



Characterization of oils for catalytic hydrodesulfurization
by Richard G Waterman

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Montana State University
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Abstract:

Catalytic hydrodesulfurization studies were carried out on four oils in the 400 to 700-F boiling range utilizing cobalt molybdate catalyst. All studies were made with bench scale equipment.

The effects of contact time, temperature, treat-gas composition, treat-gas rate, hydrogen partial pressure, and oil partial pressure were studied. Desulfurization was found to increase with an increase in contact time, but the rate of reaction decreased. The rate of desulfurization increased with temperature; however, temperatures above 700 F tend toward catalyst deactivation. At constant pressure an increase in hydrogen partial pressure increases desulfurization, and increasing the treat-gas rate from 1000 to 2000 ft³/bbl also increased desulfurization. The increase with gas rate was attributed to lower oil partial pressure at the higher gas rate. A decrease in desulfurization with an increase in pressure at constant contact time was noted when the hydrogen concentration of the treat-gas was greater than approximately 85% when using a gas rate of 2000 ft³/bbl, and approximately 55% when using a gas rate of 1000 ft³/bbl.

The charge oils and three desulfurized samples were analyzed by a mass spectrometer. It was found that thiophenes are more reactive than benzothiophenes which are more reactive than dibenzothiophenes. Di-benzothiophene content was correlated with the ease of desulfurization.

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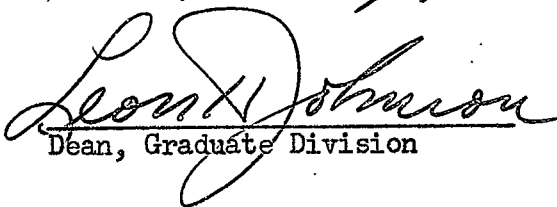
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Head, Major Department



Chairman, Examining Committee



Dean, Graduate Division

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TABLE OF CONTENTS

Abstract	page 3
Introduction	4
Equipment.	10
Materials	10
Methods	11
Discussion	15
Table XVI - Comparison of Sulfur Removal From Aramco Light Waxy Distillate.	24
Summary	26
Acknowledgment	28
Literature Cited	29
Appendix	30

ABSTRACT

Catalytic hydrodesulfurization studies were carried out on four oils in the 400 to 700 F boiling range utilizing cobalt molybdate catalyst. All studies were made with bench scale equipment.

The effects of contact time, temperature, treat-gas composition, treat-gas rate, hydrogen partial pressure, and oil partial pressure were studied. Desulfurization was found to increase with an increase in contact time, but the rate of reaction decreased. The rate of desulfurization increased with temperature; however, temperatures above 700 F tend toward catalyst deactivation. At constant pressure an increase in hydrogen partial pressure increases desulfurization, and increasing the treat-gas rate from 1000 to 2000 ft³/bbl also increased desulfurization. The increase with gas rate was attributed to lower oil partial pressure at the higher gas rate. A decrease in desulfurization with an increase in pressure at constant contact time was noted when the hydrogen concentration of the treat-gas was greater than approximately 85% when using a gas rate of 2000 ft³/bbl, and approximately 55% when using a gas rate of 1000 ft³/bbl.

The charge oils and three desulfurized samples were analyzed by a mass spectrometer. It was found that thiophenes are more reactive than benzothiophenes which are more reactive than dibenzothiophenes. Dibenzothiophene content was correlated with the ease of desulfurization.

INTRODUCTION

For many years the petroleum industry has been confronted with problems arising from the presence of sulfur compounds in petroleum. The problems are becoming more apparent for several reasons: more high-sulfur crude oils are being used because the more desirable low-sulfur crudes are being depleted; the petroleum industry has become more competitive with the consumer desiring high quality products; and, many of the more recently developed refining processes are hampered by the presence of sulfur.

Among the problems caused by the presence of sulfur compounds in various intermediates and products are:

1. The corrosive effects encountered in refining, storage, transportation, and in burning or combusting of the products
2. The objectionable odors of some compounds such as mercaptans and hydrogen sulfide
3. The reduction of octane number of gasolines induced by certain types of sulfur compounds such as disulfides, polysulfides, and mercaptans
4. The lowering of lead susceptibility by nearly all types of sulfur compounds (on a 60 iso-octane-40 n-heptane blend containing 3 cc. of tetraethyllead per gallon, the octane number was depressed about 4 octane numbers with thiophenes present to 14 octane numbers with thiophene mercaptans present. These compounds were present in concentrations equivalent to 0.1%

sulfur in the fuel (7))

5. The adverse effects of sulfur compounds on product stability
6. The acrid fumes given off when burned as in the case of fuel oils.

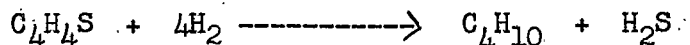
The consequences of most of these problems are easily recognized, but the manner in which the presence of sulfur alters some refining processes is not so apparent. Catalytic processing is becoming more popular in the petroleum industry and a variety of catalysts are in use; however, many of these catalysts are poisoned by the presence of sulfur compounds, that is, the sulfur compounds cause a decrease in catalyst activity. Nickel, cobalt, copper, iron, and platinum, used for dehydrogenation, platinum and palladium, used for gasoline reforming, are some of the catalysts poisoned by sulfur (3).

Before it was necessary to utilize the high-sulfur crudes, methods were employed, such as doctor treatment, to convert the objectionable odor compounds (mercaptans) to other types of compounds such as disulfides. This, of course, left the sulfur in the oil. If complete sulfur removal was required, the oil was generally treated with sulfuric acid, which also resulted in the loss of some desirable constituents.

Certain catalysts in an atmosphere of hydrogen (hydrodesulfurization) will decompose sulfur compounds, the sulfur can be eliminated as hydrogen sulfide, and losses of the feed stock are negligible. The crux of this type of processing was an economic source of hydrogen. Catalytic reforming, in which predominately naphthenes are converted to aromatics,

provided this source of hydrogen.

A typical hydrodesulfurization reaction involving thiophene is given below:



Many of the present day oil refineries receive their crude oils from various oil fields throughout the world. These crudes may differ only slightly in composition and sulfur content, or they may be greatly different. Because of the differing composition or other reasons, different oils may behave differently under similar operating conditions and can create many problems within a refinery. Generally, the reactions of the various oils to the processing conditions are determined before usage and the crudes are systematically scheduled into the refinery. This is not always possible, however; and because of the changing economic conditions of the world today, a refinery may have its crude oil supply cut off without notice and have to resort to another source.

In order to determine how a particular fraction will react to the process variables, the fraction is generally subjected to the variables of the process on a pilot plant scale. This can become a very expensive and time-consuming operation. If the composition of the oil in question could be determined, for instance by a mass spectrometer, a correlation might be found between composition and process adaptability. Once the effects of process variables have been established on a particular petroleum fraction or boiling range, a composition analysis may be all that would be needed to predict conversions at various operating condi-

tions. In other words, the charge oils may be characterized by a particular constituent or constituents.

In this paper, four different oils in the diesel and burner oil range (400-700 F) were studied in conjunction with a catalytic hydrodesulfurization process. The aim of the research was to determine the effects of the operating variables on the desulfurization reaction, and to determine if the types of sulfur compounds present in the oil could be linked to the ease of desulfurization.

The catalytic desulfurization reaction has been shown to be a pseudo-first-order reaction with respect to the concentration of the sulfur-bearing compound (5, 6, 8). The reaction is termed pseudo-first-order because the concentration of the hydrogen is kept high enough at all times to be considered constant (approximately 70 moles of H₂ per mole of sulfur compound). In view of this evidence a first-order reaction was assumed for the desulfurization reaction studied in this research.

The rate equation used was

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

in which C_a = the concentration of the sulfur-bearing compound,

t = contact time,

k = rate constant.

The actual contact time will be proportional to the apparent contact time and can be expressed in terms of space velocity, i.e., grams of oil per hour per gram of catalyst (g/hr/g). The reciprocal of space velocity has the units of time (hr). However, a better approach to the apparent

contact time is to use a function of the total vapor rate, which is a combination of treat-gas and oil vapor passing over the catalyst in a given time. This allows for variation in contact time due to temperature and pressure. Since 100 grams of catalyst were used in all the runs, the vapor rate was expressed as $\frac{\text{ft}^3 \text{ vapor}}{(\text{hr})(100\text{g})}$. The reciprocal of the vapor rate was used for apparent contact time.

Equation (1) can also be written as

$$\frac{dx}{dt} = k(A-x) \quad (2)$$

in which A = initial concentration of sulfur,

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

(A-x) = the amount of sulfur remaining. (It can be determined by a simple analysis.)

In the desulfurization reaction, the reaction rate constant is affected by all the process variables and should therefore be restricted to the operating conditions in each instance. To be specific, then, the reaction rate constant, k, in Equation (2) should be restricted by the subscripts as indicated in Equation (3).

$$\frac{dx}{dt} = k_{T.pH_2.pOil.H_2.D.C.Ca} (A-x) \quad (3)$$

The subscripts indicate, respectively, temperature, hydrogen partial pressure, oil partial pressure, hydrogen concentration, the type of diluent or diluents (gases other than hydrogen) in the treat-gas, the type of catalyst employed, and the catalyst activity, all of which affect the

velocity of the desulfurization reaction. The effects of catalyst particle size and catalyst bed depth have been left out, assuming that they are both of such dimensions so as to have no effect on the reaction. In some cases, decreasing catalyst particle size and increasing catalyst bed depth will increase desulfurization. It is desirable to operate where both of these factors will give maximum desulfurization provided the pressure drop across the catalyst bed does not become troublesome.

Rearrangement and integration of Equation (2) between limits ($t = 0$ to $t = t$, and $x = 0$ to x) gives

$$\frac{\ln A}{A-x} = kt \quad (4)$$

or
$$2.3 \log_{10} \frac{A}{A-x} = kt \quad (5)$$

If the reaction is first-order, a plot of $\log \frac{A}{A-x}$ vs. t should give a straight line with slope $\frac{k}{2.3}$ and passing through the origin.

Several rather lengthy terms are used frequently throughout the paper and for convenience the following abbreviations will be used:

<u>Term</u>	<u>Abbreviation</u>
Aramco Light Waxy Distillate	Aramco
Carter Railroad Diesel Oil	RRD
Carter Medium Cycle Oil	MCO
Husky No. 350 Burner Oil	Husky
Benzothiophene	BT
Dibenzothiophene	DBT

EQUIPMENT

All experiments were carried out in a 1-inch stainless steel reactor 36 inches long. The catalyst was supported by 1/8-inch alundum pellets and the pre-heat section above the catalyst was also filled with the pellets. The reactor was electrically heated by 4 nichrome heating coils. Current was supplied to the coils by four 120-volt autotransformers. Five iron-constantan thermocouples in a coaxial 1/4-inch stainless steel thermowell were used to measure the reactor temperature. The reactor pressure was controlled by a Mason-Neilan small volume air-to-close back pressure valve in conjunction with a Fisher-Wizard proportional controller.

A schematic diagram of the conventional high pressure flow system is given in Figure 1. The oil was pumped to the top of the reactor by a proportioning plunger pump. The hydrogen was taken from a commercial hydrogen cylinder and metered to the reactor through a rotometer.

MATERIALS

The catalyst employed was designated Harshaw COMO-0301T (Harshaw Chemical Company). This is a mixture of cobalt and molybdenum oxides supported on alumina. The catalyst was crushed and sized to 10/14 mesh and calcined for 12 to 20 hours at 1100 to 1200°F in an atmosphere of nitrogen.

The four oils used were namely:

1. Aramco Light Waxy Distillate from the Arabian-American Oil Company, Arabia

2. Carter Railroad Diesel Oil and
3. Carter Medium Cycle Oil from the Carter Oil Company, Billings, Montana
4. Husky No. 350 Burner Oil from the Husky Oil Company, Cody, Wyoming.

In addition to these four oils, a blend of 50 wt.% Carter Railroad Diesel Oil and 50 wt.% Carter Medium Cycle Oil was used. The inspection data of the charge oils are given in Table I.

Hydrogen was obtained in No. 1-A cylinders from the Whitmore Oxygen Company, Salt Lake City, Utah. Mixed gases with compositions of 60% hydrogen-40% methane and 30% hydrogen-70% methane by volume were obtained in No. 1-A cylinders from the Matheson Company, Joliet, Illinois.

METHODS

One hundred grams of catalyst were used in the reactor throughout the experimental work with the exception of Run Husky-5 (Table III), in which 50 grams were used. The 100-gram catalyst charge occupied approximately 10 inches of the reactor length.

The start-up procedure consisted of charging the reactor with catalyst, heating under hydrogen flow at the operating pressure to the desired operating temperature, and then starting the oil flow. Approximately 50 to 70 hours were necessarily allowed after the oil was started for the catalyst to become fully activated (Table VI, Aramco-5). The hydrogen was single-passed through the reactor and vented.

The product oil was received in a 1000-ml flask, caustic washed to remove hydrogen sulfide, water washed, and analyzed for sulfur content. The sulfur was determined by combustion of the oil in a lamp (ASTM method D90-41T), absorption of the oxides in hydrogen peroxide, and titration of the sulfuric acid formed with sodium hydroxide. Where highly aromatic charge oils were used (Runs Carter-2, and -3) the lamp method was unsatisfactory, and the sulfur was determined by the Carter Oil Company by combusting the sample in a quartz "boat".

In general, four samples were taken for each set of reactor conditions and the third and fourth samples were analyzed for sulfur content. One and two sulfur determinations were made on the third and fourth samples, respectively. This procedure was used to determine if the system was lined out.

A bench mark was referred to throughout the runs to check on catalyst activity. The conditions of the bench mark were: space velocity, 2 g/hr/g; pressure, 200 psig; temperature 650 F; treat-gas rate, 1000 ft³/bbl of hydrogen. The runs were designed to keep the effects of catalyst deactivation negligible.

The mass spectrometer analyses of the charge oils and the Aramco samples (Tables XIII and XIV) were made by the Esso Research and Engineering Company, Linden, New Jersey.

The charge oil for all the Aramco runs was Aramco Light Waxy Distillate, and the charge oil for all the Husky runs was Husky No. 350 Burner Oil. The charge oil for Run Carter-1 was Carter Railroad Diesel Fuel,

for Run Carter-2 was Carter Medium Cycle Oil, for Run Carter-3 was a 50 wt.% blend of the Railroad Diesel and Medium Cycle Oil.

