)$ versus $\log(S)$. (r_s) was obtained by graphically differentiating the curve of conversion versus $(1/LHSV)$ at several points. Figures 14 and 15 show the respective curves. The slope of $\log(r_s)$ versus $\log(S)$ gives the pseudo reaction order. For this system the order was 1.67. Figures 16 and 17 show the data using a reaction order of 1 and 2 for catalyst DR-3 at 700°F and 800°F. It is apparent that the reaction order is something higher than 1 from the plot shown on Figure 16. However, a second order curve (Figure 17) fits the data fairly well for desulfurization at 700°F. Desulfurization at 800°F doesn't appear to be satisfied by any of the orders tested. It is felt that insufficient data at 800°F was collected to justify establishing a reaction order.

For the reaction order of 1.67, the rate equation in the integrated form is:

$$\frac{1.5}{C_s^{.67}} - \frac{1.5}{C_o^{.67}} = K_s$$

A plot of $1.5/C_s^{.67}$ (Figure 18) versus t yielded a straight line, indicating that the reaction order is correct. The activity energy was found to be 7500 cal/mol from Figure 19. The final form of the rate equation is:

$$-r_s = 2.68 \times 10^3 \times e^{-7500/1.987(T)} \times (S)^{1.67}$$

Nomenclature used:

- r_s	reaction rate (wt% S)(cc-oil)/(cc-catalyst)(hr)
K_s	reaction rate constant $1.5(\text{cc-oil})/(\text{hr})(\text{cc-catalyst})(\text{wt\% S})^{.67}$
(S)	sulfur concentration, wt%
(H)	hydrogen concentration
	space time, hrs
C	concentration
T	temperature

VI SUMMARY AND CONCLUSIONS

a) For the three catalyst prepared and tested, the percent sulfur removal (conversion) appears to be independent of promoter composition. Based on this information, the most economical catalyst would have minimum amounts of nickel and tungsten on the support.

b) When the prepared catalysts (assuming no significant difference among prepared catalysts) are compared to the commercial Houdry-C catalyst, there is no difference in mean sulfur conversion of catalyst deactivation.

c) When a unit (hydro-treating) is operated at LHSV of 1.0 or lower, there is no distinct advantage in operating at a temperature higher than 700-725°F. Also, there is no gain in conversion for operating with a hydrogen recycle rate of higher than 5000 SCF/bbl.

d) The reaction order of the system is 1.67 and the rate equation is:

$$-r_s = 2.68 \times 10^3 \times e^{-7500/1.987(T)} \times (S)^{1.67}$$

VII RECOMMENDATIONS

When considering catalyst for desulfurization there appears to be no advantage in using a nickel tungsten catalyst over the Houdry-C (cobalt molybdenum). Assuming that the catalyst life of both are the same, the cost of cobalt molybdenum would carry a distinct advantage as its cost is \$1.25/lb compared with the cost of a comparable nickel tungsten catalyst at \$2.73/lb.

Should hydro-treating be installed on catalytic cracking or hydro-cracking feed preparation, the nickel tungsten catalyst would show a distinct advantage because of its superior denitrification qualities, as shown by Falk (4).

VIII APPENDIX

TABLE VI. Properties of Catalyst and Support Material

<u>Catalyst or Support</u>	<u>Surface Area (M²/g)</u>	<u>Pore Vol. (cc/g)</u>	<u>Bulk Density (#/ft³)</u>	<u>Pore Dia. (A^o)</u>	<u>Support Type and Size</u>
*Houdry-C	310 to 340	0.45	53	55	1/8" alumina extrusions
**Harshaw 4401E	212	0.39	59	--	1/8" silica- alumina ex- trusions
***Harshaw A1-1602-T	210 to 240	0.48	52	--	1/8" silica- alumina tablets

* Contains 3.0 Wt% CoO and 15.0 MoO₃

** Contains 6.0 Wt% Ni and 19.0 W on a support of approximately 50% SiO₂

*** Support material for all prepared catalysts: contains approximately 6.0% SiO₂

TABLE VII. Inspection Data of Feedstocks

<u>Feed</u>	<u>Husky #2 Diesel</u>	<u>Cowley, Wyo. Diesel</u>	<u>Conoco Diesel</u>
Density, °API	31.9	28.7	33.9
<u>ASTM Distillation</u>			
IBP	399	390	374
5%	456	437	419
10%	485	461	437
30%	540	492	482
50%	564	533	521
70%	586	577	543
90%	619	616	586
95%	644	644	608
EP	660	650	617
Ave. Mol. Wt. (Calc.)	222	205	200
<u>Chemical Analysis</u>			
Sulfur, Wt%	1.66	1.97	0.187
Nitrogen, ppm	350	----	----
Aniline, Pt.	148	----	----

TABLE VIII. Desulfurization Data from Run #2 Using Houdry-C Catalyst

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Pressure</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Mean Conversion</u>
HC-1	1.0	706		300	0.0205	97.52	
HC-2		695			0.0196	98.22	
HC-3		695	702		0.0102	99.39	*98.58
HC-4		705			0.0116	99.30	
HC-5		710			0.0225	98.47	
HC-6	2.0	703			0.043	97.41	
HC-7		703	703		0.047	97.17	97.23
HC-8		703			0.0478	97.12	
HC-9	3.0	---			0.0855	94.85	
HC-10		710			0.0710	95.72	95.26
HC-11		697	704		0.0795	95.21	
HC-12		798			0.0437	97.37	
HC-13		785	792		0.0321	98.07	97.72
HC-14	2.0	804			0.0286	98.28	
HC-15		790	797		0.0248	98.51	98.39
HC-16	1.0	800			0.0236	98.58	
HC-17		800	800		0.0314	98.11	98.34

*The value of 97.42 was used in LHSV plot (Figure 4). This value is the mean of Houdry-C from the catalyst life study.

TABLE IX. Desulfurization Data from Run #3 Using Harshaw 4401E Catalyst

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Pressure</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Mean Conversion</u>
4401E 1	1.0	700		300	0.080	95.19	
2		700			0.0875	94.73	
3		701			0.114	93.14	91.72
4		700			0.146	91.20	
5		704			0.152	90.84	
6	2.0	700			0.267	83.92	
7		704			0.262	84.22	
8		700			0.298	82.05	82.80
9		---			0.316	81.00	
10		776			0.148	91.09	
11		805			0.110	93.37	
12		795			0.119	92.83	92.24
13		800			0.140	91.67	
14	1.0	796			0.067	95.97	
15		803			0.068	95.90	
16		805			0.083	95.00	95.56

TABLE X. Desulfurization Data from Run #4 Using Harshaw 4401E Catalyst

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Wt % Sulfur</u>	<u>% Con- version</u>	<u>Mean Conv.</u>	<u>Pressure</u>	<u>Hydrogen Flow</u>
4401E								
1A	1.0	712		0.0597	96.40	Line out	300	3500
2A		698		0.071	95.72			3500
3A		698		0.1295	92.20			3500
4A		707		0.170	89.76			4200
5A		714		0.166	90.00			4200
6A		714	705	0.150	90.96	90.524		3900
7A		712		0.157	90.54			4200
8A	0.91	701		0.160	90.36			4500
9A	0.91	696		0.190	88.56			4500
10A	1.0	701		0.136	91.81			4500
11A		701		0.112	93.25		650	4000
12A		700	701	0.101	93.92	93.41		4500
13A		703		0.104	93.73		4500	
14A		700		0.134	91.93		3500	
15A		698		0.096	94.22			4100
16A		701		0.0713	95.70		1000	5000
17A		700		0.0540	96.74			4700
18A		698	703	0.052	96.87	96.74		4100
19A		702		0.0497	97.00			4500
20A		700		0.055	96.69			4500
21A		706		0.0423	97.45			4500

TABLE XI. Desulfurization Data from Run #5 Using Prepared Catalyst DR-1

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Wt % Sulfur</u>	<u>% Con- version</u>	<u>Mean Conv.</u>	<u>Hours on Stream</u>	<u>Pressure</u>	<u>Hydrogen Flow</u>
1A	1.0	734		0.0318	98.09	Line out	1.5	300	----
1B		712		0.0343	97.94		6.0		
1C		702		0.0384	97.69		11.5		3800
1D		707		0.0462	97.22		14.5		3800
1E		703		0.0358	97.84		18.5		3550
1F		707		0.0303	98.17		22.5		3600
1G		712		0.0363	97.83		28.5		3800
1H		706	706	0.060	96.39	97.541	37.5		4000
1I		701		0.0454	97.27		43.0		3800
1J		705		0.0345	97.92		46.5		4500
1K		710		0.0415	97.50		50.0		4000

TABLE XII. Desulfurization Data from Run #6 Using Prepared Catalyst DR-2

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Wt % Sulfur</u>	<u>% Con- version</u>	<u>Mean Conv.</u>	<u>Hours on Stream</u>	<u>Pressure</u>	<u>Hydrogen Flow</u>
2A	1.0	709		0.0312	98.12		13.5	300	4500
2B		707		0.052	96.87		18.5		4500
2C		703		0.051	96.93		23.5		4250
2D		698		0.064	96.15		29.5		3800
2E		698		0.062	96.27		34.5		
2F		703		0.0482	97.10		39.5		
2G		707		0.044	97.35		43.5		
2H		712		0.051	96.93		52.5		
2I		709		0.0555	96.66		57.5		
2J	0.98	700		0.063	96.20		61.5		
2K		709		0.067	95.96		65.5		
2L		707		----	----		70.5		
2M		716		0.0355	97.84	96.869	75.5		
2N	1.03	716	710	0.0508	96.94		80.5		
2O		716		0.0515	96.90		84.5		
2P		712		0.047	97.17		88.5		
2Q		712		0.056	96.63		92.5		
2R		716		0.063	96.20		97.5		5100
2S		725		0.0412	97.52		103.5		
2T		725		0.0555	96.66		109.5		

TABLE XIII. Desulfurization Data from Run #7 Using Houdry-C Catalyst

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Mean Temp</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Hydrogen Flow</u>
3A	0.99	698		----	---	3700
3B		698		0.0347	97.91	
3C		700		0.035	97.89	
3D		698		0.044	97.35	
3E		714		0.0267	98.39	
3F		716		0.025	98.49	
3G		705		0.040	97.59	
3H		716		0.035	97.89	3650
3I	1.01	725		0.053	96.81	
3J		710		0.052	96.87	3700
3K		709		0.0686	95.87	4000
3L	1.0	709		0.0715	95.69	4000
3M		714		0.0882	94.69	3700
3N		716	708	0.063	96.20	3550
3O		702		0.0893	94.62	3100
3P		707		0.0937	94.36	1050
3Q		700		0.126	92.41	900
3R	1.09	701		0.148	91.09	1050
3S		707		0.118	92.89	
3T		706		0.120	92.77	
3U		707		0.122	92.65	
3V		707		0.105	93.67	2200
3X		709		0.0905	94.55	
3Y		698		0.0762	95.41	
3Z		698		0.155	90.66	
3AA		702		0.064	96.15	4550
3BB		707		0.0486	97.07	
3CC		701		0.0495	97.02	5150
3DD		707		0.037	97.73	5000
3EE		716		0.0292	98.24	5500

TABLE XIV. **Desulfurization Data from Run #8 Using Prepared Catalyst DR-3.

