



Catalytic hydrodesulfurization of West Texas crude oil fractions
by Lawrence E Orr

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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The unique discovery of this study was that the ability of cobalt-molybdate catalyst to desulfurize a given diesel fuel is impaired when that catalyst is employed to desulfurize either higher or lower boiling range fractions. The scope of this study limited this phenomenon to distillates from West Texas crude oil.

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CRUDE OIL FRACTIONS

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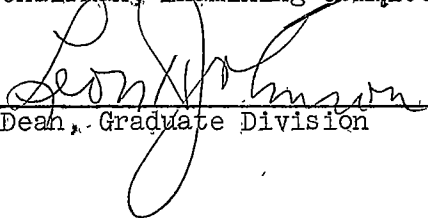
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ABSTRACT

The petroleum refiner of today is faced with the problem of making high quality products from low quality, high sulfur content crude oils. Sulfur compounds in petroleum fractions give rise to many problems in transportation, storage, and product quality.

The catalytic hydrodesulfurization of several fractions of West Texas crude oil was studied at various pressures, temperatures, and space velocities. The conversion of sulfur to hydrogen sulfide in the light straight run and reforming naphtha fractions was found to be nearly constant for each of these fractions. The pressure, temperature, and space velocity effects were found to be significant for all of the remaining crude oil fractions. Some of the two-factor interaction effects were found to be statistically significant, but were small in comparison with the effects of the individual factors.

The unique discovery of this study was that the ability of cobalt-molybdate catalyst to desulfurize a given diesel fuel is impaired when that catalyst is employed to desulfurize either higher or lower boiling range fractions. The scope of this study limited this phenomenon to distillates from West Texas crude oil.

BACKGROUND

The petroleum refiner of yesterday had what seemed to be an everlasting supply of high quality, low sulfur content crude oils at his disposal. The petroleum refiner of today is faced with a very challenging problem--how to make high quality products from low quality, high sulfur content crude oils. High sulfur content crudes present many problems in refining and in meeting product specifications.

The types of sulfur compounds commonly found in crudes are hydrogen sulfide, sulfides, disulfides, cyclic sulfides, mercaptans, alkyl sulfates, sulfonic acids, sulfoxides, sulfones, and thiophenes.⁶ The hardest type of sulfur compounds to remove from petroleum fractions are ring-type sulfur compounds.⁵ A large percentage of the sulfur compounds found in catalytically cracked distillates are ring-type sulfur compounds.

The presence of sulfur in crude oil fractions presents many problems. Conversely, certain sulfur compounds are used as additives in some lube oils.⁶ Some of the problems arising from the presence of sulfur compounds in crudes and crude oil fractions are:

1. The corrosive effects of sulfur compounds present many problems in the refining of crudes; storage of crudes, crude oil fractions, and products; transportation of crudes, crude oil fractions, and products; and the utilization of products. 2,6,8

2. Certain sulfur compounds, such as hydrogen sulfide and mercaptans, possess very obnoxious odors. These compounds must be removed from petroleum products before the products can obtain consumer acceptance. 2,6,8
3. Feed stocks which have a high sulfur content are difficult to crack catalytically, because most of the cracking catalysts used in refineries are poisoned by the sulfur compounds. 2
4. Sulfur compounds have adverse effects on the stability of products. 2,6,8
5. Many of the sulfur compounds have a depressing effect on the octane number of gasolines. 2,6,8
6. The susceptibility or responsiveness of gasolines to tetraethyllead is greatly harmed by the presence of small amounts of sulfur compounds. 2,6,8
7. Many of the sulfur compounds give off acrid fumes when burned. 2,6,8
8. Certain sulfur compounds are used as additives in lube oils. These sulfur compounds, however, must be corrosive at certain temperatures to function properly. The presence of

the wrong type of sulfur compound would reduce the effective life of the lube oil. ⁶

The sulfur which is removed from crude oil fractions may be recovered and sold, in many cases.

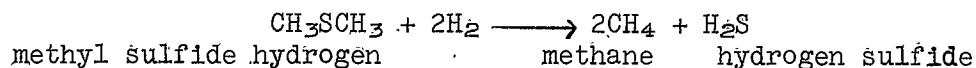
There are many methods in existence for removing or changing the form of sulfur compounds found in petroleum distillates. Many of these methods deal with highly reactive sulfur compounds present in relatively low concentrations. The doctor treatment, lead sulfide treatment, and copper sweetening have all been used to combat the problem of odorous sulfur compounds present in gasolines. These processes convert mercaptans into less objectionable disulfides. ² These disulfides, however, have undesirable effects on the knock rating and lead susceptibility of the gasolines. The petroleum refiners have naturally turned to methods which almost completely remove sulfur compounds. Since catalytic reforming has produced an abundant supply of hydrogen in recent years, the trend has been to hydrogen-treat more petroleum stocks. ¹⁰ Catalytic hydrodesulfurization has proven to be the best method for removing all types of sulfur compounds. The product gasoline shows improved lead response, less corrosiveness, and better stability. ⁵

Catalytic hydrodesulfurization consists of passing a sulfur-bearing feed over a catalyst in the presence of hydrogen. The sulfur is removed from the sulfur-bearing compounds by combining with hydrogen to form hydrogen sulfide. The hydrogen sulfide is a gas and is vented.