From the operating conditions of the experimental work (200-400 psig, 600-700 F) and the boiling range of the charge oils (400-700 F), it is apparent that all the oil will not be vaporized in the reactor. The method used to calculate the percentage of the oil vaporized was taken from the Esso Blue Book (4). This involves some empirical correlations that have been developed for predicting equilibrium vaporization curves from distillation data. To quote from the Esso Blue Book, the method is outlined as follows:

1. Determine the Flash Reference Line (FRL) and the Flash Vaporization Curve (FVC) from the ASTM distillation of the feed stock used.
2. Calculate the number of moles of hydrocarbon and gas entering the reactor.
3. By the method of trial and error, assuming a given percentage of the oil vaporized, calculate its partial pressure under the prevailing reactor pressure.
4. Shift the flash curve parallel to itself from atmospheric pressure to the calculated partial pressure of the hydrocarbon in the mixture as determined under (3). The amount by which the flash curve should be shifted is most conveniently determined from the 40% FRL point and the partial pressure of the oil by means of Chart 4-53 of the Blue Book.
5. Compare the temperature at the assumed per cent vaporized on the shifted curve with the actual reactor temperature. If this temperature is higher than the reactor temperature, then less oil is vaporized than had been assumed; conversely, if the temperature on the shifted curve is lower than the reactor temperature, more oil was vaporized. Accordingly, repeat steps (3), (4), and (5) with another assumed percentage of oil vaporized until the corresponding temperature on the shifted flash curve coincides with the reactor temperature."

Figures 2 and 3 are plots of percent vaporized vs. temperature for the five charge oils. These figures show that the percent vaporized increases as temperature and gas rate increase, but decreases as pressure increases.

DISCUSSION

In the study of a catalytic reaction, it is desirable to know if the reaction is affected by diffusion. The reaction may be limited by the diffusion of the reactants from the main gas stream to the catalyst surface and the diffusion of the products from the catalyst to the main gas stream. The effects of this type of diffusion may be kept to a minimum by using high velocities through the catalyst bed and thus lowering the film resistance on the catalyst surface. The effects of diffusion across the surface film can be tested by making two series of runs with a different weight of catalyst in each series, preferably the catalyst charge differing by a factor of two (2). The same operating conditions are used in each series and by varying the space velocity a set of pairs of points are obtained; the points in each pair are at the same space velocity but at different linear velocities. If diffusion is limiting, a plot of the data from the two series will give two separate curves; but, if diffusion is not limiting, the points from both series should fall on the same curve. This method was used with 100 grams and 50 grams of catalyst and Husky oil for charge oil. The results of the runs (Husky-1, Table II and Husky-5, Table III) are plotted in Figure 4, which shows that within experimental accuracy the conversions were the same for both runs and that film diffusion is not a limiting factor in this study. The reaction may also be limited by diffusion from the catalyst surface to the active sites in the pores of the catalyst. As the catalyst size is decreased, the resistance to internal diffusion is decreased until

an optimum size is reached where a further decrease in catalyst size will no longer increase the reaction rate. It was believed that the catalyst size used in this research (10/14 mesh) was within this optimum size.

Catalyst activity is a variable in catalytic reactions and it becomes necessary to take into account unless it is constant. Figure 5 shows that the cobalt molybdate catalyst deactivates very rapidly with Aramco charge oil at 850 F, 2 g/hr/g, 200 psig, and 1000 ft³/bbl of hydrogen; these conditions, except temperature, are representative of those used in the experimental runs. Deactivation was noted at 750 F, also, (Table V), but was negligible at 700 F and lower. The experimental runs were carried out at 600 650, and 700 F.

Assuming that the desulfurization reaction is pseudo-first-order, the data for the five charge oils were plotted according to first-order kinetics (Figures 6, 7, 8, 9, 10, 11). These figures show at once the plot of $\log \frac{A}{A-x}$ vs. contact time is not a straight line but is definitely curved and indicates that the desulfurization of these oils does not behave as a pseudo-first-order reaction. These figures also show that the rate of desulfurization is dependent on contact time, temperature, pressure, treat-gas rate, and treat-gas composition. Although the effects of pressure, gas rate, and gas composition were studied only on the Aramco oil, it is expected that these variables will affect all four oils, qualitatively, the same.

Figures 6, 7, 8, 9, 10, and 11 show that as contact time increases, the conversion increases but the rate of desulfurization decreases. This

is probably due to the several sulfur compounds in the oil, each desulfurizing at a different rate. Initially the more easily desulfurized compounds are reacting very readily leaving the less reactive sulfur compounds representing a greater percentage of the remaining sulfur. There is no indication that the less reactive compounds react only after the more reactive compounds have been exhausted, but rather, that they are all reacting simultaneously. This would, of course, explain why the overall desulfurization reactions of these oils do not adhere to first-order kinetics.

An increase in temperature increases the rate of desulfurization. In order to obtain some type of temperature-conversion correlation, an Arrhenius-type temperature plot was made (Figure 12). Two rate constants, k_1 and k_3 , were estimated for each curve by drawing tangents to the curves in Figures 6, 7, 8, and 9; the initial rate constants, k_1 , were obtained by drawing tangents to the curves where they intersected the origin, and the rate constants at a contact time of $\frac{3(\text{hr})(100\text{g})}{\text{ft}^3}$, k_3 , were obtained by drawing tangents to the curves where they crossed the abscissa value of 3. The units of k are $\frac{\text{ft}^3}{(\text{hr})(100\text{g})}$, and it should be remembered that k is restricted by the operating conditions as mentioned before.

The logarithms of the k values are plotted versus reciprocal absolute temperatures for each charge oil in Figure 12. It may be seen from this figure that the slopes of the k_1 plots are greater than the slopes of the k_3 plots for all four oils. These differences in slopes indicate that an increase in temperature has less effect on increasing desulfurization as

the desulfurization becomes more complete. This is probably due to a preponderance of the less reactive, or more refractory, sulfur compounds remaining in the oil.

The effects of hydrogen concentration in the treat-gas, treat-gas rate, pressure, hydrogen partial pressure, and oil partial pressure on the desulfurization of the Aramco oil were studied at 650 F, and the effects of pressure and gas-rate at 700 F. The diluent in the treat-gas was methane. All the data were compared at a constant contact time of $\frac{2(\text{hr})(100\text{g})}{\text{ft}^3}$ since most of the data were obtained near this value. The conversion values at the contact time of 2 were taken from the curves of Figures 10 and 11. The data are tabulated in Table XII.

Figure 13 shows that at a given pressure and gas rate, an increase in hydrogen concentration increases desulfurization, which is the same as saying that at a constant oil partial pressure, an increase in hydrogen partial pressure increases desulfurization (Figure 14). However, when operating at 400 psig and a gas rate of 2000 ft^3/bbl , increasing the hydrogen concentration above 60% appears to have no effect on increasing desulfurization. Figures 13 and 14 also show that at constant pressure, increasing the gas rate from 1000 to 2000 ft^3/bbl increases desulfurization.

The effect of increasing conversion with an increase in hydrogen partial pressure is also indicated in Figure 15, in which the $\log \frac{A}{A-x}$ is plotted versus the ratio of hydrogen partial pressure to oil partial pressure at 200 psig. This plot holds for gas rates of 1000 and 2000 ft^3/bbl of 100% H_2 , 60% H_2 - 40% CH_4 , and 30% H_2 - 70% CH_4 , indicating that the

ratio of the hydrogen partial pressure to the oil partial pressure is more important than the absolute value of the hydrogen partial pressure. Similar data scattered quite badly at 400 psig (Table XIV).

When comparing desulfurization at different pressures the reaction appears more complex. In Figure 16 the $\log \frac{A}{A-x}$ is plotted versus reactor pressure; all the data are compared at a constant contact time, (reciprocal vapor rate) of $2 \frac{(\text{hr})(100\text{g})}{\text{ft}^3}$ (Table XII). Figure 16 shows that where 100% hydrogen treat-gas was used, and where 60% H_2 - 40% CH_4 treat-gas at $1000 \text{ ft}^3/\text{bbl}$ was used, an increase in pressure decreased desulfurization. (This decrease in desulfurization with an increase in pressure may appear confusing at first since it is generally accepted that an increase in pressure increases desulfurization, which is true if the data at different pressures are compared at constant space velocities (Table XI). The increase in desulfurization with pressure at constant space velocity is due to an increase in contact time with an increase in pressure. For instance, 200 psig, 650 F, $1000 \text{ ft}^3/\text{bbl}$, and a space velocity of 2 g/hr/g gives a contact time of $3.6 \frac{(\text{hr})(100\text{g})}{\text{ft}^3}$, while 400 psig and the same conditions give a contact time of $7.35 \frac{(\text{hr})(100\text{g})}{\text{ft}^3}$. However, when the data at different pressures are compared at constant contact time the effects of pressure may show up as having an adverse effect on desulfurization.) Since both hydrogen partial pressure and oil partial pressure increase with reactor pressure, and since it has been shown that desulfurization increases with increased hydrogen partial pressure, and yet desulfurization decreases, then some type of preferential adsorption of oil

molecules is indicated. In other words, the decrease in desulfurization with an increase in pressure at constant contact time is attributed to the increase in oil partial pressure. Figure 17, which is a plot of $\log \frac{A}{A-x}$ vs. oil partial pressure, shows this adverse effect of increasing oil partial pressure when using 100% hydrogen or when operating at 1000 ft³/bbl of 60% H₂ - 40% CH₄.

If a diluent is used in the treat-gas (60% H₂ - 40% CH₄ and 30% H₂ - 70% CH₄) an increase in pressure increases desulfurization (except for 1000 ft³/bbl of 60% H₂ - 40% CH₄) as indicated in Figures 16 and 17. This change in the effect of pressure may be explained by referring to Figure 13. This figure shows that for a given contact time when operating at 650 F and a gas rate of 2000 ft³/bbl, an increase in pressure will increase desulfurization when the concentration of hydrogen in the treat-gas is less than approximately 85%; but, when the concentration of hydrogen in the treat-gas is greater than 85%, an increase in pressure will decrease desulfurization. When operating at a 650 F and a gas rate of 1000 ft³/bbl, an increase in pressure will increase desulfurization when the hydrogen concentration is less than approximately 55%; and will decrease desulfurization if the hydrogen concentration is greater than 55%. These values of 85% and 55% may vary with different diluents in the treat-gas. The curve in Figure 16 at 1000 ft³/bbl of 60% H₂ - 40% CH₄ is above the 55% value, and therefore an increase in pressure decreases desulfurization.

The results of the pressure effects may be explained with the following assumptions: The desulfurization reaction is the result of the

sulfur-bearing compound reacting with hydrogen atoms which are formed by activated adsorption of hydrogen molecules on the catalyst. If the oil molecules are preferentially adsorbed, there would be less surface for the adsorption of the hydrogen molecules. The result of a decrease in desulfurization with increasing oil partial pressure could be explained this way. The decrease in desulfurization with an increase in pressure may also be due to more liquid being present at the higher pressures, and thus a higher density of liquid oil molecules per catalyst site. However, the adverse effect of pressure on desulfurization at constant contact time has been noted in similar catalytic desulfurization reactions where the process was a vapor phase operation (6, 7). The results indicate that at a constant pressure an increase in hydrogen partial pressure increases desulfurization, and this is probably due to the higher hydrogen concentrations preventing the oil molecules from being so readily adsorbed. If a diluent is present in the treat-gas, in this case methane, it will compete with the hydrogen for the catalyst sites and the amount of hydrogen adsorbed will be decreased. The effect of increasing total pressure will then increase desulfurization (if it is below the concentrations mentioned) since the increasing effect of the hydrogen partial pressure is more pronounced than the decreasing effect of the oil partial pressure (Table XII). It is not known whether the methane actually competes for the catalyst sites or merely "shields" the hydrogen from the catalyst.

The compositions of the four oils used and three samples of the desulfurized Aramco oil were determined by mass spectrometer analyses. The

aromatic fractions were separated from the saturate fractions by silica gel percolation. These analyses are tabulated in Tables XIII and XIV. Essentially no sulfur was present in the saturate fractions and where small amounts are indicated, they were neglected. The mass spectrometer could not analyze for thiophenes, and so, presumably, the sulfur not accounted for by benzothiophenes and dibenzothiophenes is in the form of thiophene and its homologues. For convenience, the BT and DBT will be referred to as aromatic sulfur in this paper, and the sulfur unaccounted for by the mass spectrometer analysis will be referred to as thiophenes.

Aromatic sulfur compounds are harder to remove than aliphatic sulfur compounds, and it was believed that the more aromatic the charge oil, and hence the more aromatic the sulfur compounds, the more difficult it would be to desulfurize. A 50-50 wt.% blend of MCO and RRD was desulfurized; the MCO is 78% aromatic and has 2.66 wt.% sulfur, while the RRD is only 30% aromatic and has 1.0 wt.% sulfur. The rate of desulfurization of the blend was expected to be less than the rate of the RRD and greater than the rate of the MCO; instead, the reverse was noted. When the compositions of the oils were examined it was seen that 82% of the sulfur in the MCO was aromatic sulfur, BT, whereas 68% of the sulfur in the RRD was aromatic but was a combination of BT and DBT. It appears then that the aromaticity of the sulfur compounds in the oil is not so much the criteria for desulfurization, but more explicitly the type of aromatic sulfur compounds involved. Since BT is common to both the MCO and RRD but DBT is only present in the RRD, the decrease in the rate of desulfurization of the blend

is evidently due to the presence of the DBT. A small amount of DBT is apparently quite effective in retarding the desulfurization rate because the DBT in the aromatic fraction of the blend was approximately 0.72 wt. %.

When comparing the estimated rate constants of the four oils in Table X or the $\log \frac{A}{A-x}$ values at constant contact time in Table XV, it is seen that the oils desulfurize with increasing difficulty as follows: MCO, RRD, Aramco, Husky. The DBT content of the oils increases in this same order (Table XIII) with the exception of the Aramco, which has 0.6% more DBT than the Husky. However, the Husky oil is only slightly more difficult to desulfurize than the Aramco and is probably due to the large quantity of BT (10.4 wt. %) associated with the DBT (6.8 wt. %), (the Aramco has 7.8 wt. % BT and 7.4 wt. % DBT).

Although the presence of all the various sulfur compounds in the charge oil effects the rate of desulfurization, the presence of DBT seems to particularly limit the reaction rate and the degree of desulfurization can be approximated from the DBT content of the oil. The correlation between desulfurization and DBT content was made by comparing the degree of desulfurization at constant contact time for the five charge oils at 600, 650, and 700 F, 200 psig, and 1000 ft³/bbl of hydrogen (the data for the MCO was compared only at 600 and 650 F). The contact times (1/V.R.) of 1.0 and 3.0 (hr)(100g) were compared for each oil; the data are tabulated in Table XV. Figure 17 shows that the degree of desulfurization can be estimated from the DBT content of oils boiling in the 400-700 F range. Correlation is quite good at the lower conversions, but some scattering

is evidenced at the higher conversions.

The effects of the sulfur compounds in the oil are tabulated below in Table XVI. When 49% of the initial sulfur had been removed (Aramco-5, Sample 27), 79% of the thiophenes, 60% of the BT, and 35% of the DBT had been removed. When 89% of the initial sulfur had been removed (Aramco-5, Sample 12), all the thiophenes, 91% of the BT, and 63% of the DBT had been removed. These values indicate that the thiophenes are more reactive than the BT, more reactive than the DBT.