<u>Sample</u>	<u>LHSV</u>	<u>Temp</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Hydrogen Flow</u>	<u>Hours on Stream</u>
8A	1.015	672	0.072	95.65	3500	2
8B		680	0.082	95.05		8
8C		710	0.0815	95.08		12
8D		716	0.0675	95.93		18
8E		707	0.0527	96.83		22
8F		703	0.061	96.52		26
*8G		700	0.0515	96.90	4000	31
8H		703	0.0428	97.42		37
8I		703	0.0543	96.73		44
8J		700	0.0597	96.41		48
8K		698	0.062	96.27	3800	52
8L		701	0.0584	96.48		56
8M		707	0.043	97.41		61
8N		703	0.0414	95.51		66
8O		700	0.031	98.17		70
8P		700	0.0455	97.26	4000	74
8Q		710	0.030	98.19	3650	79
8R		709	0.0436	97.46		84
8S		709	0.0389	97.66	4000	90
8T		701	0.0445	97.32		94
8U		700	0.0592	96.44		98
8V		707	0.063	96.20		103
8W		702	0.0605	96.35	3650	108
8X		716	0.045	97.29	4000	115
8Y		731	0.0492	97.08		119
8Z		737	0.0414	97.50		121
8AA		765	0.0225	98.64		126
8BB		752	0.0487	97.08		132
8CC		748	0.0474	97.14		137
8DD		752	0.041	97.53		140
8EE		797	0.031	98.13		147
8FF		806	0.0257	98.45		150
8GG		801	0.0460	97.23		153
8HH		797	0.027	98.37		155
8II		790	0.0425	97.44		161
8JJ		718	0.0447	97.29		164
8KK		669	0.0815	95.08		168

*Data of samples 8G to 8KK used in determining temperature effect on conversion for Figure 6

**Pressure held constant at 300 psig

TABLE XV. Desulfurization Data from Run #9 Using Houdry-C Catalyst

<u>Sample</u>	<u>Temperature</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Hours on Stream</u>
9A				
9B	706	0.0370	97.77	17
9C	707	0.0485	97.07	27
9D	706	0.0394	97.63	35
9E	697	0.042	97.46	42
9F	706	0.0462	97.22	51
9G	713	0.0366	97.80	59
9H	707	0.0318	98.08	67
9I	715	0.0378	97.72	75
9J	704	0.0395	97.62	83
9K	690	0.0392	97.64	91
9L	698	0.053	96.80	99
9M	706	0.0552	96.68	107
9N	713	0.046	97.23	115
9O	706	0.0357	97.85	123
9P	711	0.0354	97.86	131
9Q	698	0.0353	97.88	139
9R	702	0.0495	97.02	147
9S	715	0.0535	96.77	155
9T	---	----	---	163
9U	706	0.0436	97.37	171
9V	711	0.030	98.19	179
9W	706	0.0493	97.03	187
9X	707	0.0457	97.25	203
9Y	700	0.042	97.46	211
9Z	706	0.0548	96.70	219
9AA	---	0.0405	97.56	227
9BB	704	0.0380	97.71	235
9CC	715	0.051	96.93	243
9DD	709	0.0515	96.90	251
9EE	706	0.0442	97.34	259
9FF	706	0.0445	97.38	267
9GG	---	0.047	97.17	275
9HH	709	0.0447	97.30	283
9II	713	0.0473	97.14	291
9JJ	704	0.0515	96.90	299
9KK	698	0.047	97.16	307
9LL	711	0.056	96.62	323
9MM	706	0.0351	97.88	331
9NN	---	0.046	97.22	343
9OO	706	0.0384	97.50	355
9PP	707	0.0463	97.21	367

TABLE XV (continued)

<u>Sample</u>	<u>Temperature</u>	<u>Wt% Sulfur</u>	<u>% Conversion</u>	<u>Hours on Stream</u>
9QQ	---	0.0595	96.42	379
9VV	701	0.038	97.71	403
9XX	700	0.061	96.33	415
9YY	707	0.0362	97.82	427
9ZZ	706	0.0357	97.85	439
9AAA	711	0.0457	97.25	451
9BBB	713	0.043	97.40	475
9CCC	716	0.056	96.62	487
9DDD	707	0.046	97.23	499
9EEE	707	0.046	97.23	511
9FFF	709	0.0383	97.69	523
9GGG	713	0.0475	97.14	535
9HHH	705	0.0446	97.31	547
9III	704	Line plugged; no samples.		
9JJJ	700			
9KKK	699	0.0361	97.82	595
9LLL	707	0.0407	97.55	607
9MMM	707	----	---	
9NNN	707	0.0463	97.22	631
9OOO	713	0.0390	97.55	643
9QQQ	711	0.0391	97.65	650
9RRR	711	0.0388	97.68	655
9SSS	704	0.0442	97.34	667
9TTT	705	0.0409	97.54	679
9UUU	700	0.0430	97.41	691

Hydrogen Flow constant at 7000 SCF/bbl and Pressure at 300 psig.

LHSV constant at 1.00.

TABLE XVI. Desulfurization Data from Run #10 Using Prepared Catalyst DR-3.

<u>Sample</u>	<u>LHSV</u>	<u>Temp.</u>	<u>Wt% Sulfur</u>	<u>% Con- version</u>	<u>Hours on Stream</u>
10A	1.00	695	0.0397	97.61	6
10B		695	0.0358	97.84	18
10C		695	0.0471	97.16	30
10D		697	0.0563	96.61	42
10E		650	0.0715	95.70	54
10F		702	0.0435	97.38	66
10G		697	0.0390	97.65	78
10H		709	0.024	98.55	90
10I		703	0.0412	97.52	102
10J		706	0.0485	97.08	114
10K		701	0.0352	97.88	126
10L		697	0.0385	97.68	138
10M		690	0.0337	98.03	150
10N		702	0.0327	97.53	162
10O		702	0.041	96.53	174
10P		703	0.0507	96.94	186
10Q		700	0.0472	97.16	198
10R		711	0.0378	97.72	210
10S		711	0.0342	97.72	222
10T		695	0.045	97.28	234
10U		697	0.0328	98.03	246
10V		709	----	---	258
10W		697	0.0367	97.80	270
10X		706			282
*10Y		733	0.031	98.13	294
10Z		755	0.0134	99.19	300
10AA		752	0.0260	98.34	306
10BB		751	0.0250	98.50	320
10CC		741	0.0495	97.02	322
10DD		775	0.0166	99.00	332
10EE		706	0.0384	97.69	342
10FF		702	0.0283	98.31	356
10GG		706	0.0395	97.63	366
10HH		706	0.0164	99.10	380
10II		709	0.0455	97.26	390
10JJ		---	0.0425	97.44	404

TABLE XVI (continued)

<u>Sample</u>	<u>LHSV</u>	<u>Temp.</u>	<u>Wt% Sulfur</u>	<u>% Con- version</u>	<u>Hours on Stream</u>
10KK	1.75	698	0.089	94.65	
10LL		702	0.0815	95.08	
10MM		709	0.0615	96.30	
10NN		715	0.0785	95.27	
1000		800	0.0575	96.54	
10PP		806	0.0258	98.45	
10QQ		808	0.0424	97.44	
10RR		806	0.055	96.68	
10SS		800	0.046	97.23	
10TT	3.35	815	----	---	
10UU		810	0.088	95.70	
10VV		817	0.100	93.97	
10XX	3.35	816	0.089	94.65	
10YY		755	---	---	
10ZZ		730	0.116	93.00	
10AAA		702	0.187	88.70	
10BBB	1.02	702	0.0542	96.74	
10CCC		700	0.0455	97.25	
10DDD	1.00	713	0.062	96.26	
10EEE		706	0.0296	98.22	524
10FFF		700	----	---	
10GGG		680	0.083	95.00	
10HHH		670	0.0815	95.08	
10III		665	0.102	93.85	
10JJJ		700	0.300	81.90	
10KKK		717	---	---	596
10LLL		706	0.0266	98.40	620
10MMM		697	0.0569	96.56	644
10NNN		697	0.073	95.60	

Hydrogen Flow constant at 7000 SCF/bbl and Pressure at 300 psig

*Data used for Temperature conversion (Figure 6) and LHSV versus conversion (Figure 4)

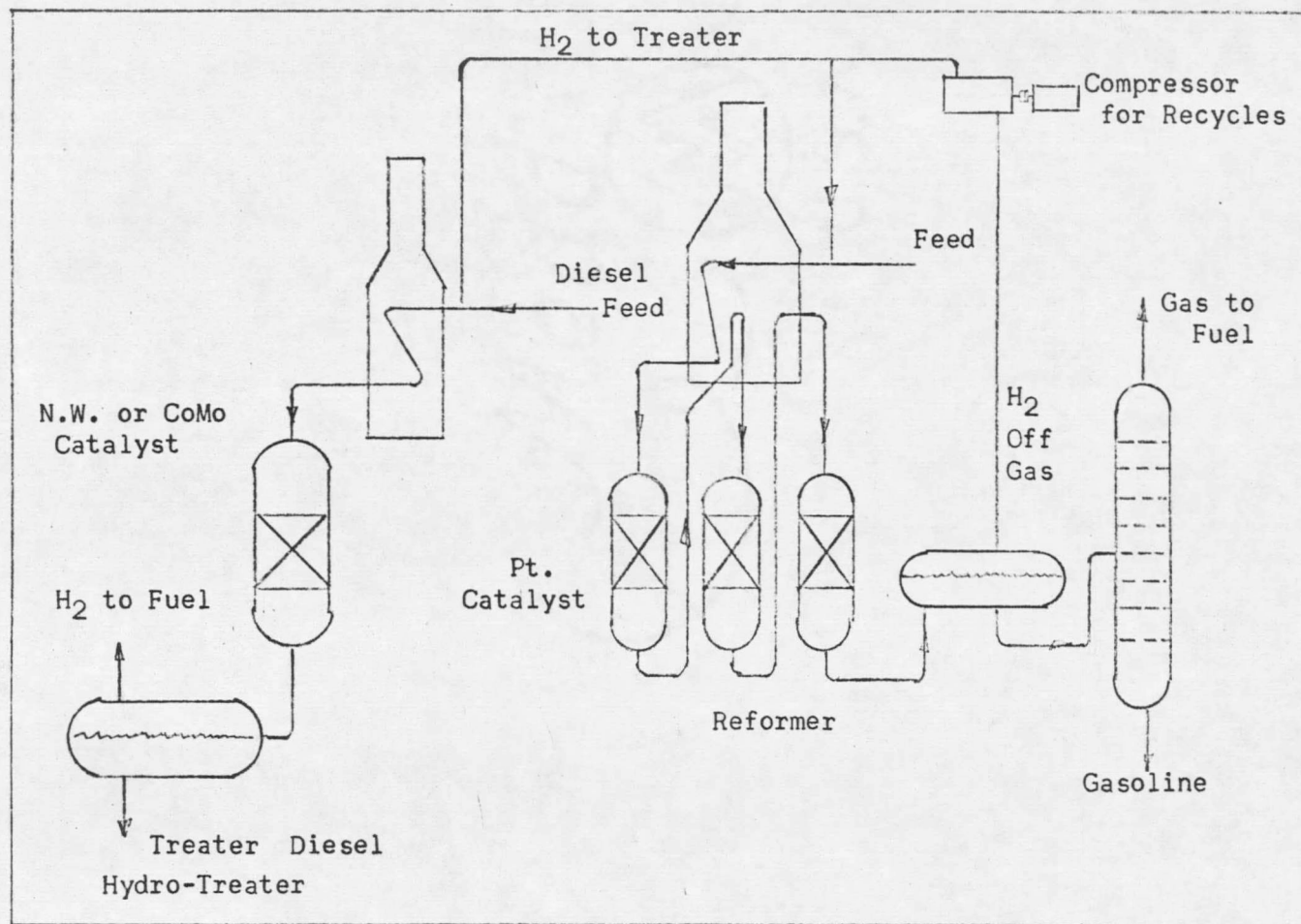


Figure 1. Typical Commercial Reformer and Hydro-Treating Scheme.