-This study deals with the catalytic hydrodesulfurization of West Texas crude oil fractions. The amount of conversion of sulfur to hydrogen sulfide obtained by the use of catalytic hydrodesulfurization was studied at various pressures, temperatures, and space velocities for several fractions from West Texas crude oil.

THEORY

A typical hydrodesulfurization reaction is:



A first order reaction is defined as one for which the rate of reaction can be described by the following equation:

$$\frac{dC_a}{dt} = -kC_a \quad (1)$$

Where C_a = Concentration of one reactant,

k = reaction rate constant,

and t = contact time.

Many reactions between two reactants which take place in the presence of an excess of one reactant follow first-order rate equations over certain ranges.⁹ These reactions are termed "pseudo" first-order reactions. If the hydrogen concentration is kept high enough to be considered a constant in hydrodesulfurization reactions, many of these reactions have been shown to follow a first-order rate equation over certain ranges.

Equation (1) may also be written as:

$$\frac{dx}{dt} = kA(1-x) \quad (2)$$

Where A = initial concentration of sulfur,

x = fraction of sulfur reacted at any time, t ,

$A(1-x)$ = concentration of sulfur remaining at time, t .

The reaction rate constant, k , is actually a function of many variables, and is a constant only for a given set of conditions. The variables which affect the reaction rate constant are temperature, pressure, hydrogen partial pressure, oil partial pressure, and catalyst activity.

Equation (2) may be rearranged and integrated between the limits $t = 0$, $x = 0$, and $t = t$, $x = x$ to give:

$$\ln \frac{1}{1-x} = kt \quad (3)$$

or $2.3 \log_{10} \frac{1}{1-x} = kt \quad (4)$

The contact time, t , is measured by the use of the apparent, or hypothetical residence time. For tubular flow reactors, this variable can be expressed as the reciprocal space velocity. The space velocity is expressed as the volume of feed per volume of catalyst per unit of time. The reciprocal of space velocity would have the units of time and is proportional to the actual contact time.

The catalyst activity is a comparison of the effectiveness of catalyst which has been used and the effectiveness of new or fresh catalyst. The activity of the catalyst decreases with its use. This loss in activity is caused by a number of different factors. The deposition of "coke" on the catalyst surface, thus covering the active sites of the catalyst, is a reason for activity loss. Many substances, either in the reactants

stream or produced by the reaction, lower the activity of the catalyst. These substances are known as catalyst poisons.

When $\log_{10}(1/1-x)$ or $\log_{10}(1-x)$ is plotted versus reciprocal space velocity for first-order reactions at a specific set of conditions, the resulting plot is a straight line. The reaction rate constant may then be obtained by measuring the slope of this line.⁹

METHODS

The data were obtained in a fixed-bed catalytic reactor at various pressures, temperatures, and space velocities (feed rates). The feed stocks used were six fractions of West Texas crude oil supplied by the Continental Oil Company. These fractions were light straight run naphtha, reforming naphtha, No. 1 kerosene, heavy diesel fuel, heavy gas oil, and the overhead composite. The overhead composite was a mixture of the other five fractions. The inspection data for the above feed stocks are listed in Table I in the Appendix.

The reactor was operated at temperatures of 650, 700, 750, and 800 degrees Fahrenheit, and pressures of 200, 400, 600, and 800 pounds per square inch gauge. The space velocities used were 2, 4, 6, and 8 cc feed per cc catalyst per hour. Each of the six feed stocks were catalytically hydrodesulfurized at all possible combinations of the above pressures, temperatures, and space velocities. A hydrogen rate of 900 standard cubic feet per barrel of feed stock was used. Previous experiments had indicated that this would be an excess of hydrogen. ⁷

The catalyst used was Houdry "series C" 1/8-inch extruded cobalt-molybdate catalyst. The catalyst consists of a mixture of cobalt and molybdenum oxides on an alumina support. The amount of catalyst used for each run was 50 cc.

A run consisted of treating a specific feed stock at a fixed temperature, a fixed pressure, and each of the four space velocities.