TABLE XVI

COMPARISON OF SULFUR REMOVAL FROM ARAMCO LIGHT WAXY DISTILLATE

Run	Aramco-9	Aramco-5	Aramco-5
Sample	26	12	27
Wt.% S in Sample	0.09	0.145	0.65
% of Init. S (1.27 wt.%) Removed	93	89	49
<u>Aromatic Fraction (Wt.%)</u>			
Benzothiophenes	0.6*	0.7	3.1
Dibenzothiophenes	1.3	2.7	4.8
Sulfur	0.36	0.61	2.01
% S as BT	37	23	36
% S as DBT	63	77	43
% S as "Thiophenes"	0	0	21
% BT removed	92	91	60
% DBT removed	82	63	35
% "Thiophenes" removed	100	100	79

*This value uncertain

It is not known exactly why these compounds react at different rates; it may be due to steric hindrance or to an increase in specific adsorbability with increasing molecular weight of the sulfur-bearing compounds.

At 700 F the plot of the $\log \frac{A}{A-x}$ vs. contact time (Figure 8) for the MCO is nearly a straight line, which is approaching a first-order reaction.

This could be expected since 82% of the sulfur is present as BT, the remainder being thiophenes. At this temperature the thiophenes are converted very readily and the desulfurization would be that of one compound. The desulfurization of BT has been shown to be a pseudo-first-order reaction (5, 8).

SUMMARY

If the effects of the variables involved in the catalytic hydro-desulfurization of petroleum fractions boiling in the range of 400 to 700 F are established, an analysis of the types and quantities of the sulfur compounds in the fraction will permit the prediction of the conversion to be expected at a given set of operating conditions. Thiophene and its homologues are more easily removed than benzothiophenes which are more easily removed than dibenzothiophenes. The presence of dibenzothiophenes, even in small quantities, appears to particularly retard the rate of desulfurization of oils in the 400 to 700 F range. With the knowledge of the dibenzothiophene content in the charge oil, it is possible to estimate the degree of desulfurization.

The effects of the operating variables may be summarized as follows:

1. As contact time increases, conversion increases but the rate of reaction decreases.
2. An increase in temperature will increase the rate of reaction; however, this increasing effect of temperature is less pronounced at higher conversions. Temperatures of 700 F and lower are compatible with prolonged catalyst activity.
3. At a constant pressure an increase in hydrogen partial pressure increases desulfurization, but the ratio of hydrogen partial pressure to oil partial pressure appears more important than the actual value of hydrogen partial

pressure.

4. If the effects of pressure are compared at constant space velocity, an increase in pressure will increase desulfurization. However, if desulfurization is compared at apparent constant contact time, pressure may or may not have an increasing effect on desulfurization. The decrease in desulfurization with an increase in pressure at constant contact time is attributed to an increase in oil partial pressure; however, the presence of a diluent in the treat-gas may reduce the hydrogen partial pressure to a point where increasing the total pressure is more beneficial from the standpoint of increasing hydrogen partial pressure than is the adverse effect of increasing oil partial pressure, and an increase in pressure then increases desulfurization.

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APPENDIX

Table I	Charge Oil Inspection Data	page 32
Table II	Tabulated Data From Runs Husky-1, -2, -3	33
Table III	Tabulated Data From Run Husky-5 With 50 Grams of Catalyst	34
Table IV	Tabulated Data From Run Aramco-2	35
Table V	Tabulated Data From Run Aramco-9	36
Table VI	Tabulated Data From Runs Aramco-1, -3, -5, -10, -12, -13, -14	37
Table VII	Tabulated Data From Run Carter-1	40
Table VIII	Tabulated Data From Run Carter-2	41
Table IX	Tabulated Data From Run Carter-3	42
Table X	Tabulated Data For Arrhenius-Type Plots	43
Table XI	Tabulated Data From Runs Aramco-4, -11, -15	44
Table XII	Tabulated Data For Pressure and Hydrogen Concentration Study	45
Table XIII	Mass Spectrometer Analyses of Charge Oils	46
Table XIV	Mass Spectrometer Analyses of Desulfurized Aramco Light Waxy Distillate	47
Table XV	Tabulated Data For Dibenzothiophene Correlation.	48
Figure 1	Schematic Flow Diagram of the De- sulfurization System	49
Figure 2	Effect of Temperature on Percentage Vaporized of Charge Oils	50
Figure 3	Effect of Temperature, Pressure, and Treat-gas Rate on Percentage Vaporized for Aramco Charge Oil.	51

APPENDIX (Cont.)

Figure 4	Testing for Diffusion	page 52
Figure 5	Catalyst Deactivation	53
Figure 6	Effect of Contact Time on Desulfurization of Husky No. 350 Burner Oil	54
Figure 7	Effect of Contact Time on Desulfurization of Carter Railroad Diesel Oil	55
Figure 8	Effect of Contact Time on Desulfurization of Carter Medium Cycle Oil and of 50 Wt.% Blend Railroad Diesel and Medium Cycle Oil	56
Figure 9	Effect of Contact Time on Desulfurization of Aramco Light Waxy Distillate	57
Figure 10	Effect of Contact Time, Pressure, Hydrogen Concentration, and Treat-gas Rate on De- sulfurization of Aramco Light Waxy Distillate at 650 F	58
Figure 11	Effect of Contact Time, Pressure, and Treat- gas Rate on Desulfurization of Aramco Light Waxy Distillate at 700 F.	59
Figure 12	Effect of Temperature on Desulfurization	60
Figure 13	Effect of Hydrogen Concentration on Desulfurization	61
Figure 14	Effect of Hydrogen Partial Pressure on Desulfurization	62
Figure 15	Effect of Hydrogen & Oil Partial Pressures on Desulfurization	63
Figure 16	Effect of Reactor Pressure on Desulfurization	64
Figure 17	Effect of Oil Partial Pressure on Desulfurization	65
Figure 18	Effect of Dibenzothiophene on Desulfurization	66

TABLE I

CHARGE OIL INSPECTION DATA

Charge Oil	Aramco Light Waxy Distillate	Husky No.350 Burner Oil	Carter RR Diesel Oil	Carter Medium Cycle Oil	50Wt% Carter RR Diesel 50Wt% Carter MCO
Gravity °A.P.I.	34.6	30.6	34.4	16.7	25
Vol. % Distilled at °F					
I.B.P.	301	458	406	468	392
5	401	526	453	488	471
10	446	547	473	494	483
20	499	568	485	499	499
30	530	582	497	502	509
40	555	591	511	506	518
50	578	601	527	508	525
60	602	611	542	512	534
70	629	623	556	516	542
80	656	638	570	521	551
90	687	663	585	528	567
95	689	---	596	535	573
E.P.	693	674	620	546	579
Wt. % Sulfur	1.27	2.11	1.0	2.66	1.76

TABLE II
 TABULATED DATA FROM RUNS HUSKY-1, -2, -3
 HUSKY-1 (200 psig)

Sample No.	Temp °F	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate (hr-100g/ft}^3\text{)}}$
2	651	50	2.0	1000	0.53	3.98	0.60	3.85
6	650	82	1.01	990	0.30	7.03	0.847	7.85
10	648	90	3.92	1020	0.97	2.18	0.338	1.9
14	649	107	1.48	1010	0.52	4.06	0.608	5.1
18	650	111	7.97	1000	1.32	1.6	0.203	0.95
22	649	128	1.99	1005	0.63	3.35	0.524	3.85
26	650	138	3.29	915	0.78	2.71	0.432	2.7
30	652	170	1.17	1065	0.35	6.03	0.78	7.4
34	650	183	2.48	1010	0.68	3.11	0.492	3.1
38	650	200	1.95	1020	0.60	3.52	0.546	3.8

HUSKY-2 (200 psig)								
4	605	228	1.96	1000	1.15	1.84	0.263	4.3
8	603	260	1.00	1000	0.83	2.54	0.405	8.4
13	600	270	3.00	1000	1.31	1.61	0.207	2.85
18	601	280	3.95	1010	1.46	1.45	0.161	2.1
22	601	289	7.94	1010	1.74	1.21	0.083	1.05
26	648	305	1.98	1010	0.58	3.64	0.561	3.8

HUSKY-3 (200 psig)								
3	700	317	1.95	1020	0.215	9.81	0.992	3.45
7	702	345	1.03	970	0.124	17.0	1.231	7.05
11	702	360	2.95	1020	0.38	5.55	0.745	2.3
15	646	376	2.02	990	0.653	3.23	0.51	3.9
19	702	386	3.93	1020	0.477	4.42	0.646	1.75
23	702	391	7.87	1020	0.863	2.45	0.39	0.85

TABLE III

TABULATED DATA FROM RUN HUSKY-5 WITH 50 GRAMS OF CATALYST

(200 psig)

Sample No.	Temp. °F	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
2	650	67	1.99	1000	0.585	3.6	0.556	3.85
6	650	131	1.00	1000	0.320	6.6	0.820	7.75
10	651	147	3.04	990	0.887	2.38	0.376	2.6
14	650	165	4.00	1000	1.08	1.95	0.290	1.95
18	651	197	1.99	1000	0.640	3.30	0.518	3.85
22	651	227	1.50	1000	0.490	4.31	0.634	5.15
25	650	235	7.90	1010	1.39	1.52	0.182	0.95
29	650	240	15.44	1040	1.65	1.28	0.107	0.44
33	648	272	2.02	990	0.673	3.14	0.497	3.8

TABLE IV
TABULATED DATA FROM RUN ARAMCO-2

(200 psig)

Sample No.	Temp. OF	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	% Conversion x/A (100)
4	650	43	1.98	1000	0.31	75.6
5	650	47	1.95	1010	0.30	76.3
8	851	59	2.02	990	0.27	78.8
9	853	63	2.0	1000	0.31	75.6
12	844	75	1.93	1020	0.40	68.5
15	851	87	2.0	1000	0.44	65.3
19	846	103	2.0	1000	0.51	59.8
25	847	127	1.98	1000	0.58	54.3
30	847	147	2.0	1000	0.59	53.6
34	847	163	1.91	1020	0.60	52.7
37	846	175	1.93	1020	0.62	51.2

TABLE V

TABULATED DATA FROM RUN ARAMCO-9

(200 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
4	650	65	2.6	970	0.217	5.85	0.767	3.5
6	750	72	9.80	1020	0.396	3.21	0.508	0.55
8	747	77	7.93	1010	0.359	3.54	0.549	0.7
13	752	87	4.06	990	0.204	6.22	0.794	1.4
17	650	105	1.99	1000	0.277	4.58	0.661	3.55
21	752	121	1.98	1010	0.096	13.23	1.122	2.85
26	750	139	1.51	990	0.093	13.65	1.135	3.85
30	648	155	1.99	1000	0.360	3.53	0.548	3.55

TABLE VI
TABULATED DATA FROM RUNS ARAMCO-1, -3, -5, -10, -12, -13, -14
ARAMCO-1 (400 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
4	700	36	2.08	970	0.07	18.2	1.259	6.8
8	702	60	0.92	1040	0.02	63.7	1.802	13.0
11	702	66	3.8	920	0.12	10.6	1.025	3.45
18	696	91	0.90	1050	0.02	63.7	1.802	13.0
24	700	99	5.1	990	0.18	7.1	0.849	2.75
29	698	109	3.7	950	0.14	9.1	0.958	3.45
33	700	127	2.06	970	0.06	21.2	1.326	6.8

ARAMCO-3 (200 psig)

8	650	50	2.02	990	0.309	4.10	0.612	3.6
13	650	70	1.02	980	0.158	8.03	0.92	7.15
17	651	86	1.5	1000	0.234	5.42	0.743	4.7
23	650	98	4.05	980	0.502	2.53	0.403	1.8
31	703	124	2.05	490	0.156	8.13	0.91	5.95
37	702	137	4.03	990	0.253	5.02	0.701	1.6
45	700	145	7.9	1010	0.454	2.80	0.448	0.75
50	650	165	2.01	1000	0.277	4.58	0.661	3.55

ARAMCO-5 (200 psig)

1	650	29	2.02	990	0.295			
2	648	37	2.02	990	0.273			
3	650	45	2.02	990	0.274			
4	646	53	2.03	990	0.276			
5	648	61	2.01	1000	0.280			
6	651	69	2.03	990	0.272			
7	648	77	1.99	1000	0.249	5.1	0.707	3.55
12	650	97	0.99	1000	0.146	8.69	0.938	7.05

TABLE VI (Cont.)
 TABULATED DATA FROM RUNS ARAMCO-1, -3, -5, -10, -12, -13, -14
 ARAMCO-5 (200 psig) Cont.