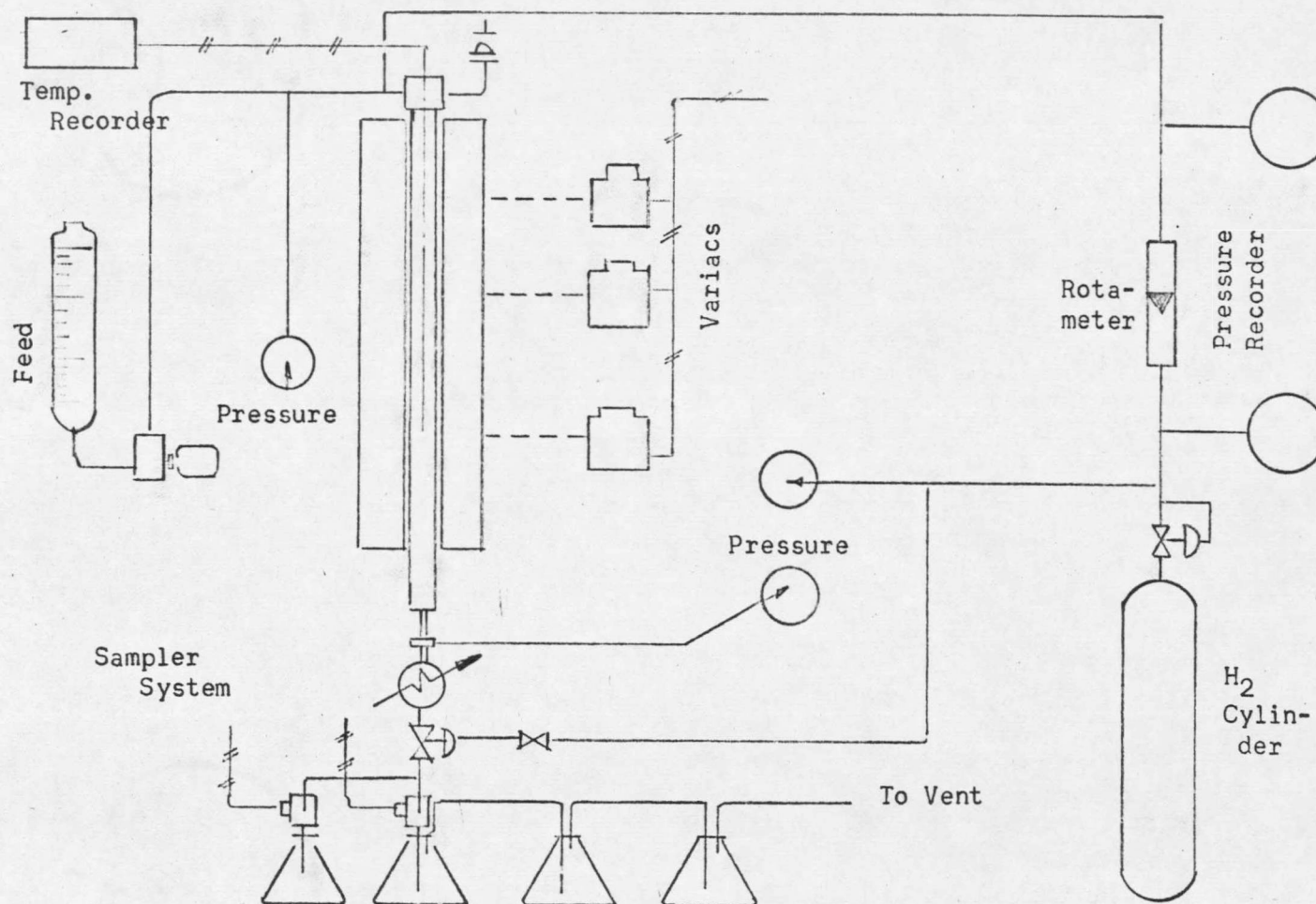


Figure 2. Schematic Diagram of Equipment.

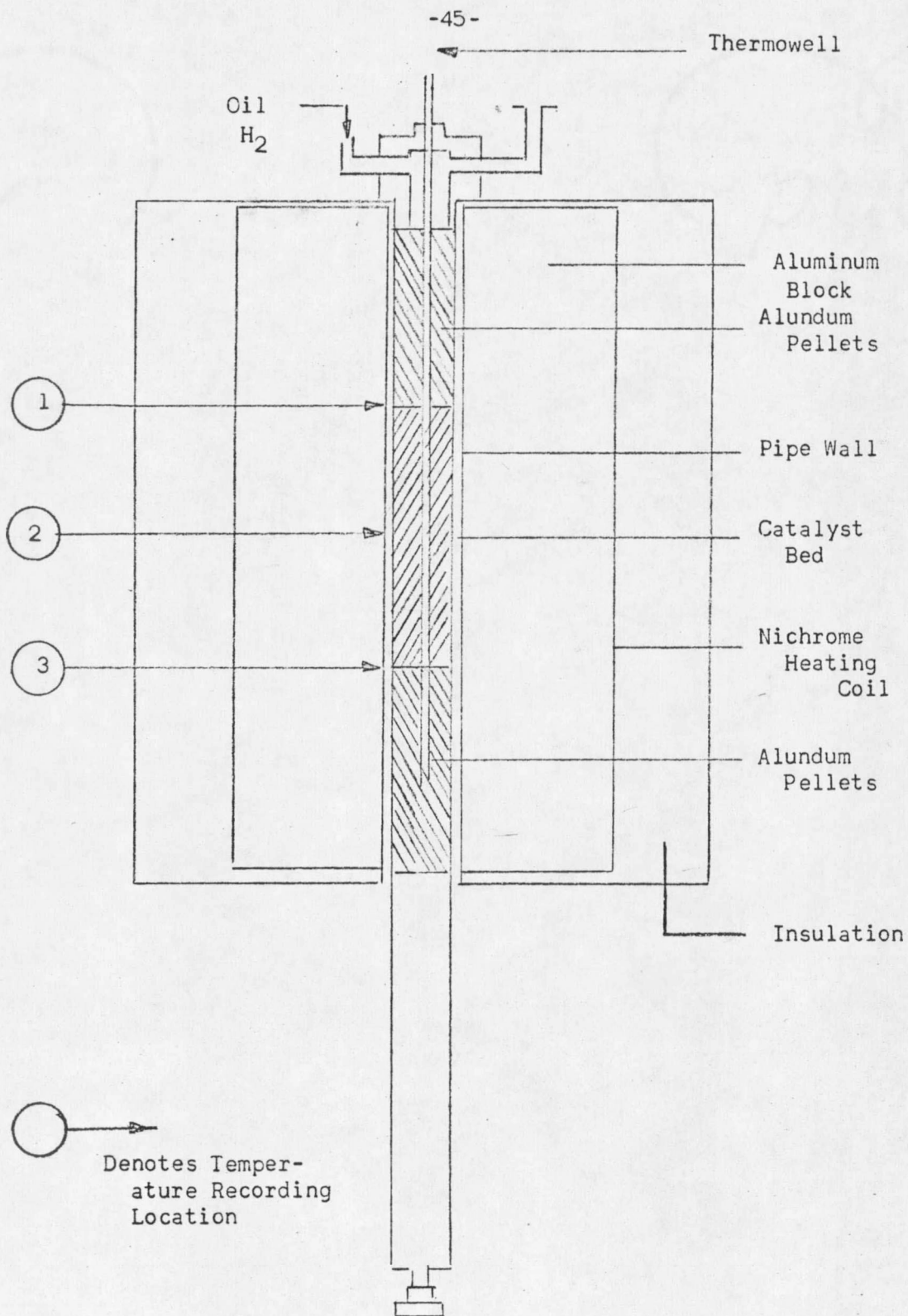


Figure 3. Reactor Detail

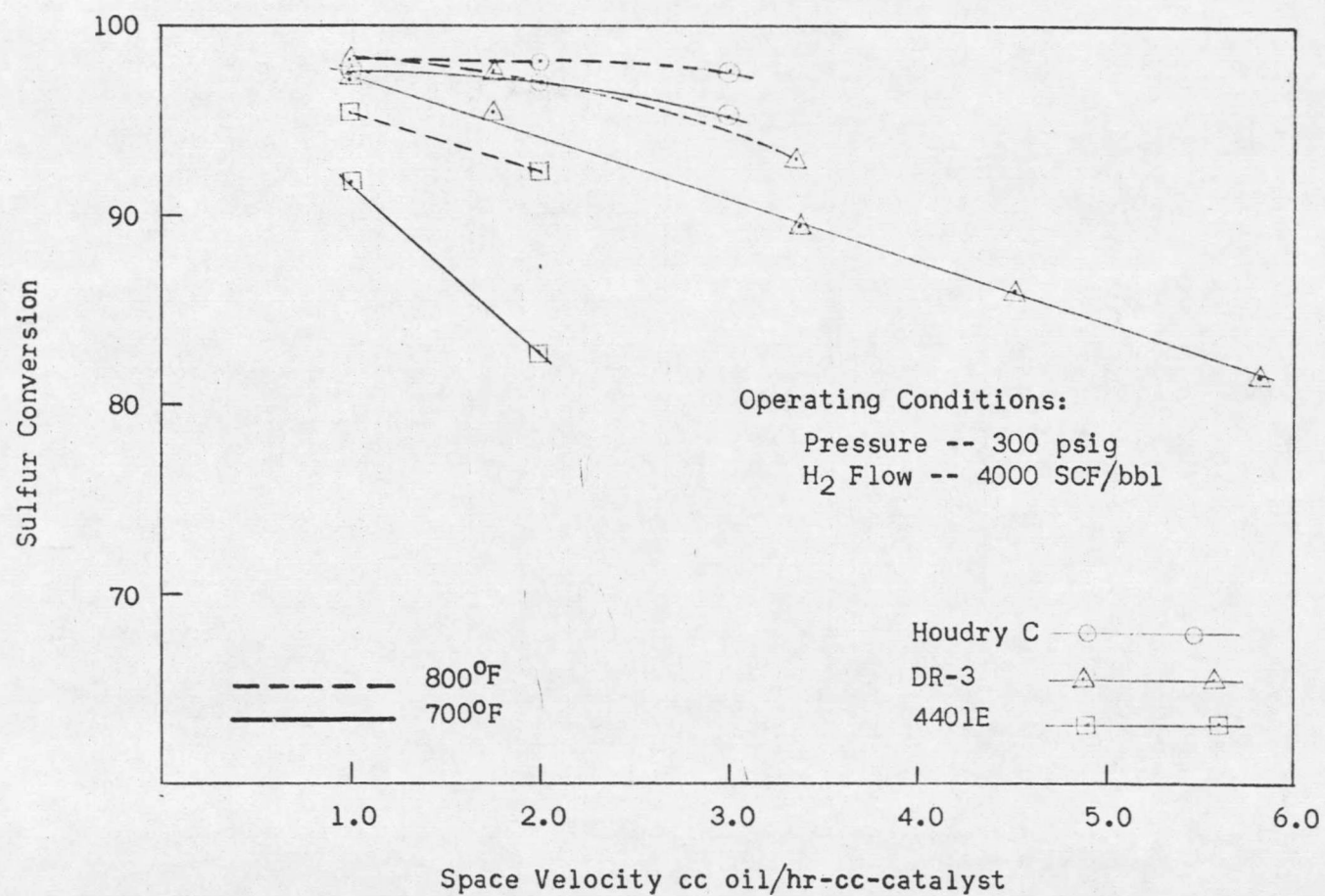


Figure 4. Effect of LHSV on Sulfur Conversion.