At the end of each run, a "bench-mark" sample was taken.

This "bench-mark" sample was taken with the reactor operating at 700°F 400 psig, and a space velocity of 4 cc. feed per cc catalyst per hour. The feed stock used for this "bench-mark" sample was heavy diesel fuel. The purpose of the "bench-mark" sample was to compare the ability of the catalyst to desulfurize heavy diesel fuel with the ability of fresh catalyst to desulfurize heavy diesel fuel at the "bench-mark" conditions (700°F, 400 psig, space velocity = 3). Figure 2 is a plot of percent conversion versus space velocity for runs made on heavy diesel fuel feed stock at 400 psig and 700°F, with fresh catalyst. The space velocity corresponding to the conversion obtained in the "bench-mark" sample was determined from this plot. This space velocity is that required to obtain the conversion found in the "bench-mark" sample, using fresh catalyst. The percent activity is calculated by dividing the space velocity at which the "bench-mark" sample was taken (4 hr^{-1}) by the space velocity determined from Figure 2. An example of this method of calculating catalyst activity would be the calculation of the catalyst activity at the end of run K-M (Table IV). The conversion obtained in the "bench-mark" sample (K-BM-M) was 91.5 percent. This conversion corresponds to a space velocity of 4.5 hr^{-1} in Figure 2, which means that, if fresh catalyst were used, the above conversion could be obtained at a space velocity of 4.5 hr^{-1} . The catalyst activity is calculated by dividing the space velocity at which the "bench-mark" sample was taken (4 hr^{-1}) by the space velocity determined from Figure 2 (4.5 hr^{-1}), and

is found to be 88.9 percent.

A sample similar to the "bench-mark" sample was taken before the "bench-mark" sample after many of the runs. This sample was taken at the same conditions as the "bench-mark" sample except that the feed stock used was the same as that used during the run instead of heavy diesel fuel. The ability of the catalyst to desulfurize the feed stock used during the run as compared to the ability of fresh catalyst to desulfurize that feed stock could be measured in this manner.

Most of the desulfurized samples were washed twice with a ten percent sodium hydroxide solution and three times with water to remove any dissolved hydrogen sulfide in the samples. The hydrogen sulfide gas was removed from the heavy gas oil samples by bubbling nitrogen through the samples. The light straight run naphtha samples could not be treated to remove dissolved hydrogen sulfide, since the samples formed a colloidal suspension with the sodium hydroxide solution, and the samples were too volatile to be treated with nitrogen.

The samples were analyzed for total sulfur content with either a Bico double-unit sulfur apparatus or by the use of the lamp method. The method for determining the sulfur content was the same as that described by the American Society for Testing Materials. ¹

EQUIPMENT

All of the runs were made in a bench-scale experimental unit. A schematic diagram of this unit appears in Figure 1. The bench-scale unit consisted of a feed section, a pre-heater, the reactor section, and the gas system.

The reactor was fabricated from one-inch I.D. stainless steel pipe. The top end of the reactor was sealed and contained fittings for the feed from the pre-heater, a pressure gauge, and a 3/16-inch stainless steel thermowell. The thermowell contained three iron-constantan thermocouples used to measure the temperatures at both ends of the catalyst zone and the temperature in the section above the catalyst zone. The bottom end of the reactor was threaded for a sleeve-plug type closure for the purpose of removing the catalyst and catalyst supports at the end of each run. The catalyst supports used were alundum pellets. The volume of catalyst was held constant at 50 cc for all of the runs, and the volume of the catalyst zone was held constant at 100 cc by mixing the catalyst with 50 cc of alundum pellets. The closure for the bottom end of the reactor contained an outlet for the product leaving the reactor. A fitting for another pressure gauge was located directly below this outlet.

The reactor was machined to fit into a block of aluminum which was 30 inches long and 5-7/8 inches in diameter. The aluminum block had been bored longitudinally and reamed so that the reactor could be inserted into

it. The outside of the aluminum block was threaded with a 5-threads per inch, round-bottom thread, for the purpose of holding three beaded-nichrome wires which were wrapped around the block. These nichrome wires were connected to three powerstats so that the voltage applied to each of the wires could be controlled. The aluminum block was contained inside an aluminum can which was approximately 32 inches long. The space between the block and the wall of the aluminum can was filled with "Zonolite" insulation. The temperature inside the reactor could be controlled very closely with this configuration.