Sample No.	Temp. F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	A (A-x) A=init S	Log ₁₀ A/(A-x)	Vapor rate (hr-100g/ft. ³)
17	648	107	4.08	980	0.483	2.63	0.42	1.8
21	648	123	1.52	990	0.219	5.79	0.762	4.75
27	651	129	7.97	1000	0.645	1.97	0.294	0.9
31	650	145	2.0	1000	0.238	5.33	0.727	3.55
36	655	155	3.01	1000	0.370	3.43	0.535	2.35
43	651	185	1.24	1010	0.152	8.35	0.921	5.5
47	655	201	2.5	1000	0.295	4.31	0.634	2.85
51	650	217	2.05	970	0.231	5.5	0.74	3.6
56	650	227	4.04	990	0.476	2.67	0.426	1.63
61	648	246	1.45	1030	0.202	6.28	0.798	4.6
65	650	262	3.0	1000	0.365	3.48	0.541	2.35
68	651	274	2.58	970	0.30	4.23	0.626	2.9
72	648	290	2.05	980	0.275	4.62	0.664	3.6
76	655	304	8.02	1000	0.667	1.9	0.279	0.9
80	650	328	1.22	1020	0.156	8.14	0.91	5.5
84	651	354	1.0	1000	0.10	12.7	1.104	7.05
88	651	370	2.01	1000	0.253	5.02	0.70	3.55

ARAMCO-10 (*400 psig, **200 psig)

5**	651	63	1.99	1000	0.318	3.99	.601	3.55
9*	650	84	1.05	960	0.122	10.40	1.017	14.8
13*	642	92	3.95	1010	0.346	3.67	.565	3.65
17*	655	109	1.48	1010	0.137	9.27	.967	9.85
21*	648	114	8.08	990	0.61	2.08	.318	1.85
25**	646	130	2.0	1000	0.325	3.91	.592	3.55
32*	658	144	1.95	1010	0.188	6.76	.830	7.3
37*	648	167	2.49	1000	0.243	5.22	.718	5.9
41**	650	183	1.95	1010	0.263	4.83	.684	3.53

TABLE VI (Cont.)
TABULATED DATA FROM RUNS ARAMCO-1, -3, -5, -10, -12, -13, -14
ARAMCO-12 (200 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
2	651	334	1.99	1000	0.26	4.88	0.688	3.55
7	597	354	2.0	1000	0.622	2.04	0.310	4.05
12	600	380	0.97	1010	0.420	3.02	0.480	7.8
16	601	396	1.49	1000	0.520	2.44	0.387	5.3
20	590	406	3.97	1000	0.851	1.49	0.173	2.0
24	653	422	2.03	990	0.253	5.02	0.70	3.6
30	601	427	8.06	990	0.98	1.30	0.114	1.0
34	597	436	2.96	1010	0.76	1.67	0.222	2.6
38	603	448	2.48	1000	0.646	1.97	0.296	3.25
42	648	461	1.98	1010	0.280	4.54	0.657	3.5

ARAMCO-13 (200 psig)

6	698	467	7.98	1000	0.495	2.56	0.408	0.75
10	703	475	4.0	1000	0.266	4.77	0.678	1.6
14	703	484	3.1	970	0.19	6.68	0.825	2.15
17	650	495	2.08	960	0.32	3.97	0.599	3.65
22	700	514	1.98	1010	0.126	10.06	1.003	3.15
26	700	526	2.48	1000	0.171	7.42	0.871	2.55
29	700	545	1.05	950	0.0258	49.2	1.692	6.65
33	653	559	1.93	1020	0.28	4.54	0.657	3.5

ARAMCO-14 (200 psig)

8	650	69	2.08	960	0.31	4.1	0.613	3.65
12	596	101	0.51	910	0.25	5.08	0.706	16.2
17	599	121	1.02	980	0.37	3.43	0.535	8.1
22	649	137	1.0	1000	0.14	9.06	0.957	7.05
26	650	153	1.95	1030	0.27	4.7	0.672	3.5
30	702	168	1.99	1000	0.12	10.6	1.025	3.2
35	702	178	4.11	970	0.28	4.53	0.656	1.65

TABLE VII

TABULATED DATA FROM RUN CARTER-1

(200 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
4	648	62	1.97	1015	0.114	8.77	0.944	3.35
8	651	92	1.02	980	0.042	23.80	1.377	6.8
12	649	112	1.53	980	0.0727	13.75	1.138	4.55
16	651	120	3.92	1020	0.2135	4.68	0.670	1.65
20	653	125	7.85	1020	0.385	2.60	0.415	0.8
24	651	141	1.96	1020	0.101	9.91	0.997	3.35
28	603	157	1.98	1010	0.278	3.59	0.555	3.8
32	603	189	0.965	1035	0.144	6.94	0.842	7.45
36	600	197	3.94	1015	0.452	2.23	0.348	1.9
41	599	203	7.85	1020	0.629	1.90	0.279	0.9
45	649	219	1.96	1020	0.081	12.34	1.091	3.35
49	702	233	1.96	1020	0.0348	28.70	1.458	2.9
53	697	253	1.49	1010	0.0261	38.30	1.583	3.9
57	700	263	3.92	1020	0.098	10.204	1.009	1.45
63	700	269	7.86	1020	0.213	4.69	0.672	0.7
68	651	285	1.99	1005	0.116	8.62	0.936	3.4

TABLE VIII

TABULATED DATA FROM RUN CARTER-2

(200 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log 10 $A/(A-x)$	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
6	648	309	1.97	1020	0.085	31.3	1.496	3.25
10	650	337	1.03	970	0.021	126.7	2.103	6.65
14	648	357	1.41	1060	0.040	65.5	1.817	4.3
19	642	367	3.98	1000	0.311	8.56	0.933	1.6
25	646	373	7.87	1020	0.820	3.25	0.512	0.8
29	648	389	2.00	1000	0.126	21.1	1.324	3.3
33	601	405	2.03	990	0.289	9.20	0.964	3.9
37	597	433	1.06	950	0.124	21.4	1.331	7.9
41	599	442	3.98	1000	0.860	3.09	0.490	1.9
46	603	448	8.07	990	1.21	2.20	0.343	0.97
50	646	464	2.00	1000	0.103	25.8	1.412	3.3
54	700	480	2.02	990	0.027	98.5	1.994	2.7
58	700	488	4.03	990	0.301	8.84	0.947	1.35
63	709	493	8.02	1000	0.410	6.48	0.812	0.67
64	709	496	8.05	990	0.510	5.22	0.718	0.68
68	700	524	1.02	980	0.014	190.0	2.279	5.45
72	651	540	2.03	990	0.205	13.0	1.140	3.9

TABLE IX

TABULATED DATA FROM RUN CARTER-3

(200 psig)

Sample No.	Temp. °F.	Total Hrs.	Space Velocity (g/hr/g)	Ft ³ /bbl Treat Gas (100% H ₂)	Avg. Wt. % S in Prod. (A-x)	$\frac{A}{(A-x)}$ A=init S	Log ₁₀ A/(A-x)	$\frac{1}{\text{Vapor rate}}$ (hr-100g/ft ³)
5	650	131	1.98	1010	0.142	12.4	1.094	3.3
9	649	159	1.06	940	0.022	80.2	1.905	6.75
13	650	175	1.50	1000	0.062	28.5	1.439	4.45
19	647	188	4.01	1000	0.303	5.82	0.765	1.65
25	645	193	7.82	1020	0.585	3.02	0.480	0.8
29	650	210	2.02	990	0.152	11.6	1.065	3.35
33	701	226	1.99	1000	0.034	49.0	1.690	2.85
41	700	263	4.04	990	0.145	12.2	1.086	1.45
45	647	279	1.99	1000	0.158	11.2	1.049	3.35

TABLE X
TABULATED DATA FOR ARRHENIUS-TYPE PLOTS

K_1	$\log_{10} K_1$	K_3	$\log_{10} K_3$	Temp. °F	$^{\circ}R^{-1} \times 10^4$
Aramco Light Waxy Distillate					
0.095	-1.002	0.07	-1.154	600	9.44
0.34	-0.468	0.135	-0.87	650	9.01
0.67	-0.174	0.215	-0.667	700	8.63
Husky No. 350 Burner Oil					
0.09	-1.045	0.052	-1.284	600	9.44
0.22	-0.657	0.108	-0.966	650	9.01
0.65	-0.187	0.155	-0.809	700	8.63
Carter Railroad Diesel Oil					
0.26	-0.585	0.108	-0.966	600	9.44
0.90	-0.045	0.16	-0.795	650	9.01
1.54	0.188	0.218	-0.661	700	8.63
Carter Medium Cycle Oil					
0.40	-0.398	0.18	-0.744	600	9.44
1.30	0.114	0.26	-0.552	650	9.01
1.85	0.268	0.53	-0.275	700	8.63

TABLE XI
TABULATED DATA FROM RUNS ARAMCO-4, -11, -15
ARAMCO-4 (650°F)

Sample No.	Space Velocity (g/hr/g)	Press. (psig)	Ft ³ /bbl Treat Gas	Treat Gas Comp. %H ₂ -%CH ₄	Avg. Wt. % S in Prod (A-x)	A (A-x) A-init S	Log ₁₀ A/(A-x)	1 Vapor rate (hr-100g/ft ³)
5	2.22	200	910	100-0	0.335	3.78	0.578	3.7
10	1.98	"	1010	60-40	0.504	2.52	0.402	3.6
14	1.99	"	2000	60-40	0.50	2.52	0.402	1.85
34	1.96	"	1020	30-70	0.774	1.64	0.216	3.52
38	1.97	"	2030	30-70	0.746	1.70	0.23	1.87
42	1.96	"	1020	100-0	0.226	5.62	0.749	3.5
18	2.04	400	970	60-40	0.38	3.35	0.525	7.45
22	2.03	"	1970	60-40	0.296	4.29	0.632	3.9
26	2.0	"	1000	30-70	0.582	2.18	0.338	7.35
30	2.04	"	1960	30-70	0.564	2.29	0.36	3.9

ARAMCO-11 (650°F)

4	2.06	400	970	60-40	0.43	2.95	0.47	7.4
10	0.97	"	1010	60-40	0.22	5.77	0.761	14.65
14	4.11	"	970	60-40	0.565	2.25	0.352	3.7
18	1.45	"	1020	60-40	0.269	4.72	0.674	9.8
22	1.98	200	1000	100-0	0.207	6.13	0.787	3.55
28	7.87	400	1010	60-40	0.778	1.63	0.212	1.8
32	3.08	"	980	60-40	0.477	2.68	0.428	4.95
36	2.45	"	1010	60-40	0.426	2.98	0.474	5.85
40	1.97	200	1010	100-0	0.25	5.08	0.706	3.5

ARAMCO-15 (650°F)

4	1.96	200	1020	100-0	0.276	4.6	0.663	3.5
8	1.97	"	2030	"	0.226	5.62	0.75	1.85
12	2.01	400	1990	"	0.162	7.84	0.894	3.8
16	1.98	"	1010	"	0.202	6.3	0.799	7.3
20	1.96	100	1020	"	0.426	2.98	0.475	1.75
24	1.95	200	1025	"	0.276	4.6	0.663	3.5

TABLE XII
TABULATED DATA FOR PRESSURE AND HYDROGEN CONCENTRATION STUDY
All Data at 650°F, Contact Time (1/V.R.) = $\frac{2 \text{ hr}(100\text{g})}{\text{ft}^3}$

Space Velocity	Treat-gas Rate ft ³ /bbl	Treat-gas Comp. %H ₂ -%CH ₄	Ft ³ /hr Oil Vapor	Ft ³ /bbl Treat-gas	Total press. psia	ppH ₂ (psia)	ppOil (psia)	ppCH ₄ (psia)	ppH ₂ ppOil	Log ₁₀ A/(A-x)
1.75	1000	100-0	0.115	0.383	115	89	26	--	3.42	0.54
3.53	"	100-0	0.084	0.413	215	179	36	--	4.97	0.49
3.53	"	60-40	"	"	"	108	"	71	3.0	0.25
"	"	30-70	"	"	"	54	"	125	1.5	0.14
1.85	2000	100-0	0.063	0.433	"	188	27	--	6.95	0.77
"	"	60-40	"	"	"	113	"	75	4.2	0.44
"	"	30-70	"	"	"	56	"	132	2.07	0.25
7.35	1000	100-0	0.054	0.445	415	370	45	--	8.2	0.36
"	"	60-40	"	"	"	222	"	148	4.93	0.23
"	"	30-70	"	"	"	111	"	259	2.46	0.21
3.75	2000	100-0	0.044	0.455	"	378	37	--	10.2	0.64
"	"	60-40	"	"	"	227	"	151	6.14	0.64
"	"	30-70	"	"	"	114	"	264	3.1	0.39

700°F, Contact Time (1/V.R.) = $\frac{2 \text{ hr}(100\text{g})}{\text{ft}^3}$

3.2	1000	100-0	0.11	0.39	215	168	47	--	3.58	0.78
5.8	500	"	0.137	0.354	215	155	60	--	2.58	0.38
6.65	1000	"	0.073	0.42	415	354	61	--	5.8	0.73

TABLE XIII
MASS SPECTROMETER ANALYSES OF CHARGE OILS

SATURATE FRACTIONS

Sample		Carter R.R. <u>Diesel</u>	Carter Med. <u>Cycle Oil</u>	Husky #350 <u>Burner Oil</u>	Aramco Light <u>Waxy Distillate</u>
Wt.% of Total Sample		70.4	21.9	56	67
Paraffins	Wt.%	43.9	58.9	40.0	68
Non-cond. Naphthenes	"	23.1	17.4	22.2	16
2 Ring Cond. Naph.	"	18.3	13.0	14.9	10
3 Ring	"	10.5	7.6	11.6	4
4 Ring	"	1.9	1.3	5.6	2
5 Ring	"	0.3	0.3	3.4	-
6 Ring	"	---	---	2.3	-
Mono Aromatics	"	2.0	1.5	---	-
Total Sulfur (Dietert)"		---	<.01	<.03	<.01

AROMATIC FRACTIONS

Wt.% of Total Sample		29.6	78.1	44	33
Alkyl Benzenes	Wt.%	24.4	6.0	17.2	29.8
Indans & Tetralins	"	20.6	6.9	14.0	17.1
Dinaphthene/Benzenes	"	11.3	4.1	13.5	7.6
Naphthalenes	"	15.7	47.6	12.6	13.3
Acenaphthenes	"	8.1	14.2	9.8	6.0
Acenaphthylenes	"	6.7	7.4	9.4	6.2
Phenanthrenes	"	3.2	1.4	6.3	4.8
Benzothiophenes	"	7.4	12.4	10.4	7.8
Dibenzothiophenes	"	2.6	---	6.8	7.4
Total Sulfur (Dietert)"		3.37	3.46	4.92	3.94
% of Total Sulfur Accounted for by M.S. analysis		68.4	82	76.3	81.7

TABLE XIV
MASS SPECTROMETER ANALYSES OF DESULFURIZED ARAMCO LIGHT WAXY DISTILLATES

SATURATE FRACTIONS

Run		Aramco-9	Aramco-5	Aramco-5
Sample		26	12	27
Wt.% of Total Sample		78	77	66
Paraffins	Wt. %	71	69	66
Non. Cond. Naph.	"	13	14	16
2 Ring Cond. Naph.	"	9+	10	10+
3 Ring " "	"	4	5	5
4 Ring " "	"	1+	1+	2
5 Ring " "	"	<1	<1	<1
Sulfur (In Saturate Fraction)		----- <0.005% -----		

AROMATIC FRACTIONS

Wt. % of Total Sample		22	23	34
Alkyl Benzenes	Wt. %	33.5	34.8	34.8
Indans/Tetralins	"	17.1	19.4	18.6
Dinaphthene/Benzenes	"	7.6	8.7	7.7
Naphthalenes	"	13.9	11.7	13.0
Acenaphthenes	"	10.4	8.9	6.7
Acenaphtylenes	"	9.3	8.4	6.9
Phenanthrenes	"	5.3	4.7	4.3
Benzothiophenes	"	0.6	0.7	3.1
Dibenzothiophenes	"	1.3	2.7	4.8
Total Sulfur (Dietert)		0.36	0.61	2.01
% Sulfur (Total) in Product		0.09	0.145	0.65
% of Total Sulfur Accounted for by M.S. analysis		100	100	82