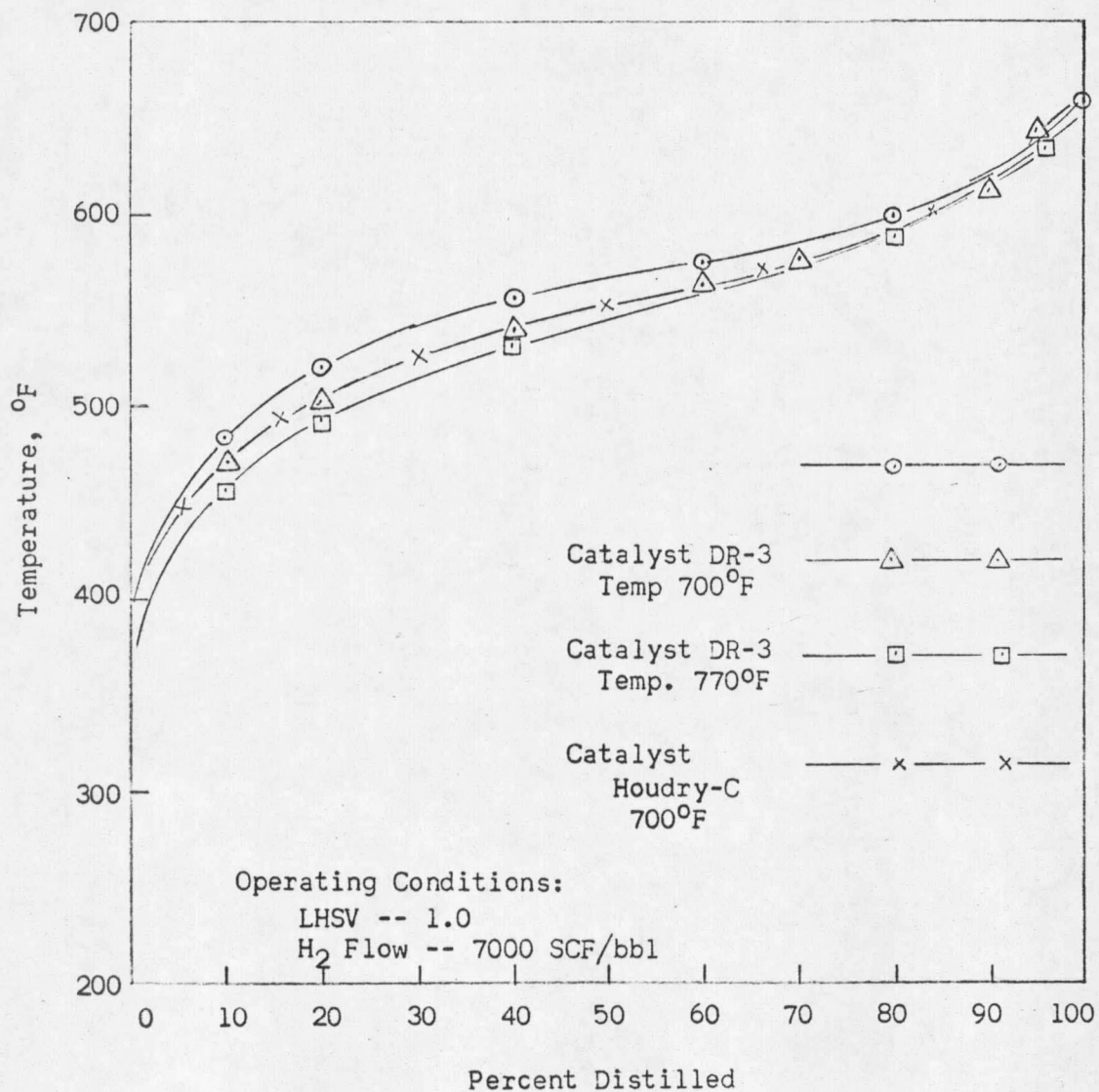


Figure 5. ASTM Distillations of Feed and Products.

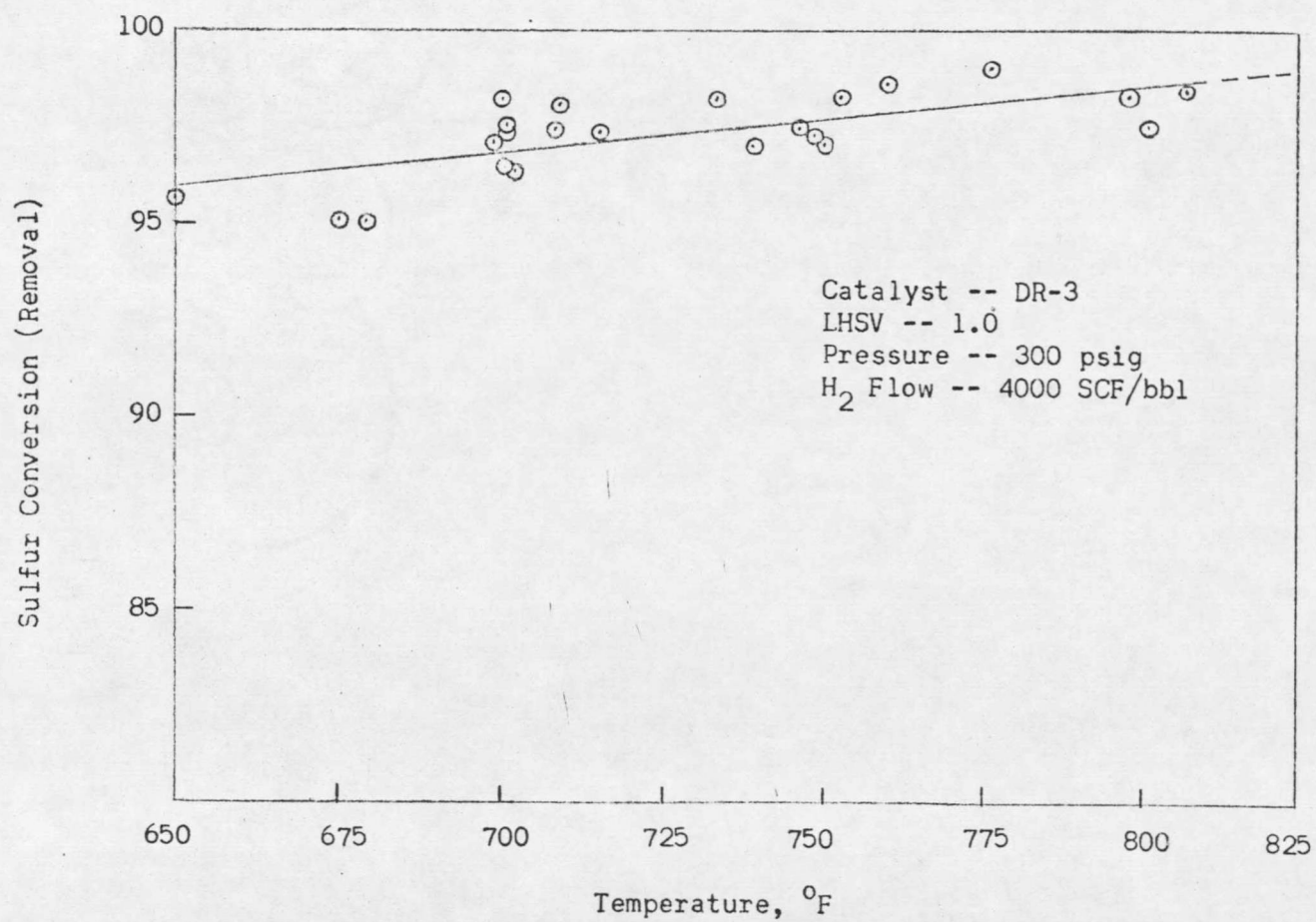


Figure 6. Temperature Effect on Sulfur Conversion.

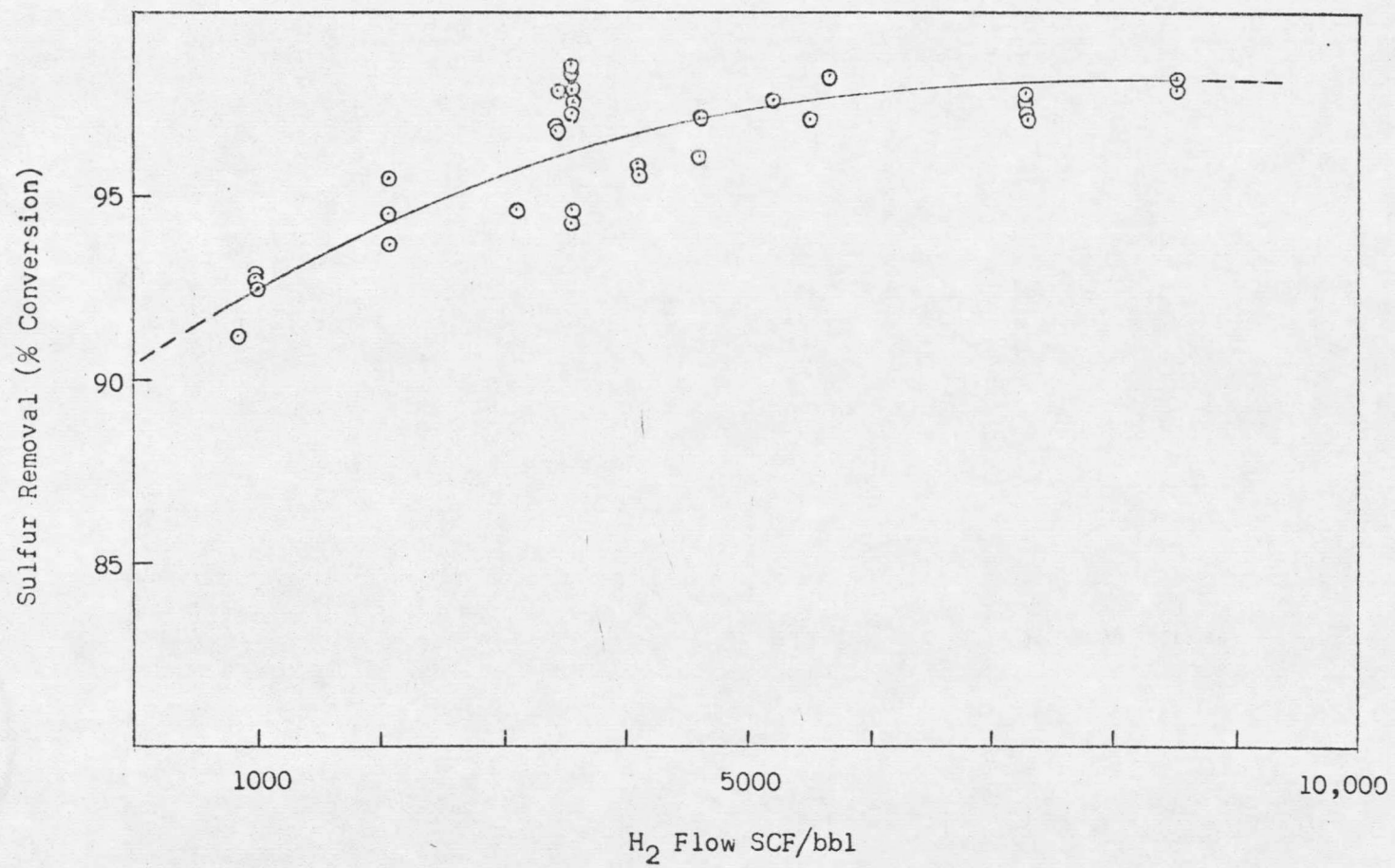


Figure 7. Hydrogen Flow Effect on Sulfur Conversion.