The feed section consisted of two large feed storage bottles, a Hills-McCanna chemical proportioning pump, and a 50 ml burette. The particular feed stock which was being desulfurized was stored in one of the storage bottles. The feed stock was pumped to the top of the pre-heater by the chemical proportioning pump. The space velocity was measured by feeding to the pump from the 50 ml burette. The second feed storage bottle was used for storing heavy diesel fuel. The heavy diesel fuel was used at the end of each run for catalyst activity comparisons.

The pre-heater was fabricated from a small section of stainless steel pipe and was packed with alundum pellets. The top of the pre-heater was fitted with inlets for the feed stock from the feed section and for hydrogen, and also contained a fitting for a pressure gauge. The bottom of the pre-heater was connected to the reactor top by means of 1/8-inch stainless steel tubing. The pre-heater was also wrapped

with beaded nichrome wire which was attached to a powerstat. The temperature in the pre-heater was measured by the use of an iron-constantan thermocouple. This thermocouple and the three thermocouples in the reactor were connected to a Leeds and Northrup indicating potentiometer, from which the temperatures could be read directly.

The hydrogen was metered into the pre-heater from a cylinder of hydrogen by the use of a Brooks rotameter. The hydrogen cylinder was equipped with a Victor hydrogen regulator. The hydrogen passed through a De-oxo purifier and a drier before reaching the rotameter. The De-oxo purifier converted any oxygen in the hydrogen stream to water. The water was removed in the drier which contained Drierite.

The desulfurized feed stock and excess hydrogen passed through a water-cooled condenser after leaving the reactor section, and then through a Grove pressure regulator which controlled the pressure in the reactor section. The product was received in a product reservoir, and the excess hydrogen plus hydrogen sulfide gas were passed through a sodium hydroxide wash and a water wash to remove the hydrogen sulfide. The excess hydrogen was then vented into the atmosphere.

DISCUSSION

Figures 3 through 21 show $\log_{10} [100(1-x)]$ plotted versus reciprocal space velocity for each of the feed stocks at the various temperatures and pressures. It is obvious from these plots that very few of the plots are the straight lines which a first-order reaction would yield. There are a number of possible reasons that the plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity did not yield straight lines. The range of space velocities used may have been too wide, and it is probable that portions of these plots, including a smaller range of space velocities, would approximate the straight lines which first-order and pseudo-first-order reactions yield. Another possible reason that the data did not indicate first-order reactions might arise from the fact that a wide variety of sulfur-bearing compounds was present in most of the feed stocks. It is possible that if each sulfur-bearing compound was desulfurized separately, that each of the reactions would be first-order reactions, or a majority of the reactions might be first-order with the remainder of the reactions being fractional or higher-order reactions. The combination of several sulfur-bearing compounds, which would normally yield first-order reactions when desulfurized individually, might give rise to an interaction effect which would cause the desulfurization of this combination of compounds to exhibit an order of reaction other than first-order. The possibility of experimental error, as a reason for the reactions not exhibiting first-order characteristics, cannot be neglected. Tables II through VII present the tabulated de-

sulfurization data for each of the feed stocks.

The investigation of the catalyst activity with respect to its ability to desulfurize heavy diesel fuel feed stock produced some unexpected results. These calculated catalyst activities are listed in Tables II through VII. These catalyst activities showed that the ability of the catalyst to desulfurize heavy diesel fuel was drastically reduced at the end of each run. The samples which were taken just prior to the "bench-mark" samples indicated in almost all cases that the catalyst was still very close to 100 percent active with respect to the catalyst's ability to desulfurize the feed stock used during the run. These samples are numbered as the -24- samples in Tables II through VII; e.g., K-24-I. The conversion obtained in these samples was compared with the conversions obtained at a temperature of 700°F., a pressure of 400 psig, and a space velocity of 4 for each feed stock. Opprecht lists desulfurization data obtained using a cobalt-molybdate catalyst for the desulfurization of several petroleum fractions.⁷ These studies indicated that the catalyst showed no appreciable loss in activity until the catalyst had been used for a length of time in the range of 70-100 hours. The catalyst was usually used for approximately 20 hours in gathering the data for this study. In view of the above findings, the catalyst activity was assumed to be constant at 100 percent with respect to the catalyst's ability to desulfurize the feed stock used during the run.

A possible explanation of the apparent decrease in the catalyst's ability to desulfurize heavy diesel fuel feed stock after having been used on heavier feed stocks is one which could be termed a "molecular sieve" theory. It is possible that the inner structure of the catalyst was filled with the heavier feed stock used during the run, and when the heavy diesel fuel flowed over the catalyst, the differences in the size of the molecules of the two feed stocks limited the amount of heavy diesel fuel which could reach the active sites of the catalyst. The lighter feed stocks may have left a layer of "coke" which prevented the heavy diesel fuel from reaching the active sites, but still permitted the smaller molecules of the lighter feed stocks to reach the active sites. These situations could possibly cause an apparent decrease in catalyst activity. A study of this nature is presently being undertaken in the Chemical Engineering Department of Montana State College.