TABLE XV
TABULATED DATA FOR DIBENZOTHIOPHENE CORRELATION

Charge Oil	Avg. M.W.	$\text{Log}_{10} \frac{A}{(A-x)}$ at $\frac{1}{V.R.} = 1.0$	$\text{Log}_{10} \frac{A}{(A-x)}$ at $\frac{1}{V.R.} = 3.0$	Wt.% Dibenzothiophene in Aromatic Fraction of Charge Oil
<u>600°F</u>				
MCO	183	0.33	0.77	0.0
RRD	208	0.21	0.48	2.6
Husky	250	0.08	0.22	6.8
Aramco	220	0.09	0.26	7.4
<u>650°F</u>				
MCO	183	0.64	1.34	0.0
50-50 Wt.%				
MCO-RRD	197	0.55	1.09	2.6
RRD	208	0.48	0.93	0.72
Husky	250	0.20	0.46	6.8
Aramco	220	0.29	0.63	7.4
<u>700°F</u>				
MCO	183	0.87	2.18	0.0
50-50 Wt.%				
MCO-RRD	197	0.76	1.74	2.6
RRD	208	0.82	1.43	0.72
Husky	250	0.45	0.9	6.8
Aramco	220	0.46	1.0	7.4

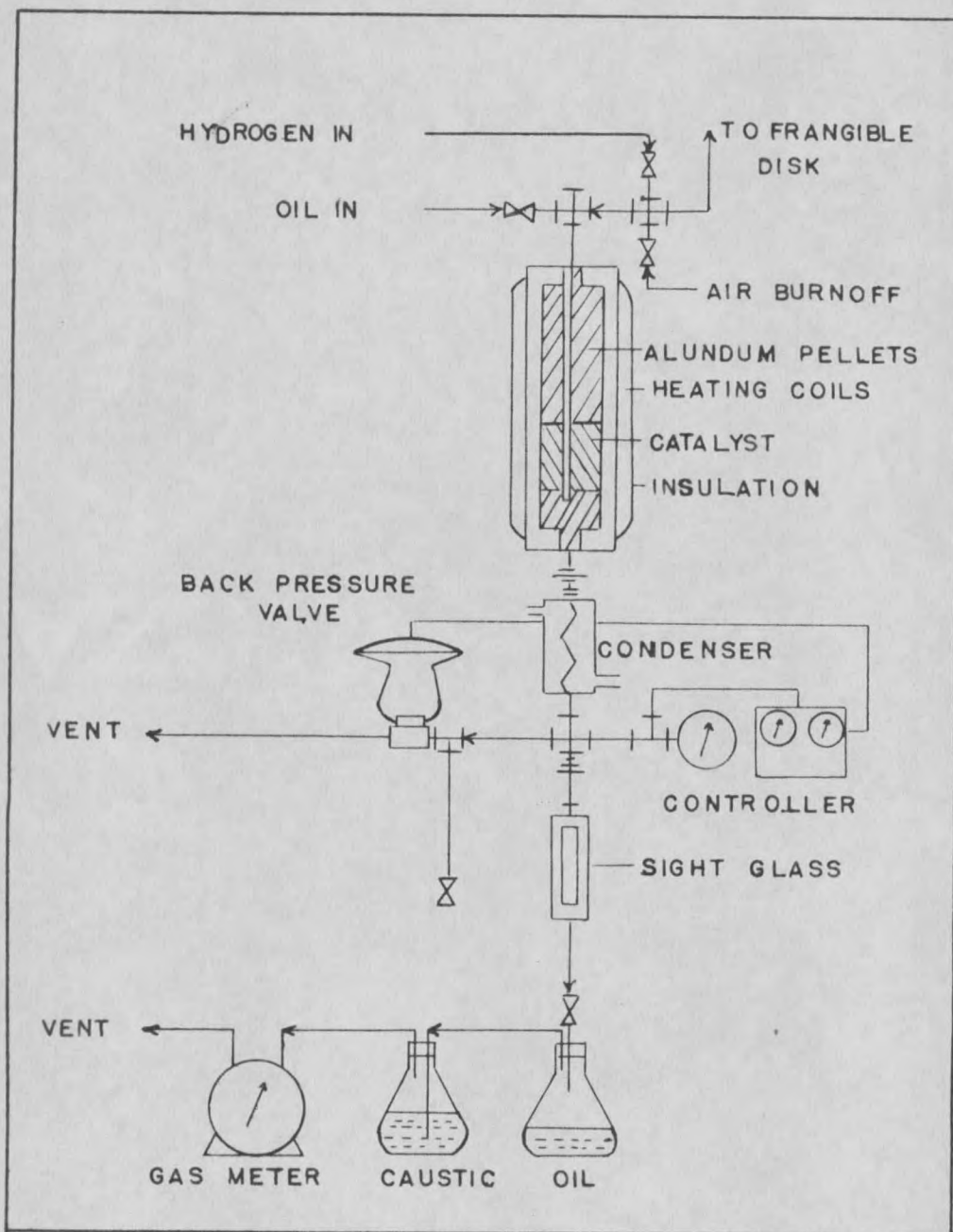


Figure 1. Schematic Flow Diagram of The Desulfurization System

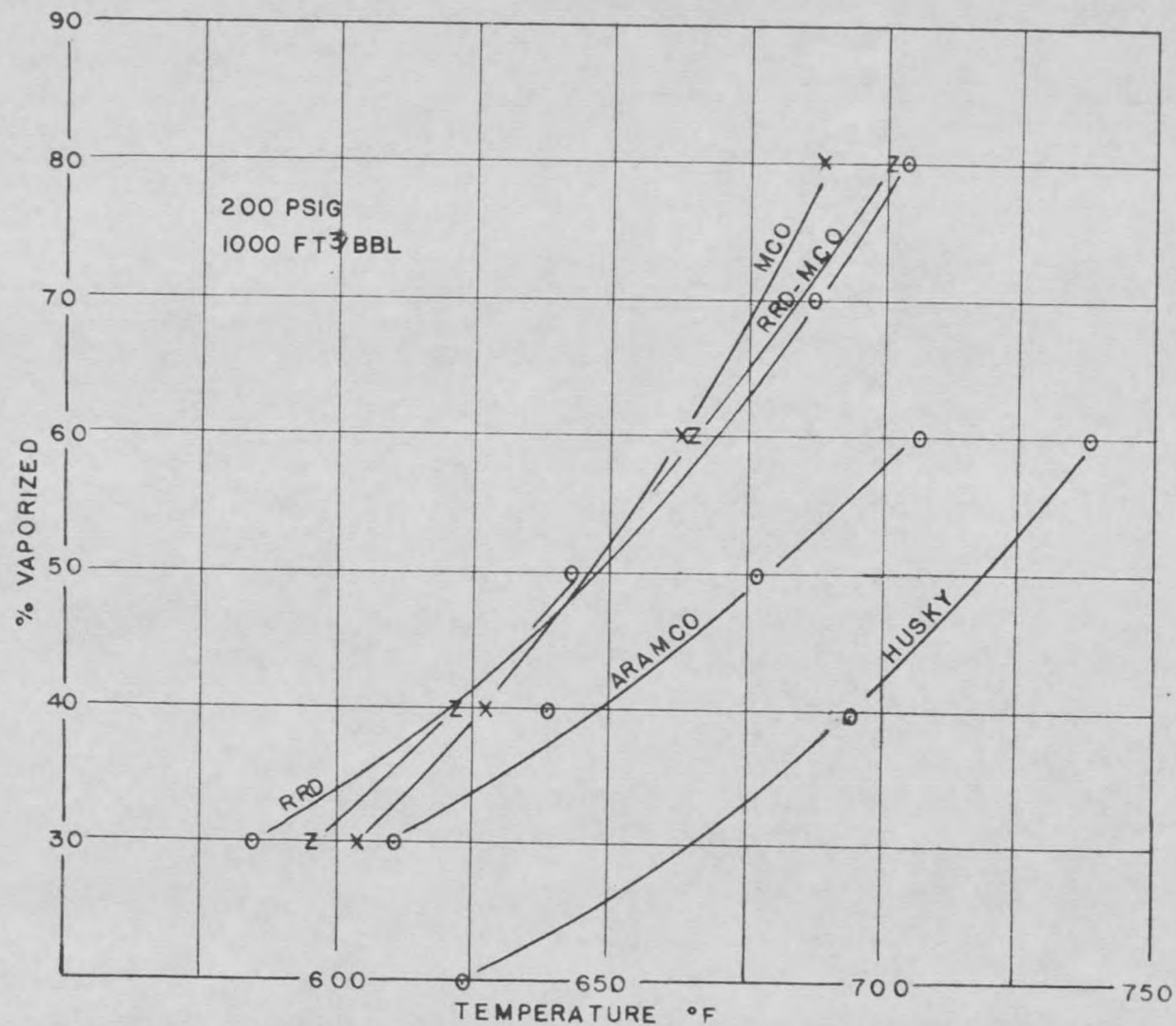


Figure 2. Effect of Temperature on Percentage Vaporized of Charge Oils

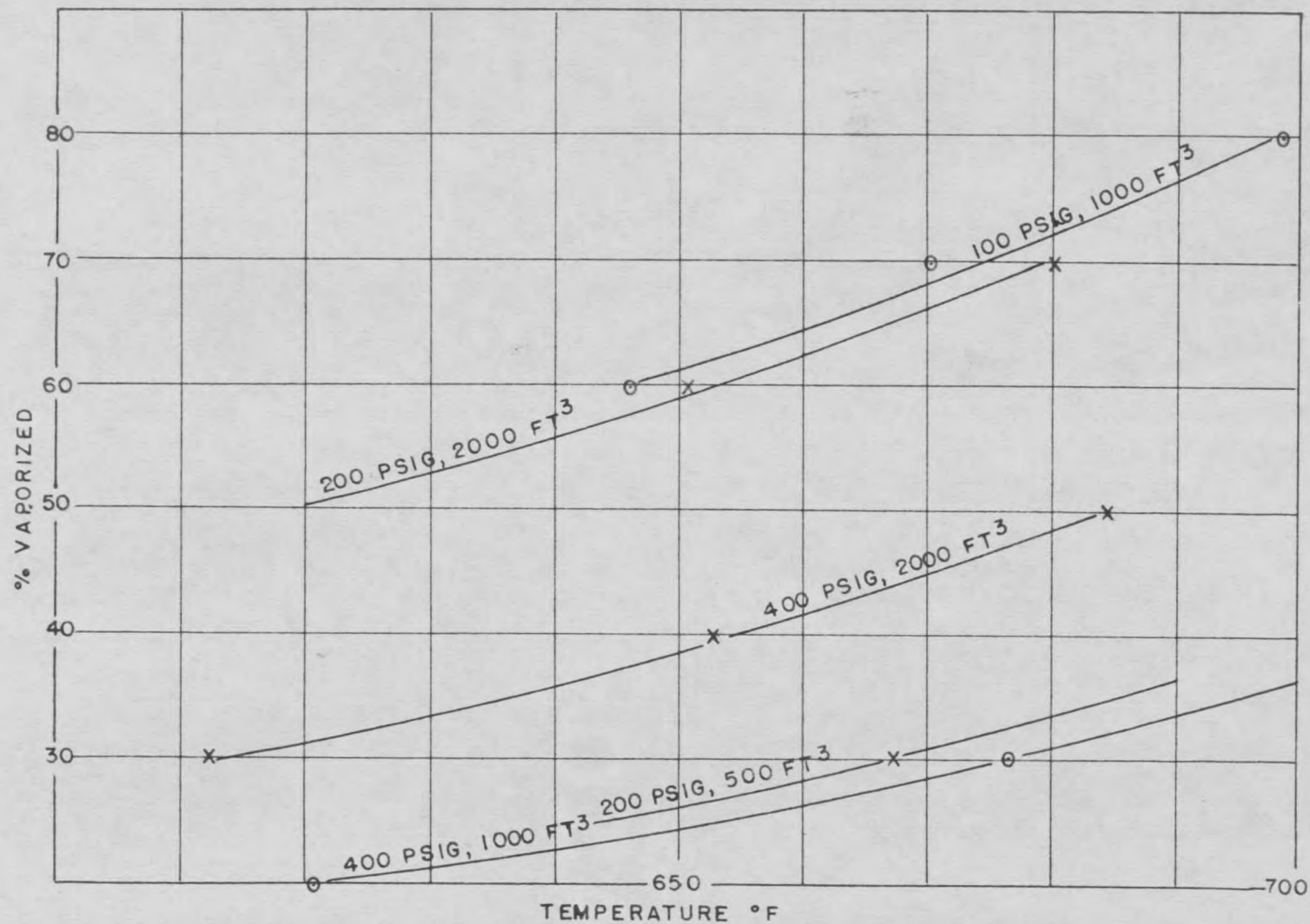


Figure 3. Effect of Temperature, Pressure, and Treat-gas Rate on Percentage Vaporized for Aramco Charge Oil.

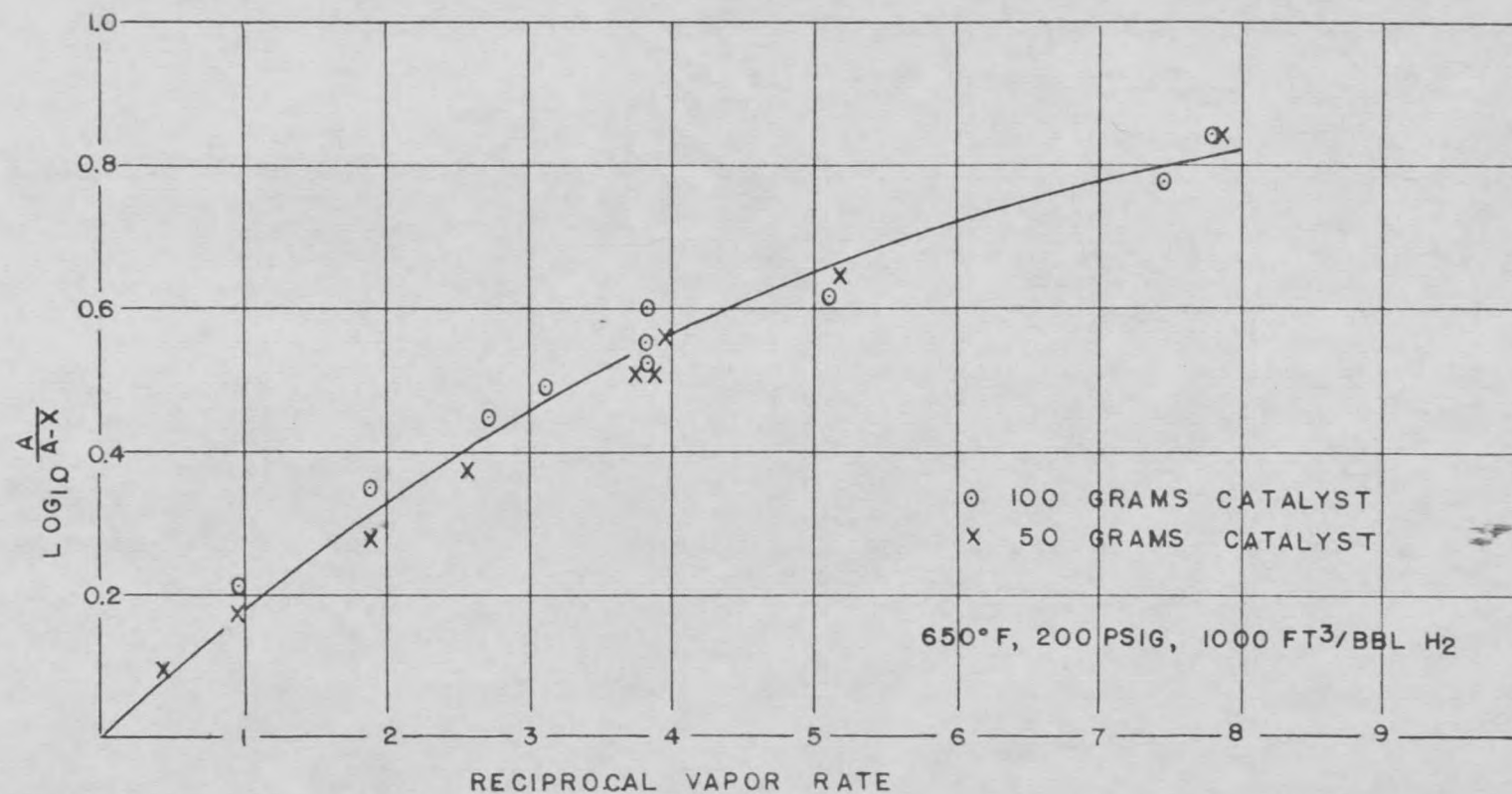


Figure 4. Testing for Diffusion.