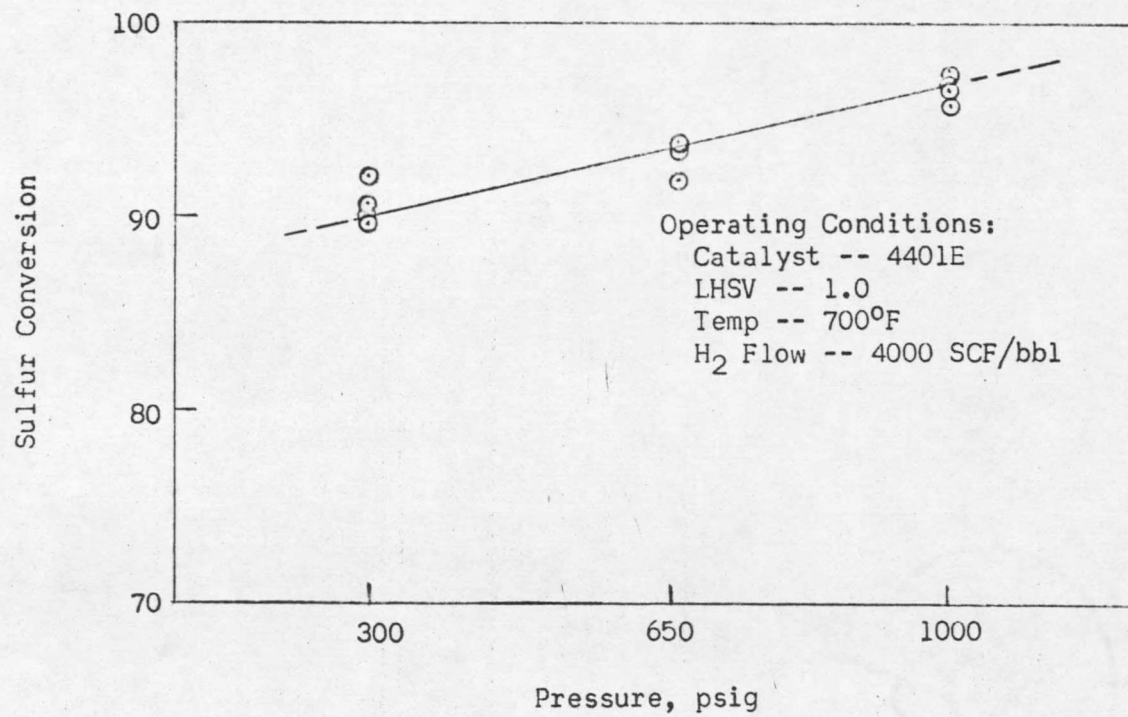


Figure 8. Effect of Pressure on Sulfur Conversion.

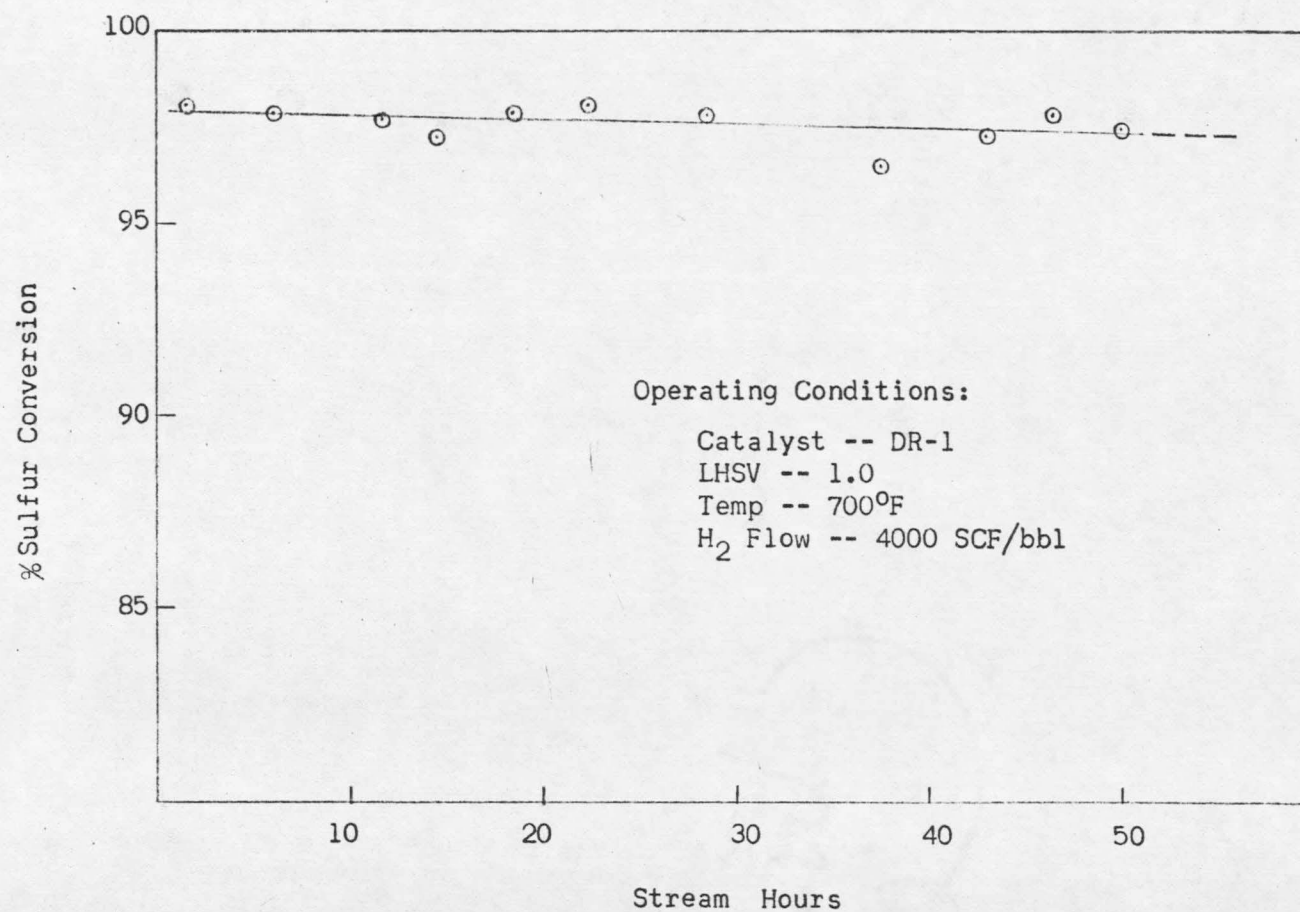


Figure 9. Conversion versus Time for Catalyst DR-1

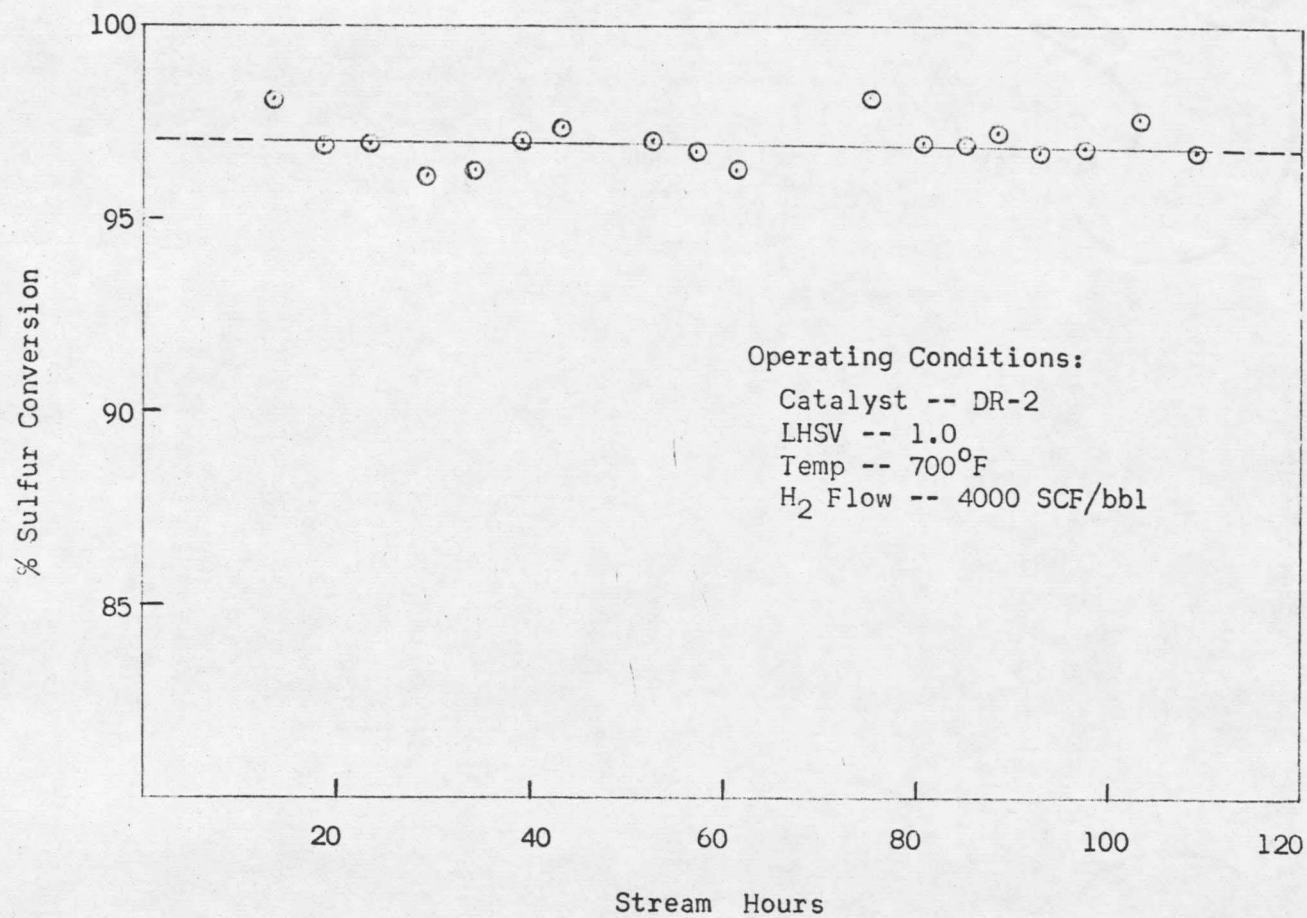


Figure 10. Conversion versus Time for Catalyst DR-2.