Since the plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity did not yield straight lines, the data could not be analyzed by the usual chemical reaction kinetics methods. The data were, however, analyzed using a statistical approach.

The data obtained from each of the feed stocks constituted a factorial experiment. A factorial experiment is one in which two or more factors are studied at two or more different levels.³ The data from each feed stock constitutes a 4 x 4 x 4 factorial experiment. The three

factors, temperature, pressure, and space velocity, are each studied at four different levels, and all possible combinations of these factors and levels are studied. In this factorial analysis, the effects of pressure, temperature, and space velocity on conversion are all studied separately, and the two-factor interactions of the above factors are also studied. The effect of a factor is the change in response produced by a change in the level of the factor. If the effect of one factor is different at different levels of another factor, the two factors are said to interact. An example of a two-factor interaction would be obtaining a greater increase in conversion when the pressure is increased from 200 to 400 psig at 700°F than the increase in conversion obtained when the pressure is changed from 200 to 400 psig at 650°F.

The three-factor interaction is assumed to be negligible for this study, and is used as an estimate of experimental error. Normally, in factorial experiments, replications of the individual observations are made, and the variance of these replications is used for an estimate of error. When there are no replications, as in this study, the higher order interactions are used as an estimate of error.³ An explanation of the notation used in the statistical tables is presented in Table VIII. A discussion of the results of the desulfurization of the individual feed stocks follows:

Light Straight-Run Naphtha

The desulfurization data for the runs made with light straight-run naphtha are presented in Table II. The conversion of the sulfur in the feed to hydrogen sulfide appears to be very nearly constant.

The analysis of variance of the data for light straight-run naphtha is presented in Table IX. An analysis of variance permits the experimenter to determine at a known level of probability which of the variables affect the observations (in this case, which variables affect the conversion of sulfur to hydrogen sulfide). The effect of a variable is said to be statistically significant if the variance ratio (F-ratio) exceeds the specified value called the critical variance ratio. The variance ratio is obtained by dividing the mean square for the particular factor by the mean square for error. The effect of factor A (pressure) in the runs made with light straight-run naphtha was found to be significant at the one percent level. (When a factorial effect is significant at the five percent level, the probability that the effect is actually not significant is 0.05, or 1 in 20). The AB interaction (interaction between pressure and temperature) was found to be significant at the five percent level.

The conversion data for light straight-run naphtha are presented in the form which is conventional for a factorial analysis in Table X. Two-way tables of means for factors A and B, A and C, and B and C are presented in Tables XI, XII, and XIII. The factor C represents space velocity.

These two-way tables are obtained by summing the observations on two factors over the levels of the third factor, and dividing by the number of observations in each sum. The means obtained in these tables are the mean values of all observations at one level of a specific factor. The mean listed in the upper right-hand corner of Table XI (88.91) is the mean of all observations at the first level of factor A, or the mean of all observations at 200 psig on light straight-run naphtha.

A multiple range test for significant differences among the means of the conversions obtained at the various levels of each of the factors was carried out. This test is attributed to D. B. Duncan⁴ and determines which of the differences between the means, considered a pair at a time, are significant and which are not. An example of this is finding which of the differences between the four means obtained at the various levels of pressure are significant. The four means obtained for light straight-run naphtha are:

Pressure:	200 psig(1)	400 psig(2)	600 psig(3)	800 psig(4)
Mean:	88.91%	88.41%	89.88%	91.02%

The first step is to obtain the standard error of a mean. This is obtained by dividing the error variance (error mean square) by the number of observations in each mean (16), and taking the square root of this quotient. The standard error of a mean for light straight-run naphtha feed stock was found to be 0.355. From tables of special significant ranges for a five percent significance level test and a one percent

significance level test, significant ranges for sample sizes of 2, 3, and 4, and 27 degrees of freedom are obtained (27 is the number of degrees of freedom upon which the standard error is based). These significant ranges, at the five percent significance level, are 2.905, 3.05, and 3.135, for sample sizes of 2, 3, and 4, respectively. The significant ranges are multiplied by the standard error of a mean to obtain the least significant ranges. These least significant ranges, at the five percent significance level, for light straight-run naphtha, are 1.031, 1.083, and 1.113 for sample sizes of 2, 3, and 4, respectively. This means that the difference between the largest and smallest of the four means must be at least 1.113 to be significant at the five percent significance level; the difference between the smallest and second largest means must be at least 1.083 to be significant at the five percent significance level, etc. The means are arranged in increasing order in Table XIV. Any two means which are not underscored by the same line are significantly different. In the analysis of variance for light straight-run naphtha, the effect of pressure (factor A) was found to be significant at the one percent significance level. Table XIV shows that the difference between the conversion obtained at 200 psig and that obtained at 400 psig is not significant at the five percent level. The differences between any other combination of two means is significant at the five percent significance level. Changing the pressure from 200 to 400 psig did not significantly affect the conversion. Changing the pressure from 400 psig to 600 psig increased the conversion by approximately one per-