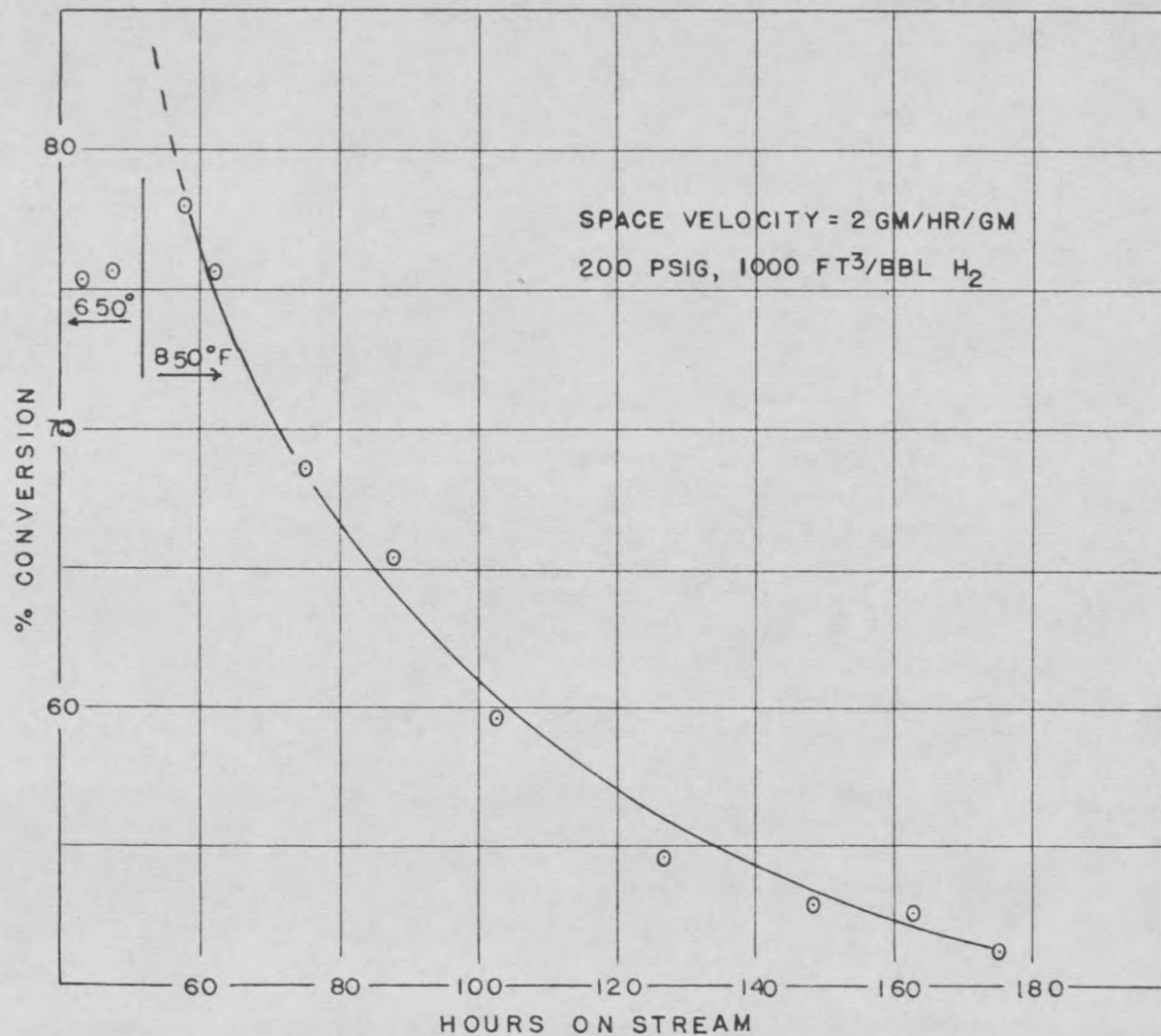


Figure 5. Catalyst Deactivation

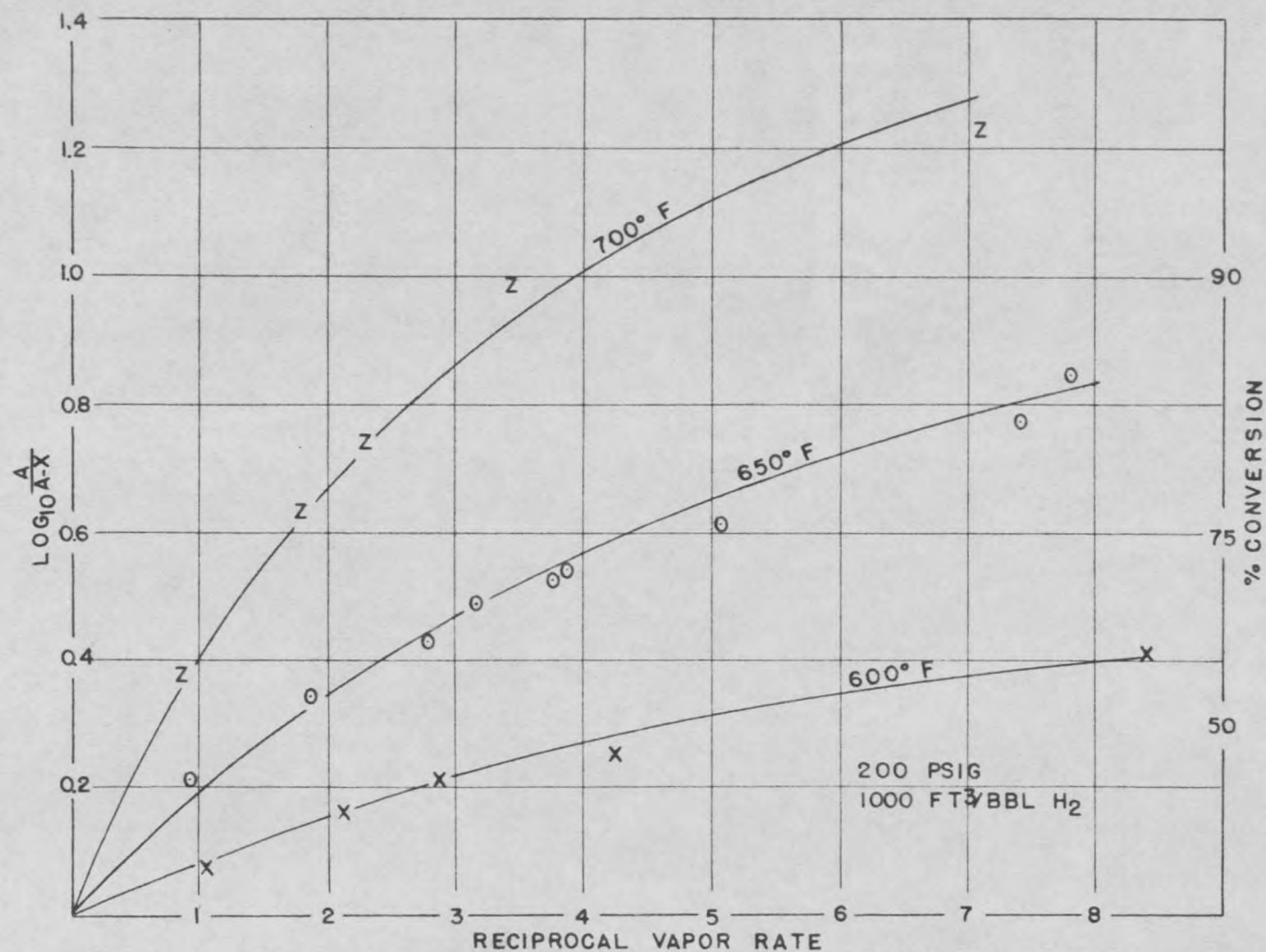


Figure 6. Effect of Contact Time on Desulfurization of Husky No. 350 Burner Oil

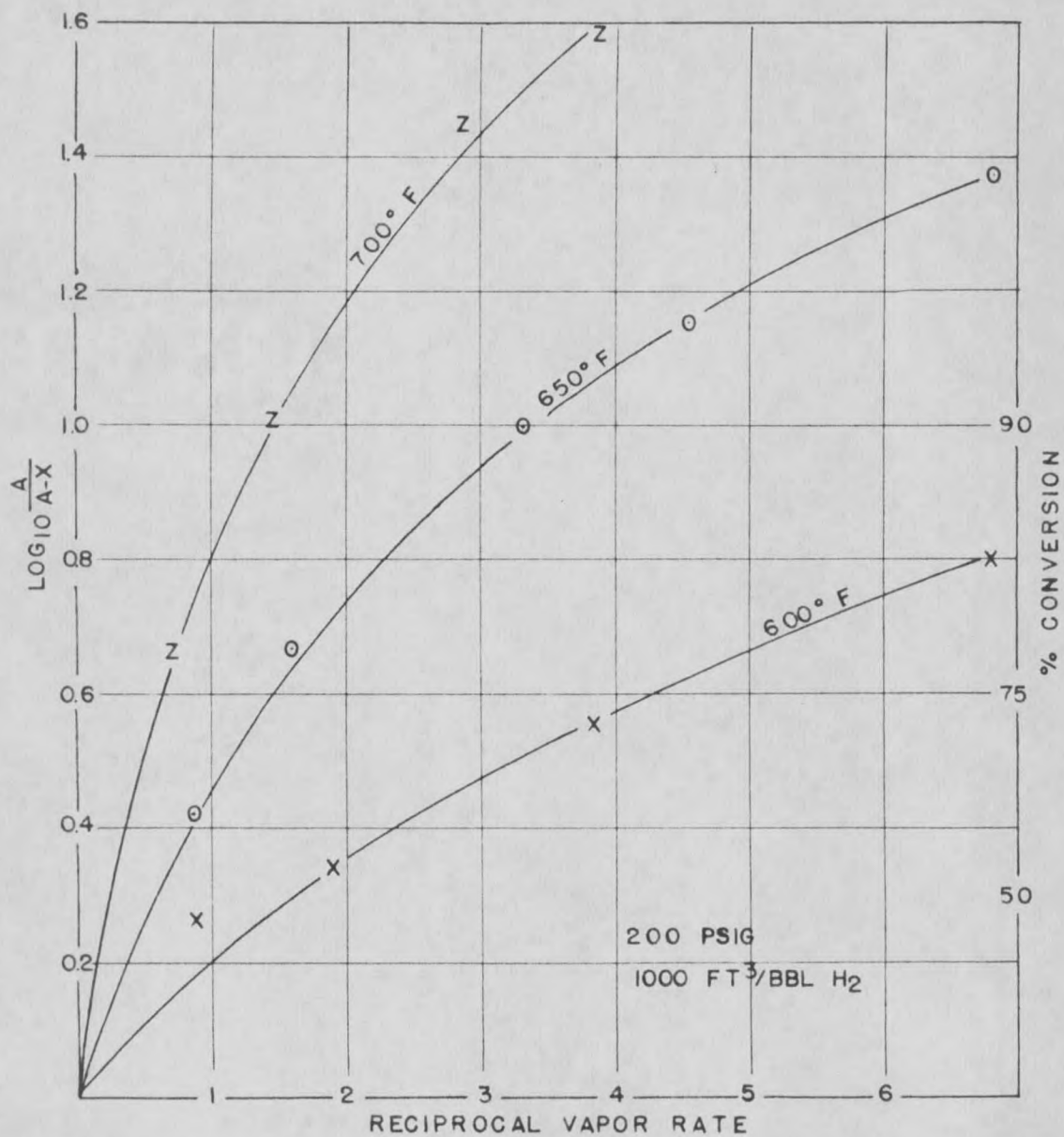


Figure 7. Effect of Contact Time on Desulfurization of Carter Railroad Diesel Oil.