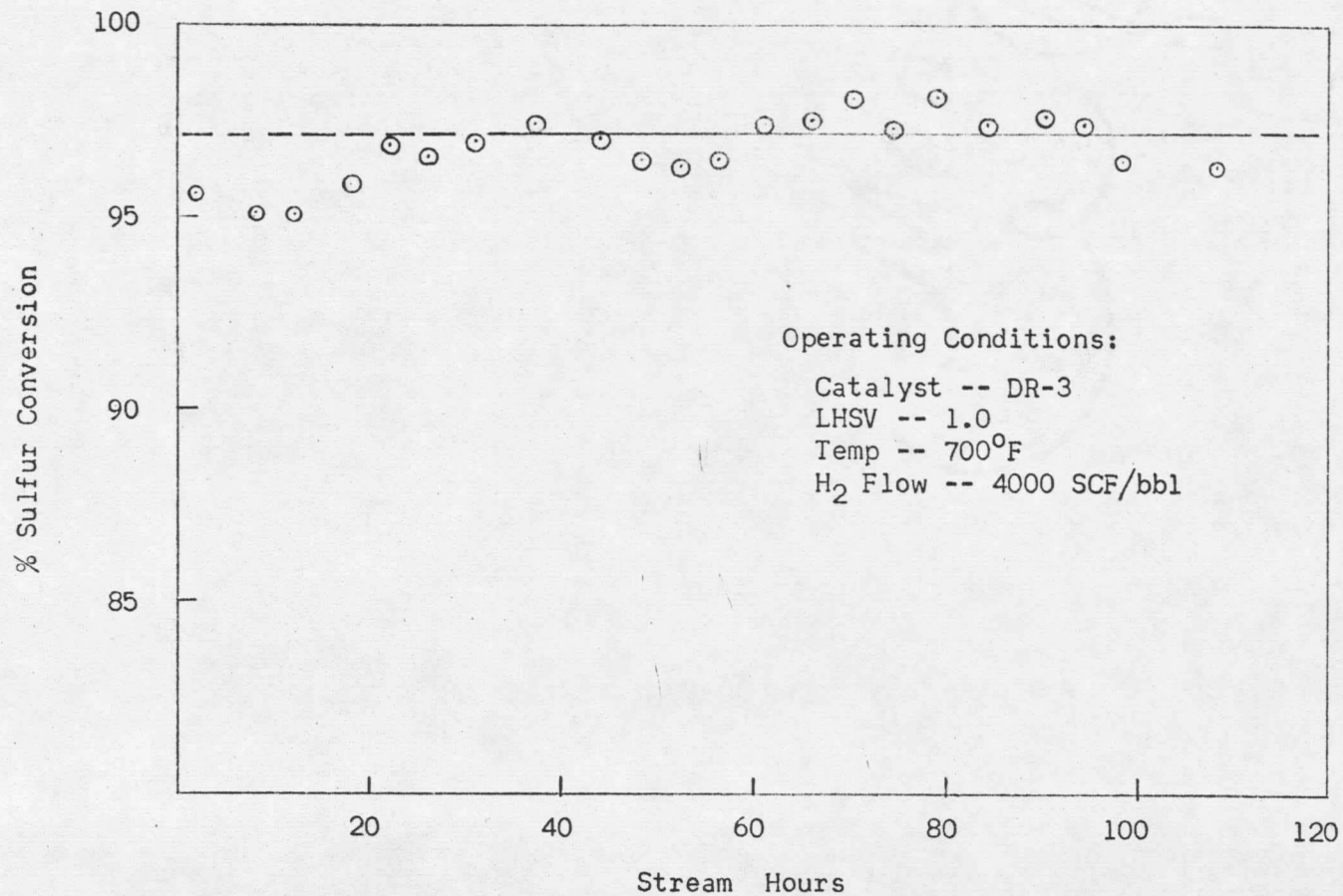


Figure 11. Conversion versus Time for Catalyst DR-3.

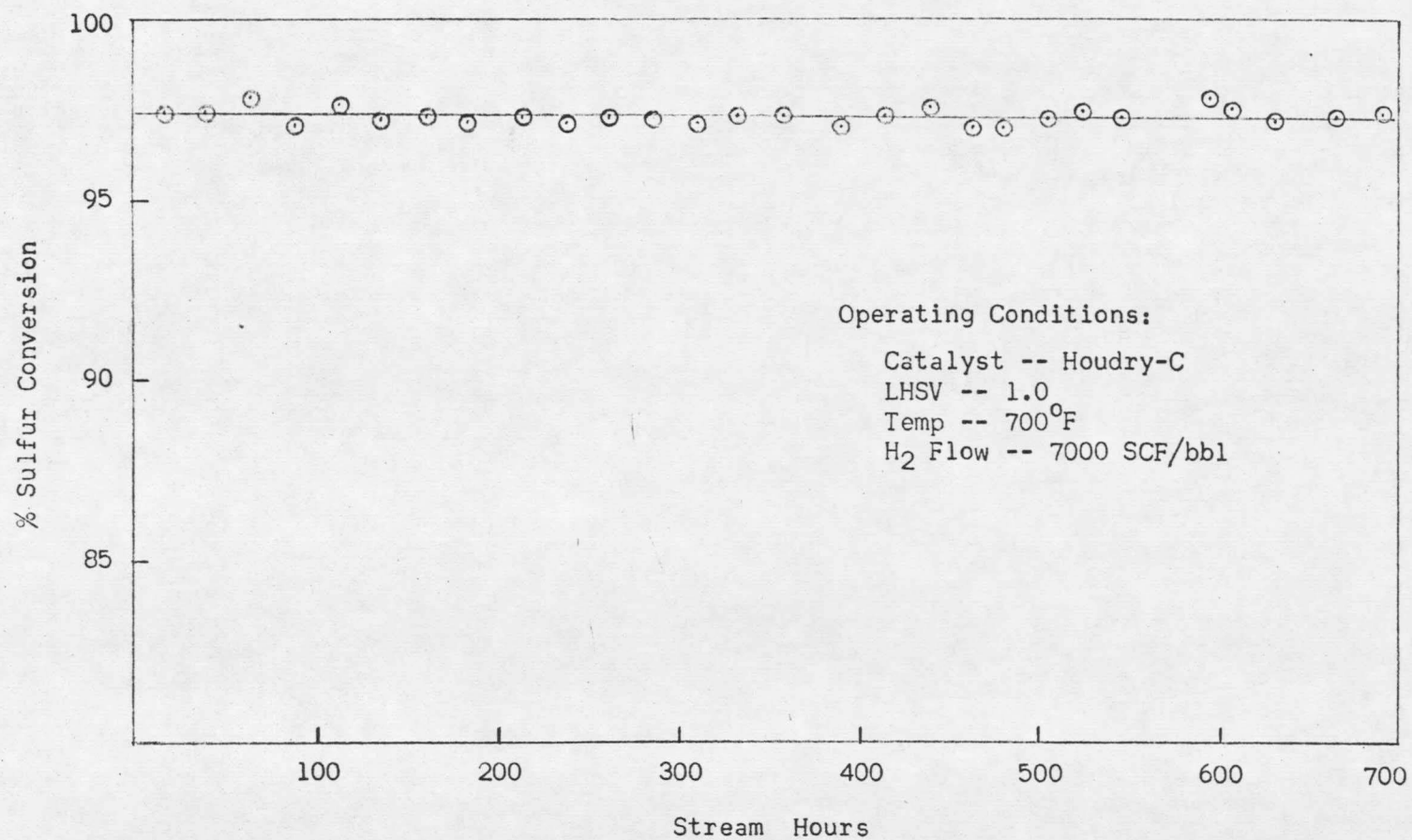


Figure 12. Catalyst Life Study Using Houdry-C.

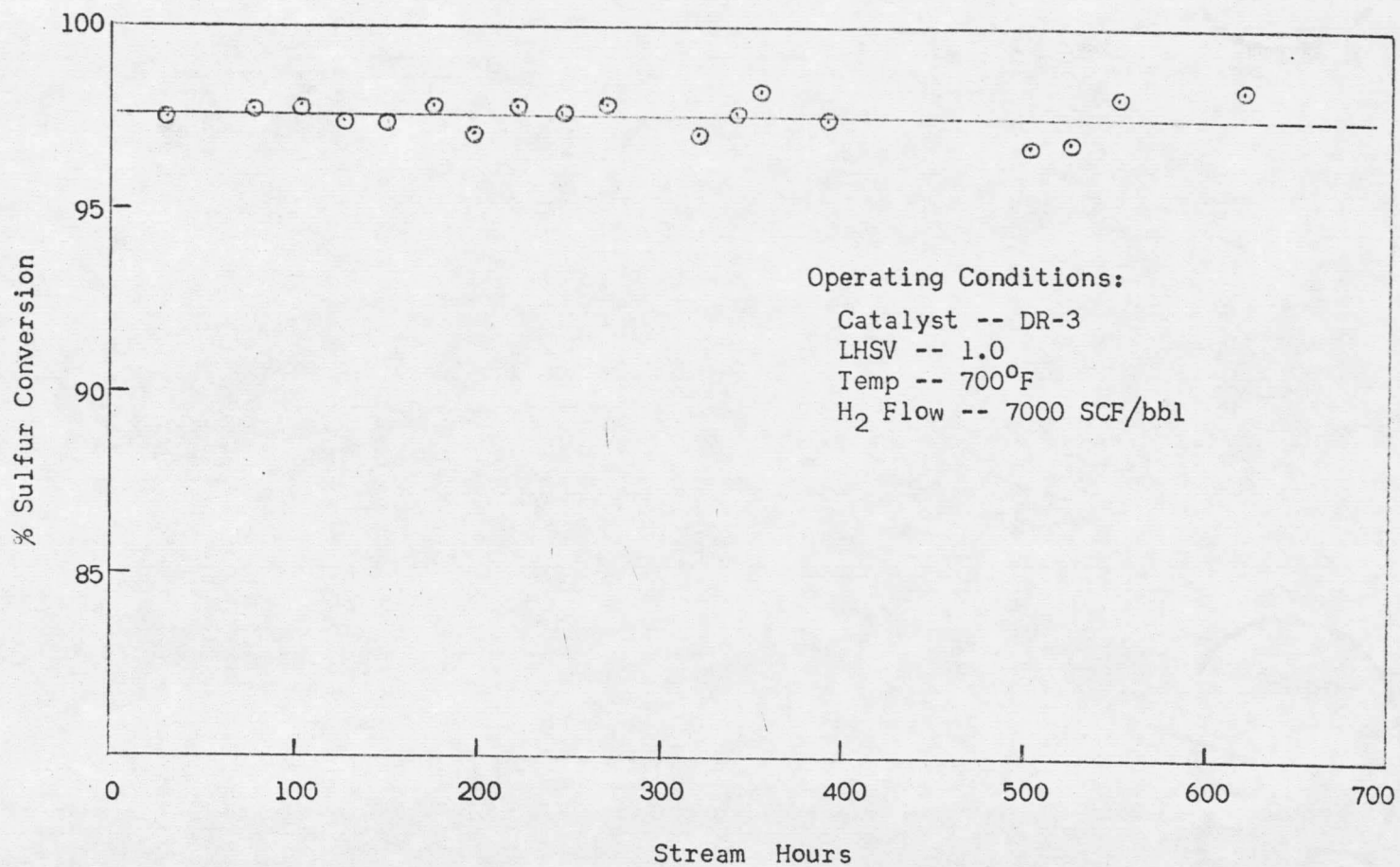


Figure 13. Catalyst Life Study using DR-3.