cent, and changing the pressure from 600 psig to 800 psig increased the conversion again by approximately one percent. The difference between the means obtained at 800 psig and 200 psig, the difference between the means at 800 psig and 400 psig, and the difference between the means at 600 psig and 400 psig were found to be significant at the one percent level.

The only significant difference found in the means of the conversions obtained at the four levels of temperature was the difference between the mean of the conversions obtained at 790°F and the mean of the conversion obtained at 750°F. The difference of these means was found to be significant at the five percent level. There were no significant differences at the one percent level, in the means of conversions obtained at the four levels of temperature.

There were no significant differences at the five percent or one percent significance level between the means of the conversions obtained at the four different space velocities.

The mean of all observations made on light straight-run naphtha was 89.56 percent conversion. This value was lower than expected. The most probable reason for this is that the light straight-run naphtha samples could not be washed to remove any hydrogen sulfide dissolved in the samples.

Figures 3 through 6 are plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity at various temperatures and pressures for light straight-run naphtha feed stock.

Reforming Naphtha

The desulfurization data for reforming naphtha feed stock are presented in Table III. The conversion data are presented in the conventional form for a factorial analysis in Table XVI. Tables XVII, XVIII, and XIX are the two-way tables of means of the conversions obtained for reforming naphtha feed stock.

Table XV presents the analysis of variance for conversion data obtained from reforming naphtha feed stock. The effect of pressure is significant at both the five percent and one percent significance levels, as is the effect of temperature. The effect of the space velocity is not significant. The interaction between temperature and pressure, and the interaction between temperature and space velocity were found to be slightly significant at the five percent significance level, but small compared to the effects of temperature and pressure.

Table XX presents the results of the multiple range tests for significant differences among the means of the conversions obtained for reforming naphtha feed stock. The standard error of a mean was found to be 0.1122. The only difference from the least significant ranges used for light straight-run naphtha feed stock is that the significant ranges taken from the special tables are multiplied by the standard error of a

mean for reforming naphtha feed stock instead of the standard error used for light straight-run naphtha feed stock. Table XX shows that increasing the pressure decreased the conversion. The difference between the largest mean (96.72 at 400 psig) and the smallest mean (95.40 at 800 psig), however, was only 1.3 percent. The means at 200, 400, and 600 psig were all fairly close, but the mean at 800 psig was lower than the other means.

The largest difference between the means at the four levels of temperature was 0.9 percent conversion. The mean obtained from the observations made at 750°F was significantly different from the other means. The means at the four levels of space velocity were not significantly different.

The mean of all observations made on reforming naphtha was found to be 96.21 percent conversion. Figures 7 through 10 are plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity at the various temperatures and pressures for reforming naphtha feed stock.

No. 1 Kerosene

The desulfurization data for No. 1 kerosene feed stock are presented in Table IV. These data were very erratic, as is shown by the plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity presented in Figures 11 through 14.

The conversion data are presented in the conventional form for a factorial analysis in Table XXII. Tables XXIII, XXIV, and XXV are the two-way tables of means of the conversions obtained for No. 1 kerosene feed stock.

The analysis of variance of the conversion data for No. 1 kerosene feed stock is presented in Table XXI. The effects of pressure, temperature, and space velocity were all found to be significant at both the five percent and the one percent significance levels. The effect of the interaction between pressure and temperature was found to be significant at both the five percent and the one percent significance levels. The effect of the interaction between pressure and space velocity was found to be significant at the five percent significance level, while the effect of the interaction between temperature and space velocity was not significant. The significance of the interaction effects was small compared to the effects of the individual factors.

Table XXVI presents the results of the multiple-range tests for significant differences among the means for No. 1 kerosene feed stock. These tests show that at the various levels of pressure, the only mean which is significantly different from the other means is the mean at 200 psig. There is an increase in conversion of approximately six percent when the pressure is increased from 200 psig to 400 psig, but there is no significant difference in the means at 400, 600, and 800 psig. The only mean which was significantly different from the other means at the

various levels of temperature was the mean at 650°F. Here again, there is an increase in conversion of approximately four percent when the temperature is increased from 650°F to 700°F, but there is no significant difference in the means at 700, 750, and 800°F. No significant difference was found in the means of the conversions obtained at space velocities of two and four hr^{-1} , and no significant difference was found in the means of the conversions obtained at space velocities of six and eight hr^{-1} . The means of the conversions obtained at two and four hr^{-1} were significantly different from the means obtained at six and 8 hr^{-1} at the five and one percent significance levels. Increasing the space velocities decreased the conversion obtained, as would be expected.