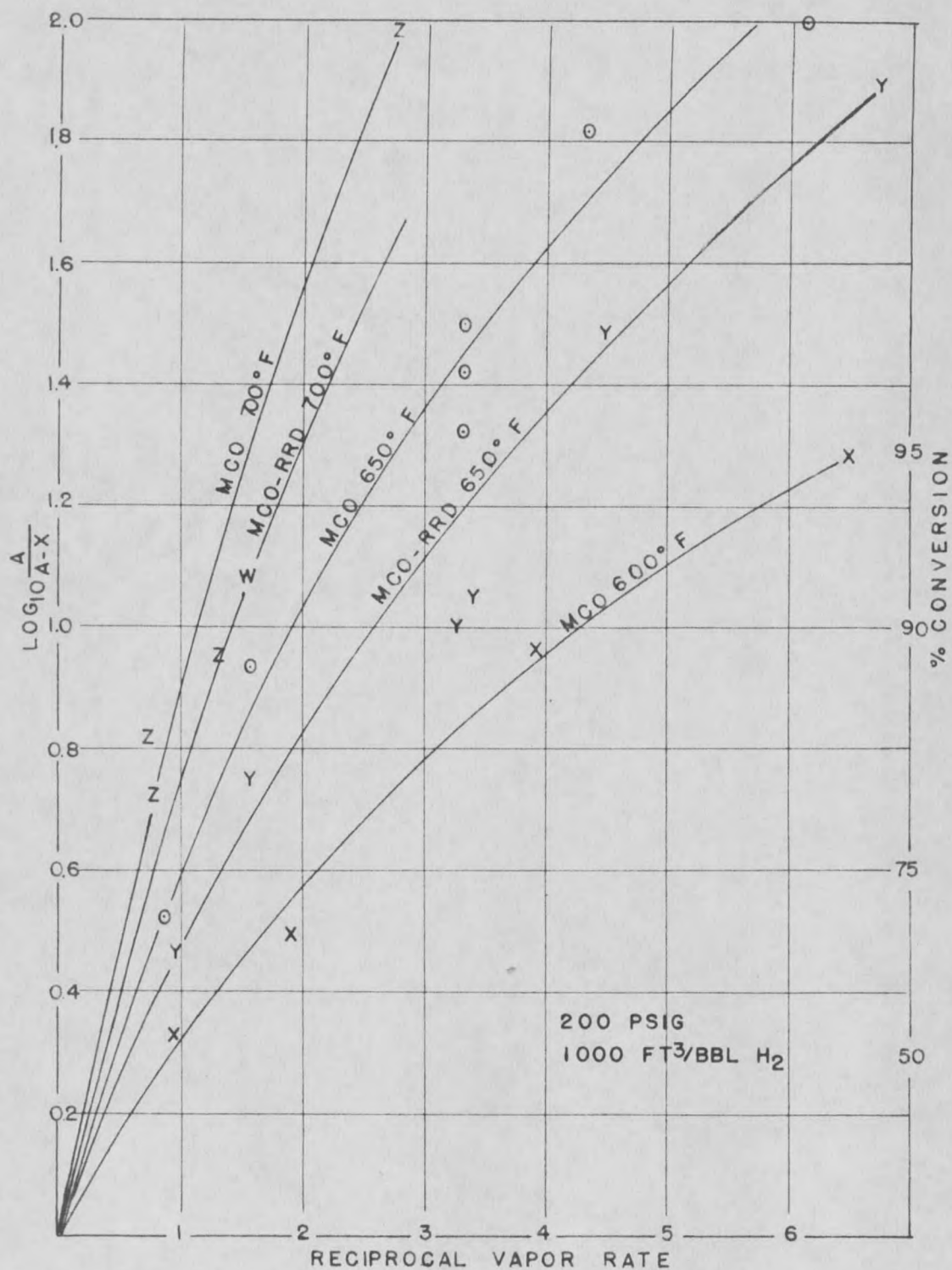


Figure 8. Effect of Contact Time on Desulfurization of Carter Medium Cycle Oil and of 50 Weight % Blend Railroad Diesel and Medium Cycle Oil.

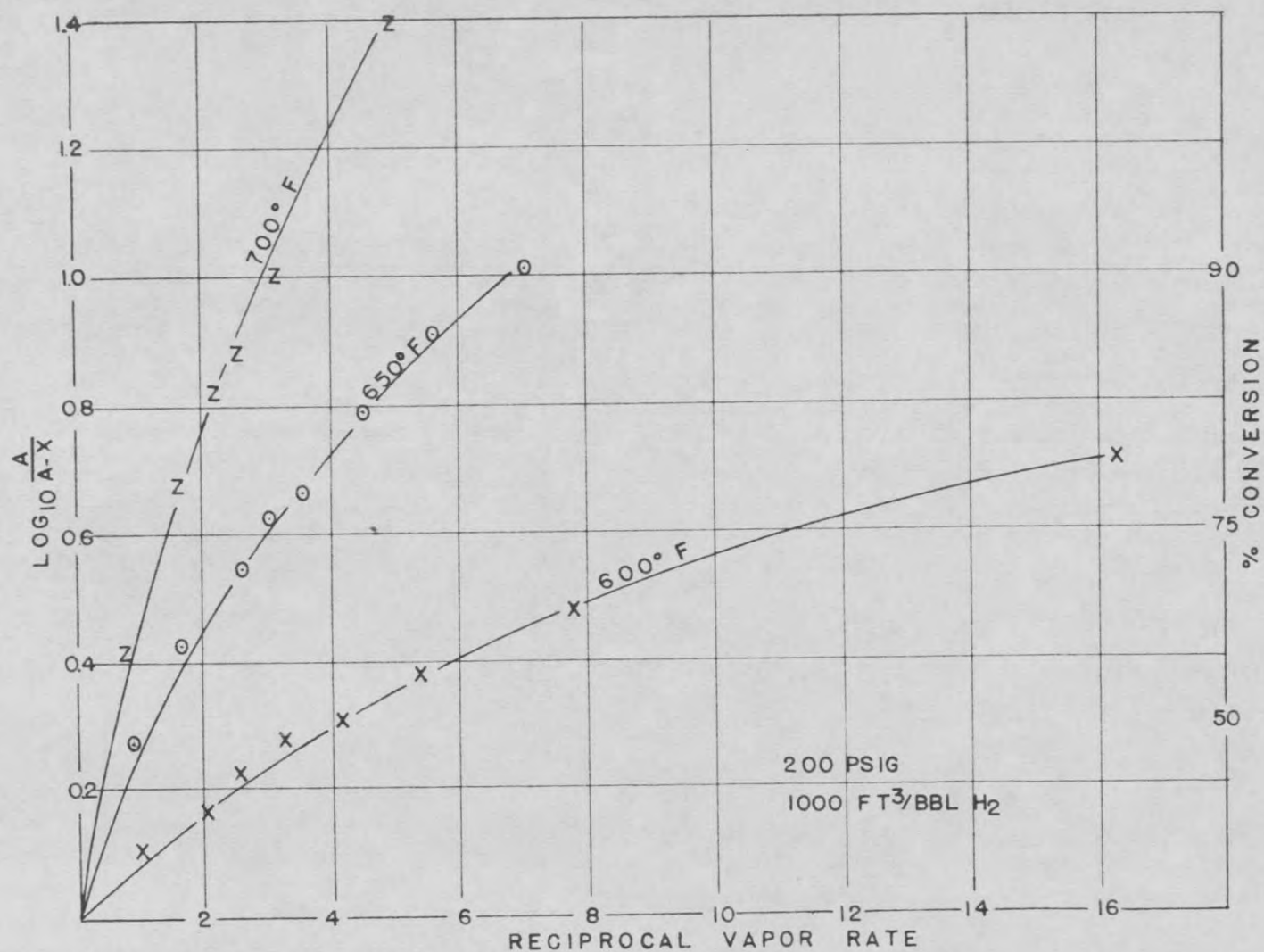


Figure 9. Effect of Contact Time on Desulfurization of Aranco Light Waxy Distillate.

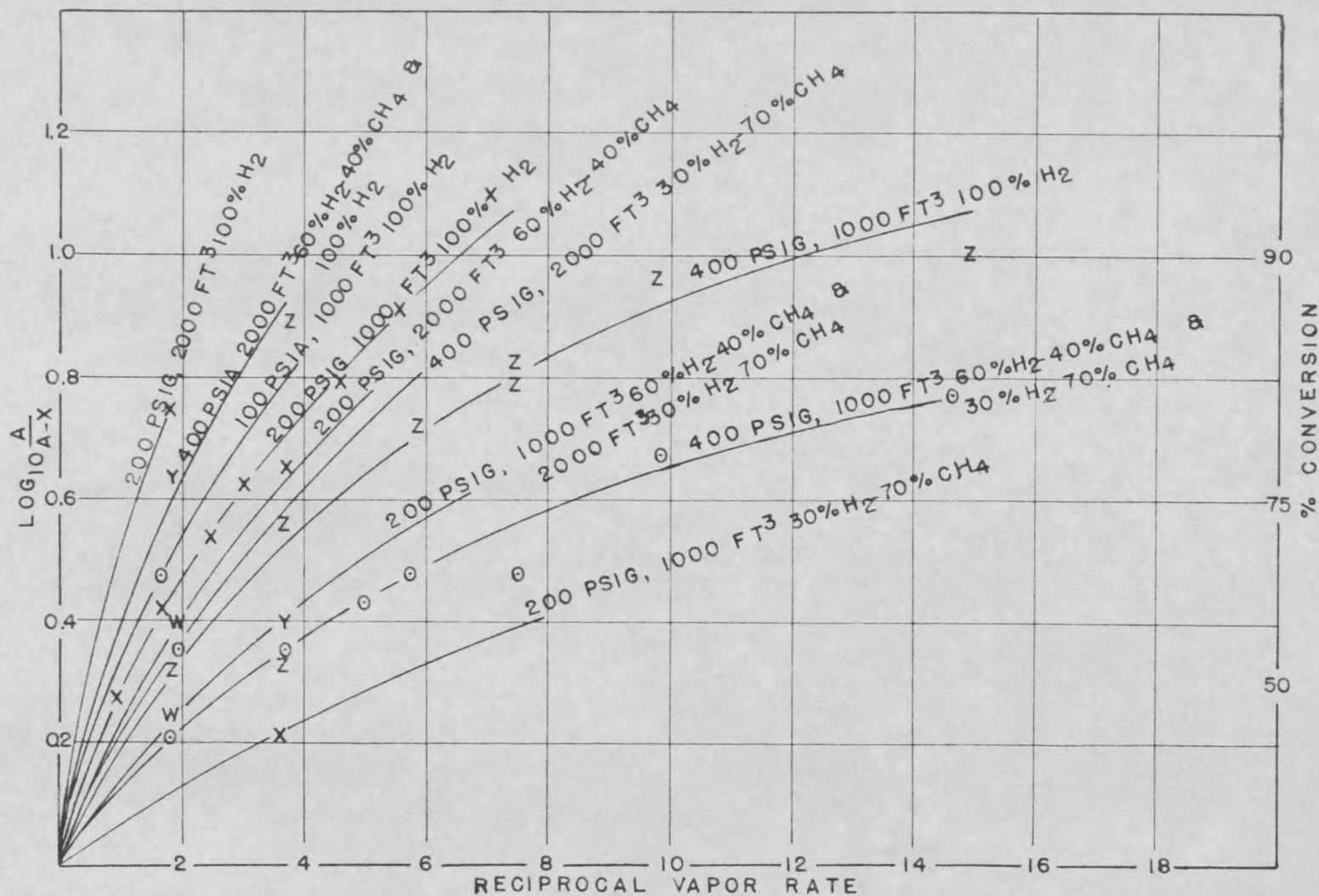


Figure 10. Effect of Contact Time, Pressure, Hydrogen Concentration, and Treat-gas Rate on Desulfurization of Aramco Light Waxy Distillate at 650 F.

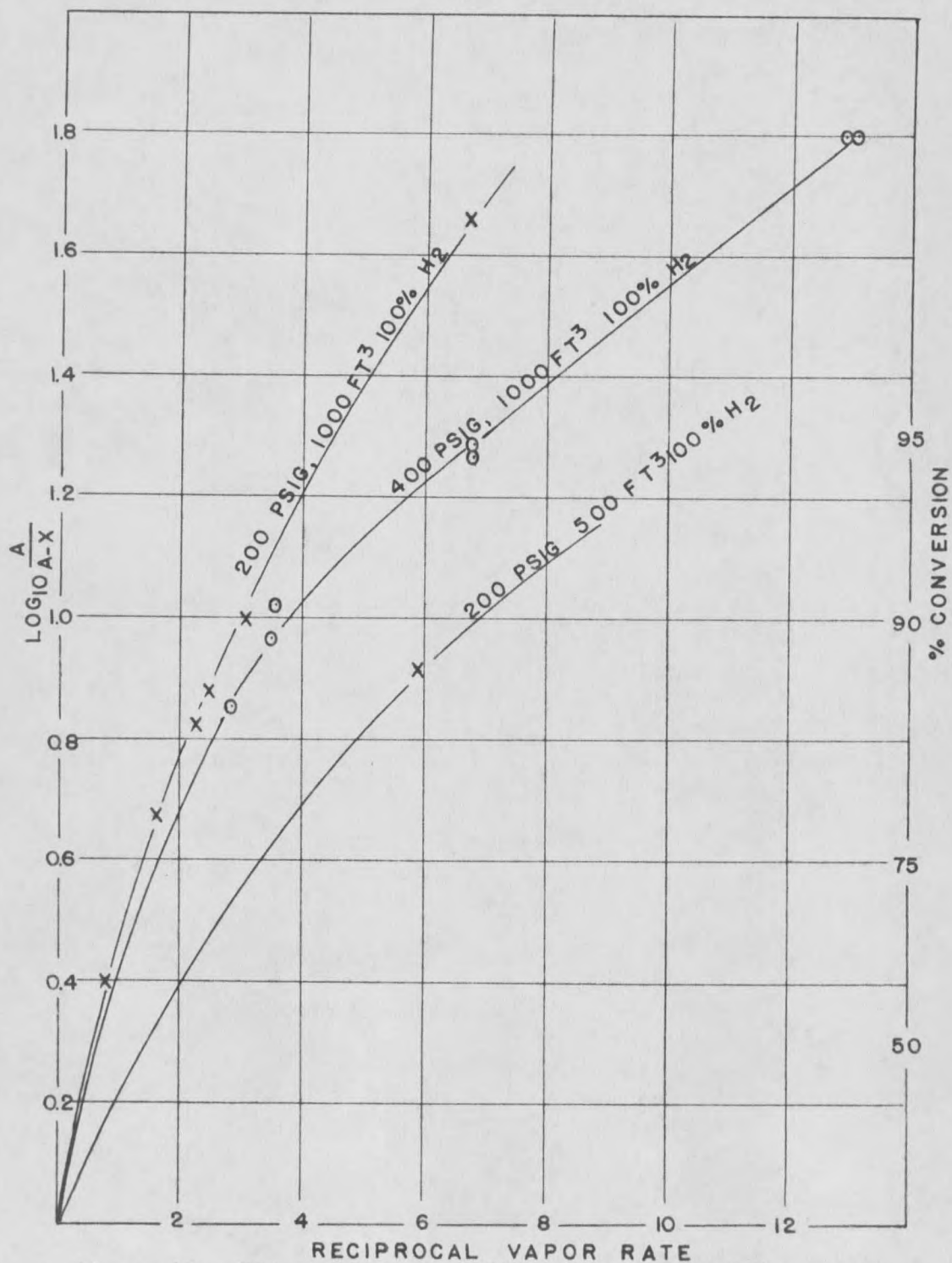


Figure 11. Effect of Contact Time, Pressure, and Treat-gas Rate on Desulfurization of Aramco Light Waxy Distillate at 700 F.