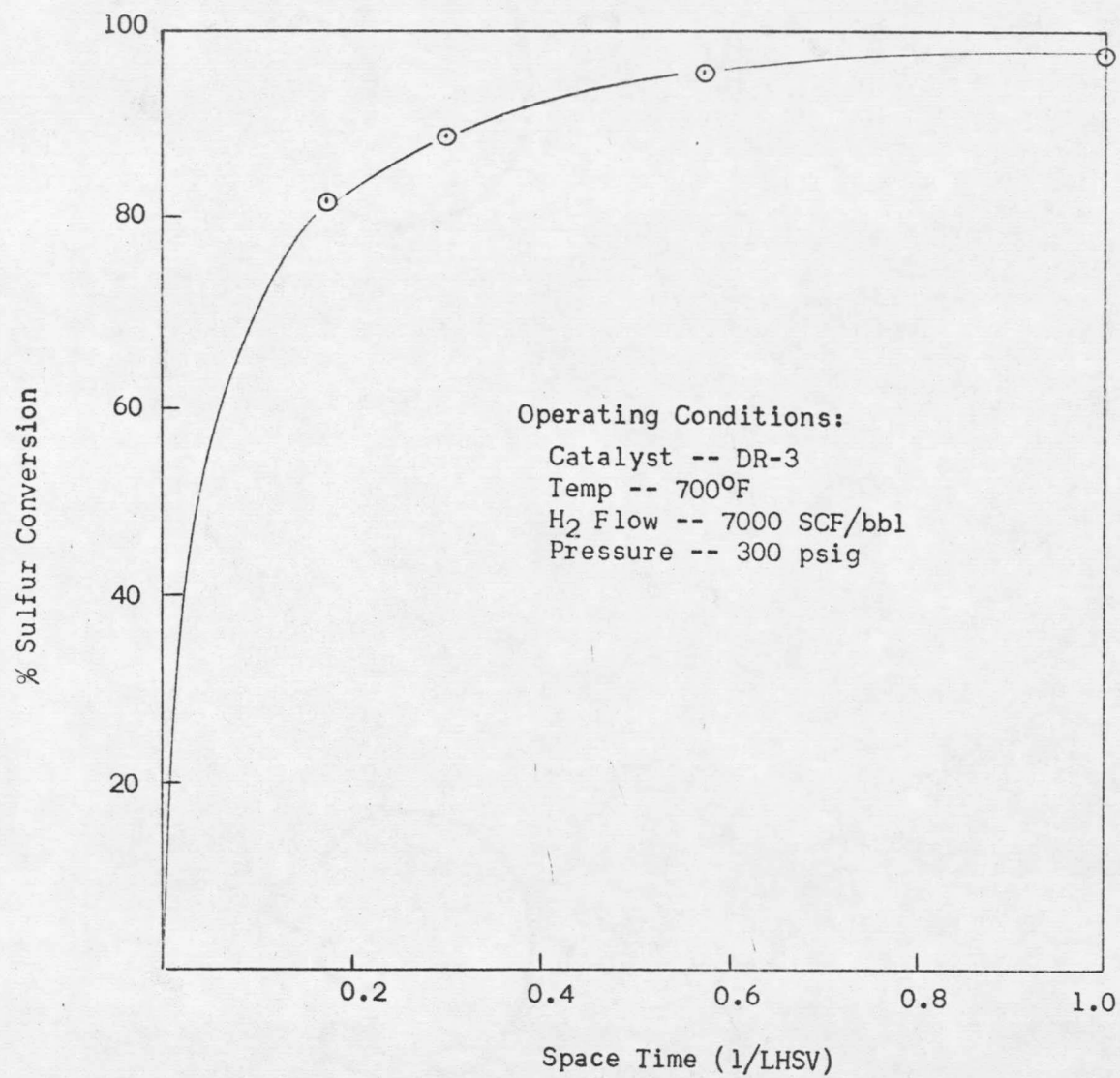


Figure 14. Effect of Space Time on Sulfur Conversion.

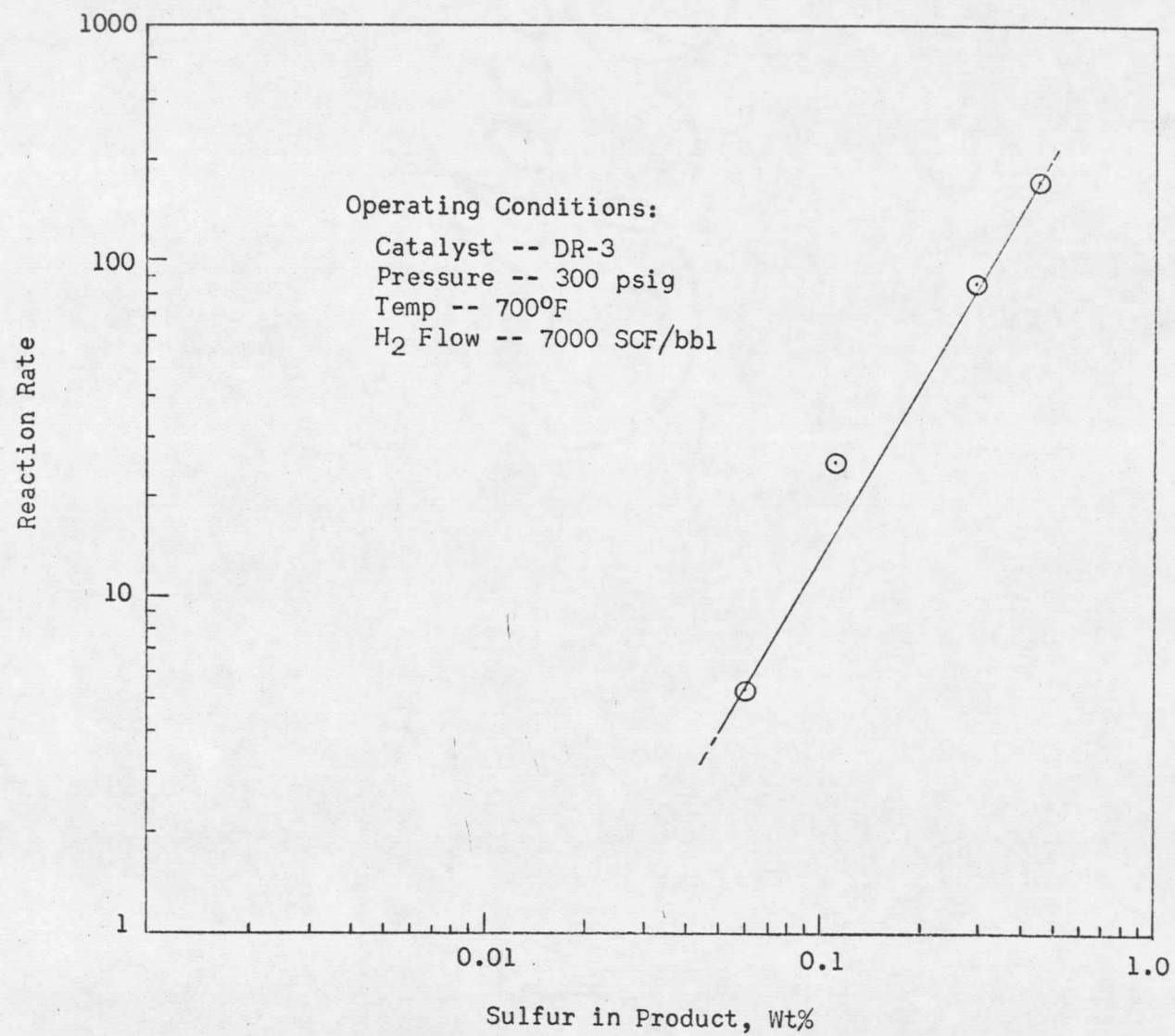


Figure 15. Pseudo Order of Reaction of Desulfurization by Differential Analysis.

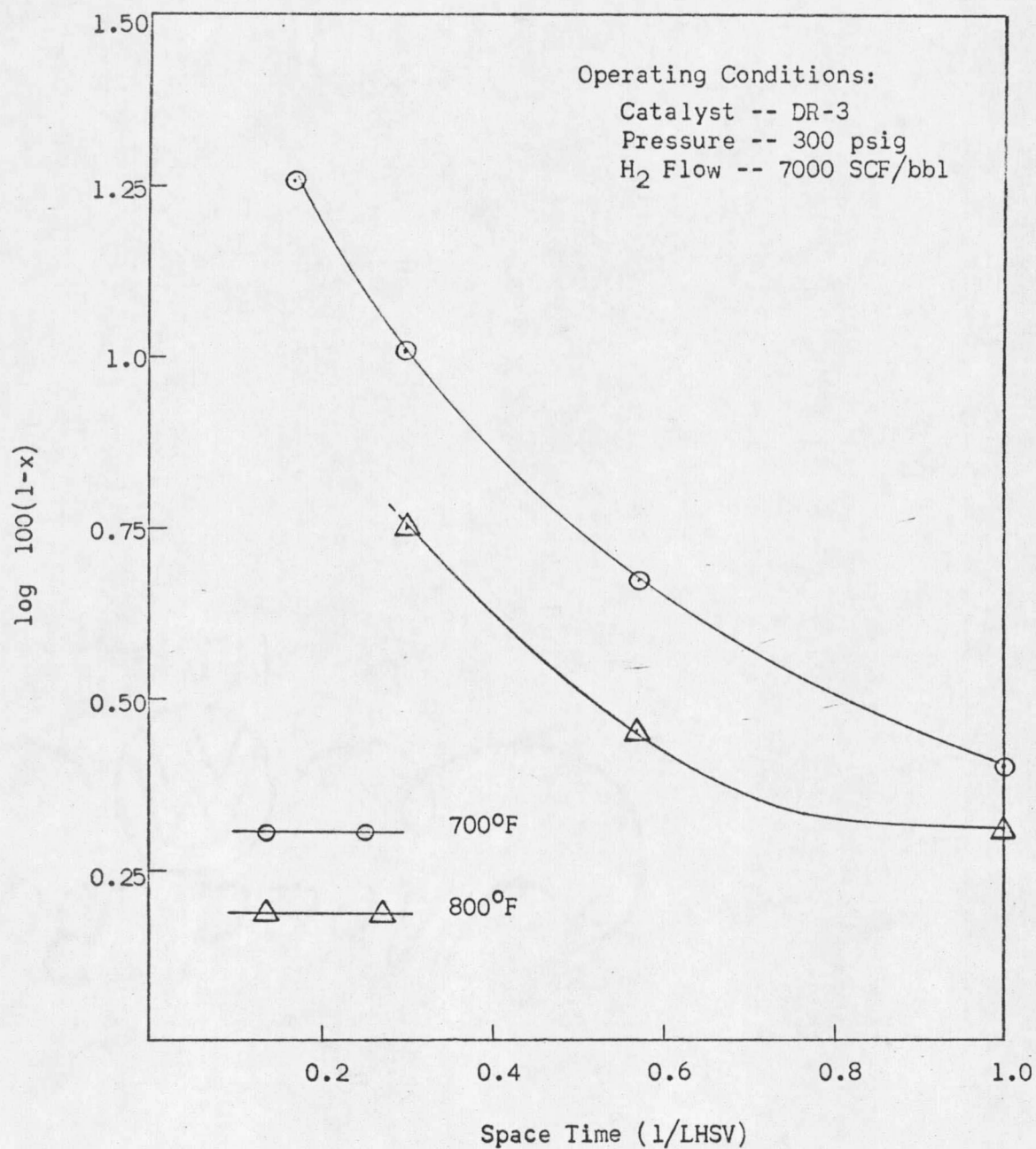


Figure 16. Test for Pseudo First Order Reaction.