The mean of all observations made on No. 1 kerosene feed stock was 94.95 percent conversion.

Heavy Diesel Fuel

The desulfurization data for heavy diesel fuel feed stock are presented in Table V. The conversion data are presented in the conventional form for a factorial analysis in Table XXVIII. Tables XXIX, XXX, and XXXI are the two-way tables of means of the conversions obtained for heavy diesel fuel feed stock.

The analysis of variance of the conversion data for heavy diesel fuel feed stock is presented in Table XXVII. All factors and all interactions were found to be significant at both the five and one percent significance levels. The effects of the interactions, however, were small in

comparison with the effects of the individual factors.

Table XXXII presents the results of the multiple range tests for significant differences among means for heavy diesel fuel feed stock. These tests show that the conversion was increased when the pressure was increased from 200 to 400 psig, but when the pressure was further increased, the conversion was decreased. The conversion was increased approximately 20 percent when the pressure was increased from 200 to 400 psig (65.93% to 86.01%), and was decreased approximately six percent when the pressure was increased from 400 to 600 psig (86.01% to 79.78%).

The difference in the means of the conversions obtained at 750 and 800°F was not significantly different. An increase in conversion of approximately 21 percent was obtained when the temperature was increased from 650 to 700°F (57.71% to 78.58%), and an increase of approximately nine percent was obtained when the temperature was increased from 700 to 750°F (78.58% to 87.59%).

The means of the conversions obtained at the various levels of space velocity were all significantly different. A decrease in conversion of 8.7 percent was obtained when the space velocity was increased from two to four hr^{-1} (89.79% to 81.09%), a decrease of 6.9 percent was obtained when the space velocity was increased from four to six hr^{-1} (81.09% to 74.19%), and a decrease of 6.6 percent was obtained when the space velocity was increased from six to eight hr^{-1} (74.19% to 67.57%).

The mean of all observations made on heavy diesel fuel feed stock was 78.16 percent conversion. Figures 15 through 18 are plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity for heavy diesel fuel feed stock.

Heavy Gas Oil

The desulfurization data for heavy gas oil feed stock are presented in Table VI. The conversion data are presented in the conventional form for a factorial analysis in Table XXXIV. Tables XXXV, XXXVI, and XXXVII are two-way tables of means of conversions for heavy gas oil feed stock.

The analysis of variance of the conversion data for heavy gas oil feed stock is presented in Table XXXVIII. The effects of pressure, temperature, and space velocity were all significant at the five and one percent significance levels. The interaction between pressure and temperature was significant at the five and one percent significance levels, but was small in comparison with the effects of the individual factors.

Table XXXVIII presents the results of the multiple range tests for significant differences among means for heavy gas oil feed stock. The difference between the means of the conversions obtained at 400 psig and 800 psig are significantly different at the five percent significance level, but the difference between the means of the conversions obtained at 400, 600, and 800 psig are not significantly different at the one percent significance level. The mean of the conversions obtained at 200 psig is significantly different from the means obtained at the other

levels of pressure. An increase in conversion of approximately 15.6 percent was obtained when the pressure was increased from 200 to 400 psig (45.31% to 60.89%). The conversion was increased approximately 1.9 percent when the pressure was increased from 400 to 600 psig (60.89% to 62.81%), and the conversion was increased approximately 1.5 percent when the pressure was increased from 600 to 800 psig (62.81% to 64.36%).

The differences in the means of the conversions obtained at the various levels of temperature were all significantly different. An increase in conversion of approximately 18.8 percent was obtained when the temperature was increased from 650 to 700°F (35.34% to 54.12%), an increase in conversion of approximately 15.1 percent was obtained when the temperature was increased from 700 to 750°F (54.12% to 69.26%), and an increase of 5.4 percent was obtained when the temperature was increased from 750 to 800°F (69.26% to 74.64%).

The differences in the means of the conversions obtained at the various space velocities were all significantly different. A decrease in conversion of approximately 13.5 percent was obtained when the space velocity was increased from two to four hr^{-1} (74.61% to 61.09%), a decrease of approximately 9.4 percent was obtained when the space velocity was increased from four to six hr^{-1} (61.09% to 51.73%), and a decrease of approximately 5.8 percent was obtained when the space velocity was increased from six to eight hr^{-1} (51.73% to 45.94%).