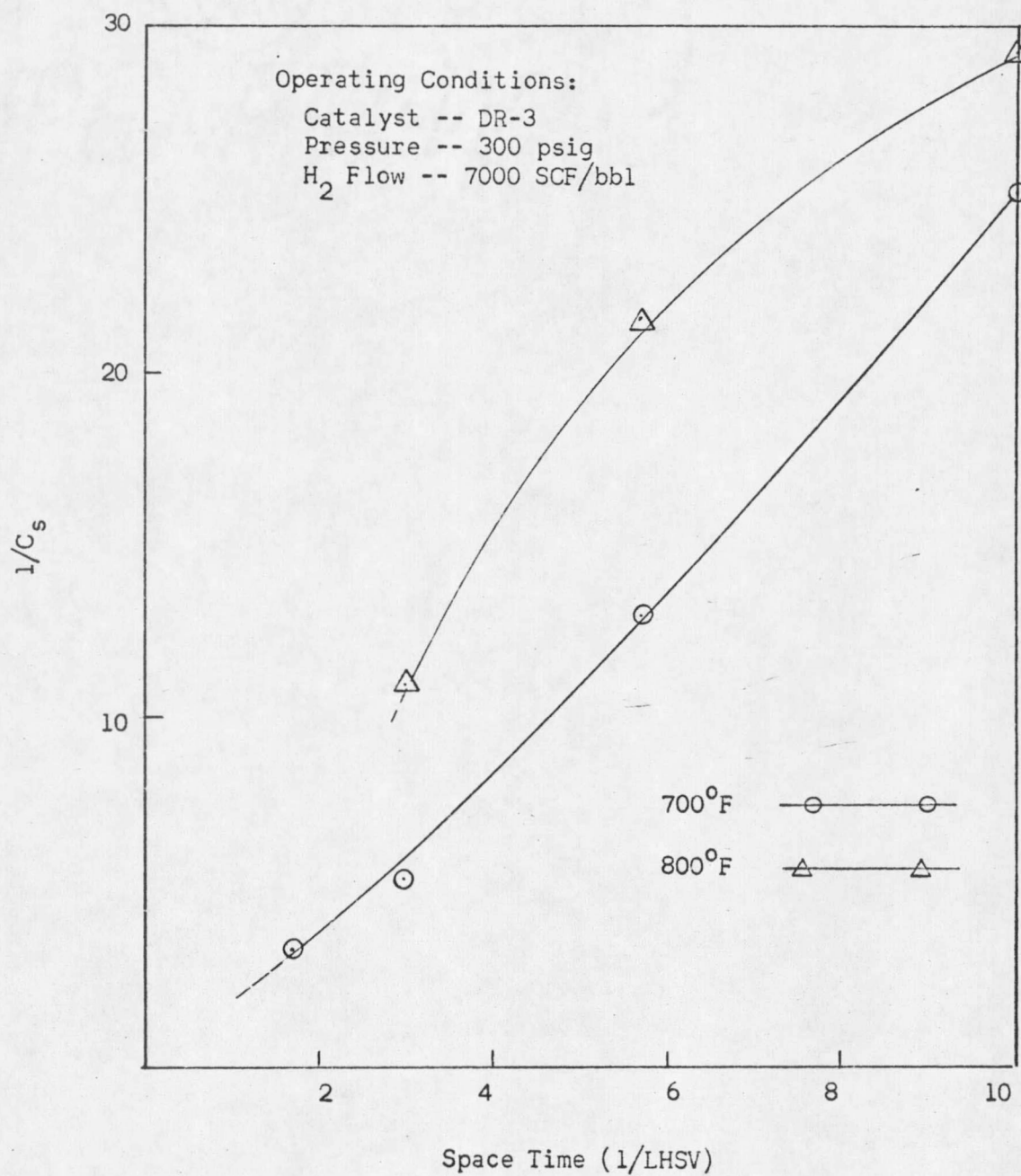


Figure 17. Test Data on Second Order Reaction.

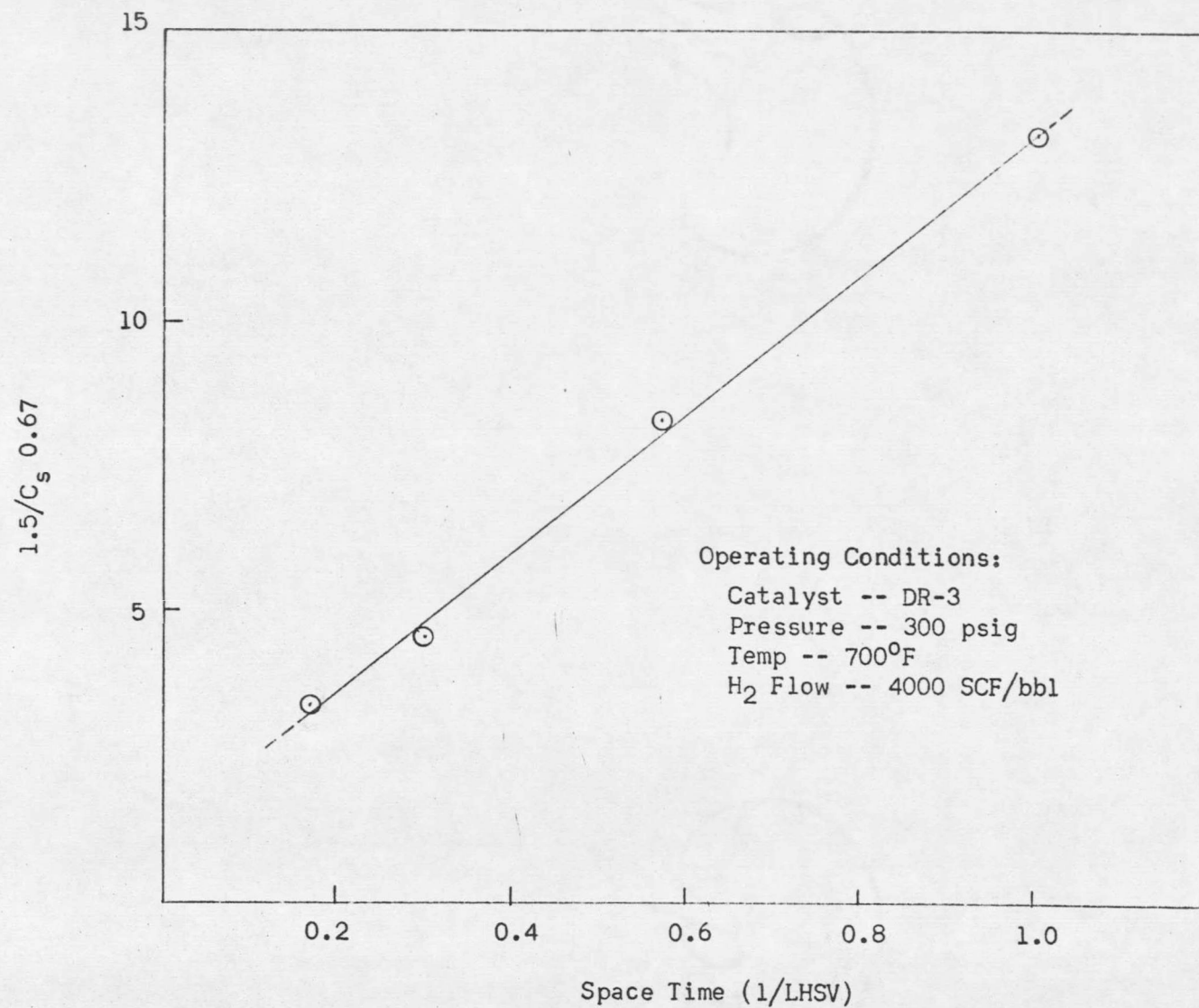


Figure 18. Test for Pseudo 1.67 Order Reaction.

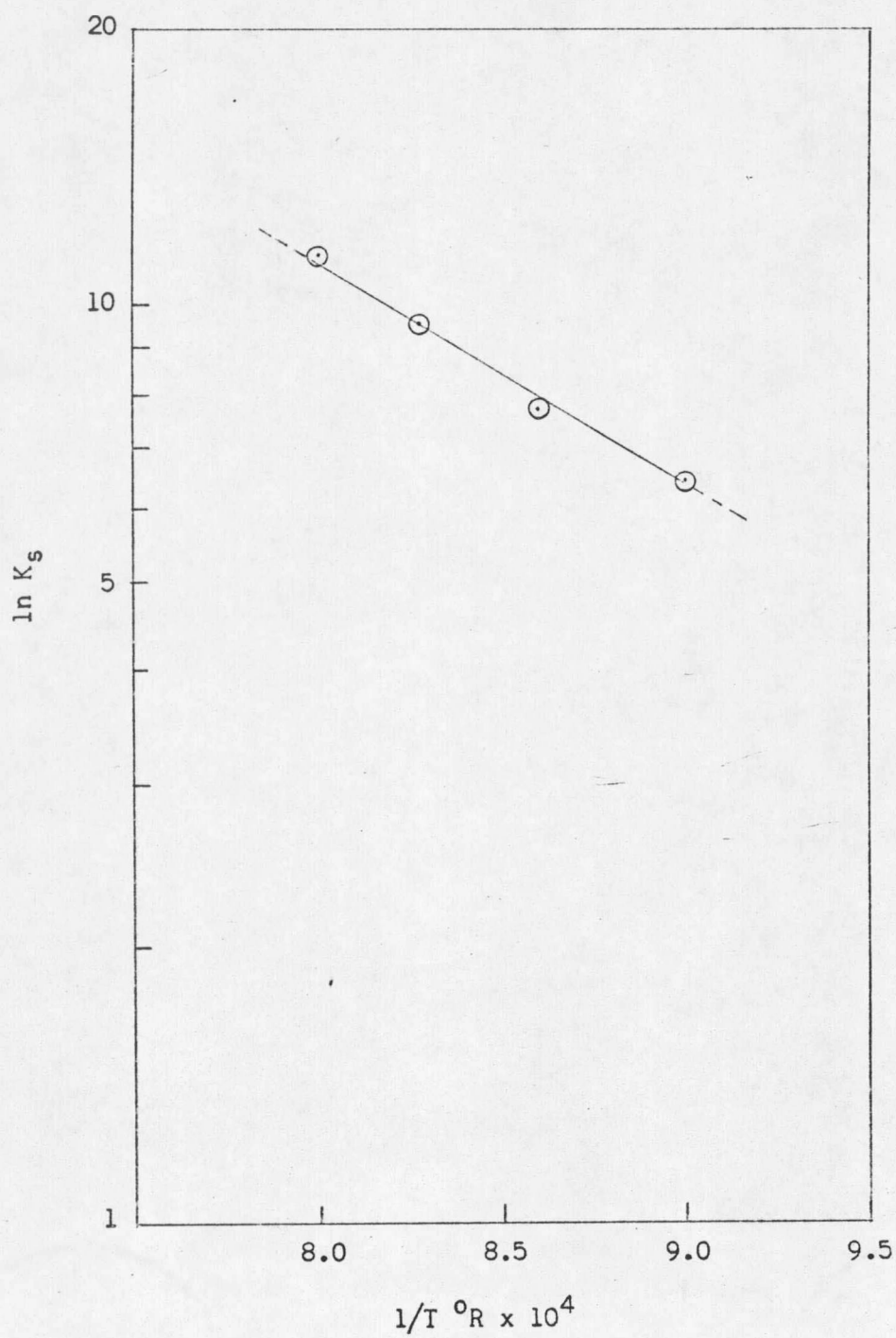


Figure 19. Activation Energy.

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