The mean of all observations made on heavy gas oil feed stock was 58.34 percent conversion. Figures 19 through 22 are plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity for heavy gas oil feed stock.

Overhead Composite

The desulfurization data for overhead composite feed stock are listed in Table VII. Table XI presents the conversion data for overhead composite feed stock in the conventional form for a factorial analysis. Tables XLI, XLII, and XLIII are two-way tables of means of conversions for overhead composite feed stock.

The analysis of variance of the conversion data obtained with overhead composite feed stock is presented in Table XXXIX. The effects of pressure, temperature, and space velocity are all significant at both the five and one percent significance levels. The interaction effects between pressure and space velocity, and between temperature and space velocity are significant, but are small in comparison with the effects of the individual factors.

Table XLIV presents the results of the multiple range tests for significant differences among the means of the conversions obtained for overhead composite feed stock. The difference between the means of the conversions obtained at 600 and 800 psig was not significant. An increase in conversion of approximately 17.6 percent was obtained when the pressure was increased from 200 to 400 psig (61.31% to 78.92%), and

an increase in conversion of approximately 4.3 percent was obtained when the pressure was increased from 400 to 600 psig (78.92% to 83.23%).

The differences among the means of the conversions obtained at the various levels of temperatures were all significant at the five percent significance level. The difference between the means of the conversions obtained at 750 and 800°F was not significant at the one percent significance level. An increase in conversion of approximately 15.9 percent was obtained when the temperature was increased from 650 to 700°F (61.78% to 77.65%), an increase of 5.1 percent was obtained when the temperature was increased from 700 to 750°F (77.65% to 82.75%), and an increase of approximately two percent was obtained when the temperature was increased from 750 to 800°F (82.75% to 84.73%).

The differences among the means of the conversions obtained at the various space velocities were all significant. A decrease in conversion of 7.4 percent was obtained when the space velocity was increased from two to four hr^{-1} (87.27% to 79.83%), a decrease of 7.2 percent was obtained when the space velocity was increased from four to six hr^{-1} (79.83% to 72.63%), and a decrease of approximately 5.4 percent was obtained when the space velocity was increased from six to eight hr^{-1} (72.63% to 67.18%).

The mean of all observations made on overhead composite feed stock was 76.73 percent conversion. Figures 23 through 26 are plots of $\log_{10} [100(1-x)]$ versus reciprocal space velocity for overhead com-

posite feed stock.

The means of the observations made on each of the various feed stocks are listed below:

<u>Feed Stock</u>	<u>Percent Conversion</u> <u>(mean of all observations)</u>
Light straight-run naphtha	89.56
Reforming naphtha	96.21
No. 1 kerosene	94.95
Heavy diesel fuel	78.16
Heavy gas oil	58.34
Overhead composite	76.73

These mean percent conversion values decrease as the boiling range of the feed stock becomes higher in all cases except for the light straight-run naphtha. As was mentioned earlier, the dissolved hydrogen sulfide could not be removed from the light straight-run naphtha samples, and this is probably the reason that the conversion obtained with light straight-run naphtha was lower than expected. The mean percent conversion for the overhead composite feed stock falls between the means of the heavier and the lighter feed stocks, as would be expected.

The interaction effects between temperature, pressure, and space velocity were small in comparison to the effects of the individual factors for all of the feed stocks. This means that these factors are almost independent. The change in conversion obtained by changing one factor is nearly independent of the level of the other factors over the range of values used in this study.

The unique discovery of this study was the severe catalyst deactivation encountered with respect to heavy diesel fuel feed stock. The averages of the catalyst activities with respect to heavy diesel fuel feed stock for each feed stock are listed below:

<u>Feed Stock</u>	<u>Average Catalyst Activity (with respect to heavy diesel fuel) After Approximately 20 Hours</u>
Light straight-run naphtha	36.6%
Reforming naphtha	52.2
No. 1 kerosene	63.3
Heavy diesel fuel	59.5
Heavy gas oil	47.7
Overhead composite	42.7

The general opinion in the oil industry has been that heavier feed stocks will deactivate a catalyst more severely than do light feed stocks. The above data indicate that the lighter feed stocks also severely reduced the catalyst's ability to desulfurize that feed stock much more than feed stocks having boiling ranges near that of the particular feed stock. The next step in this study is obviously to study this phenomenon, using different crude oils, and determine if it is a characteristic of all or many crude oils. A research project with the purpose of investigating this question is now being undertaken in the Chemical Engineering Department at Montana State College.

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