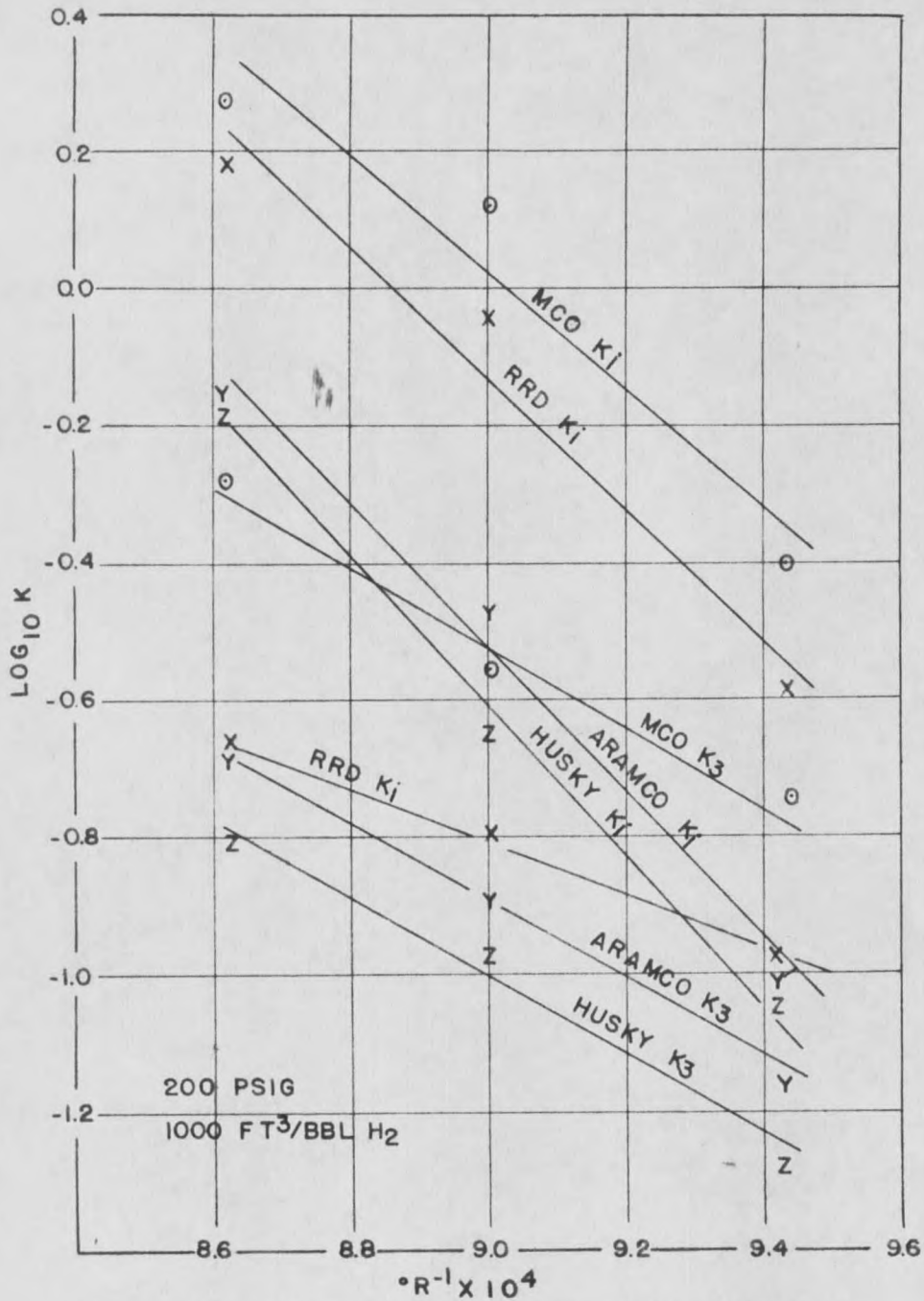
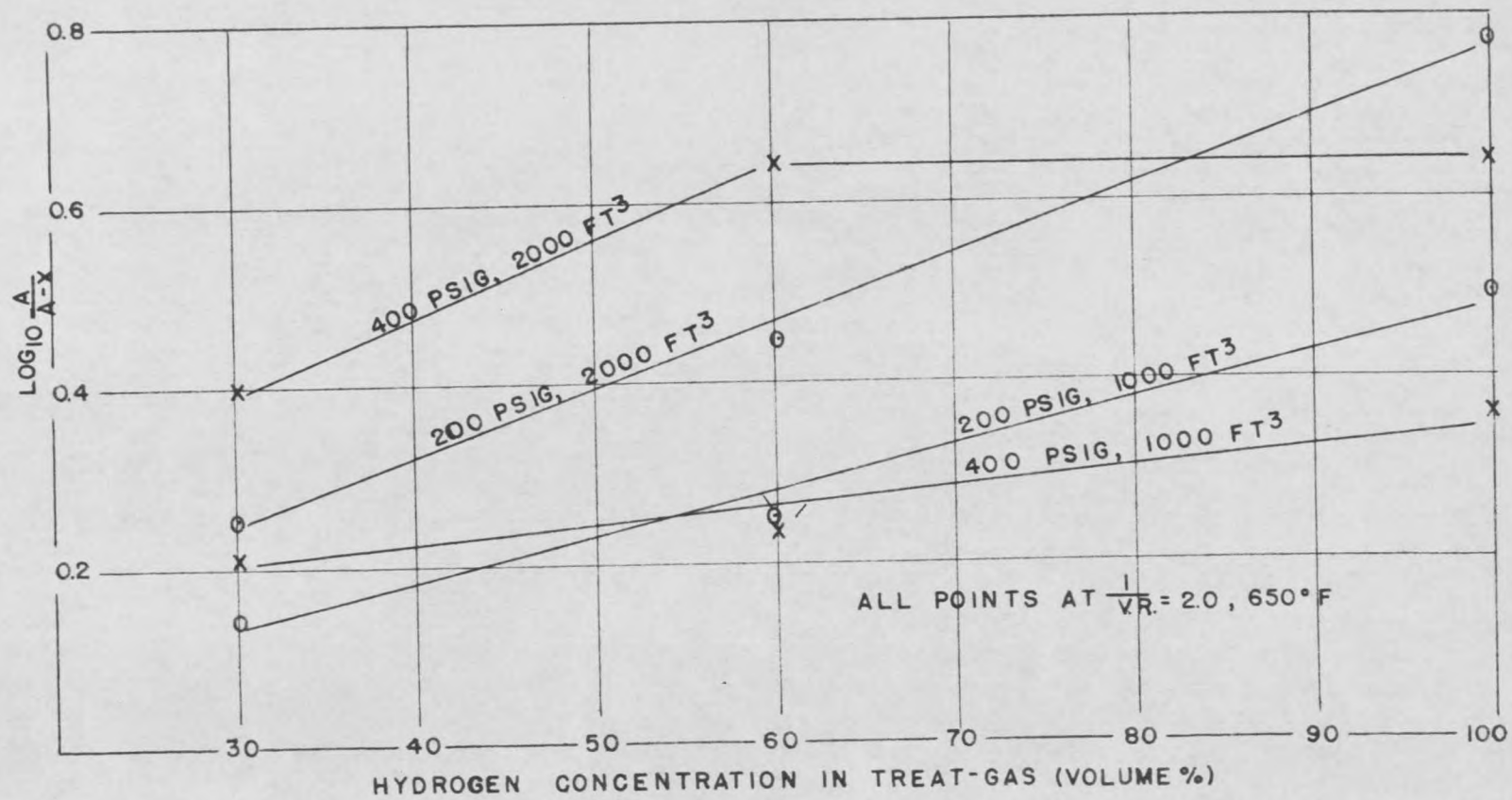


Figure 12. Effect of Temperature on Desulfurization.



- 19 -

Figure 13. Effect of Hydrogen Concentration on Desulfurization.

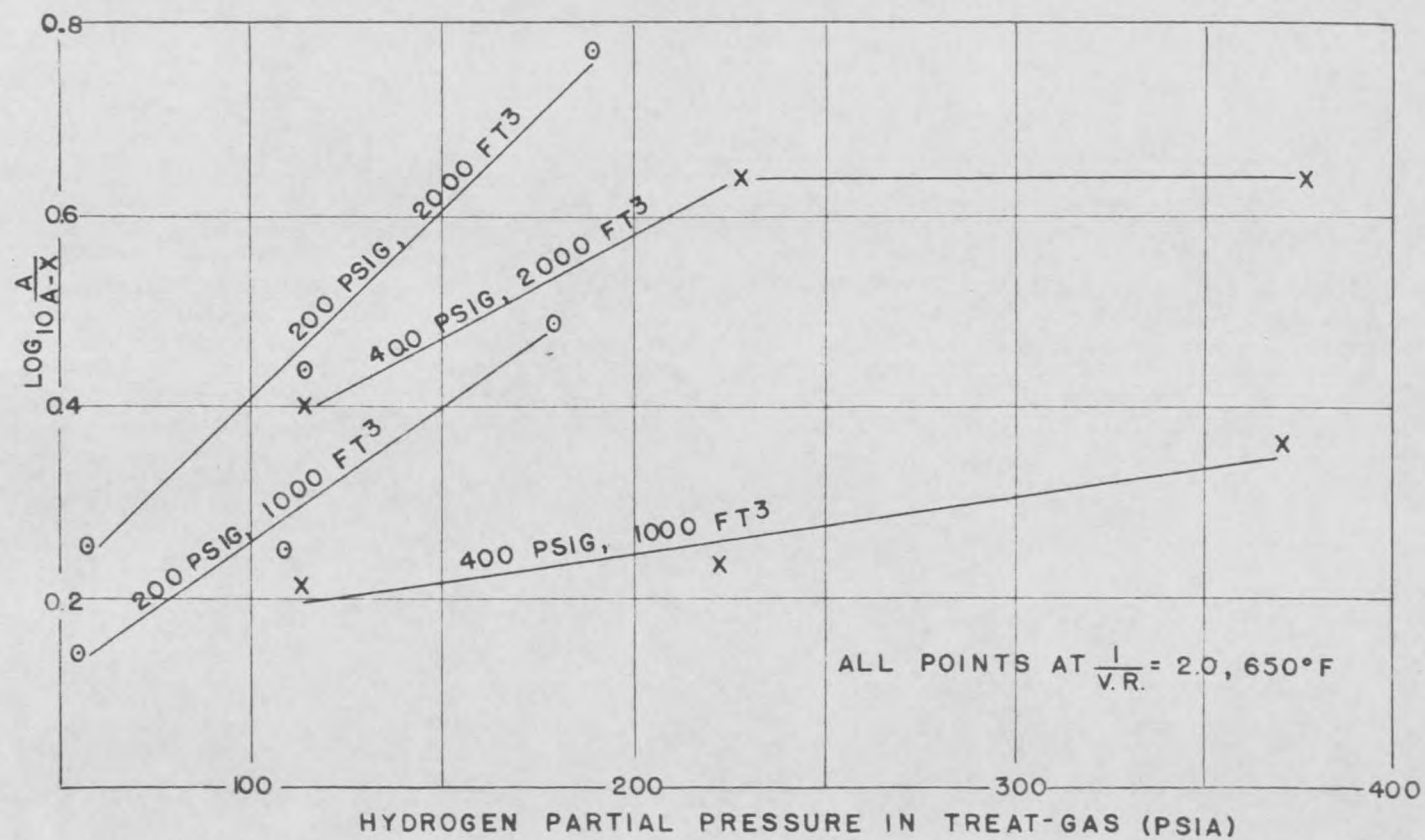


Figure 14. Effect of Hydrogen Partial Pressure on Desulfurization

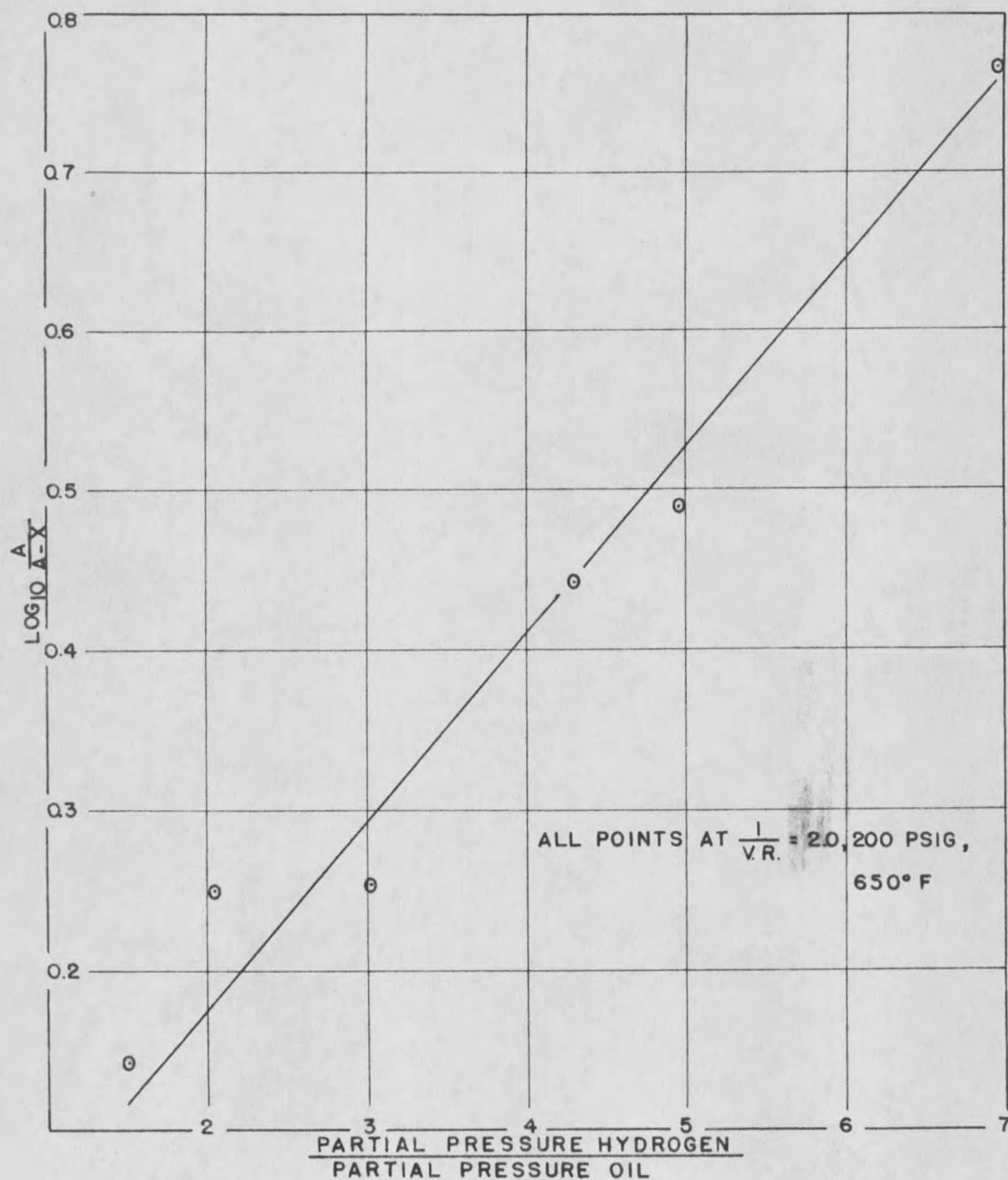


Figure 15. Effect of Hydrogen & Oil Partial Pressures on Desulfurization.

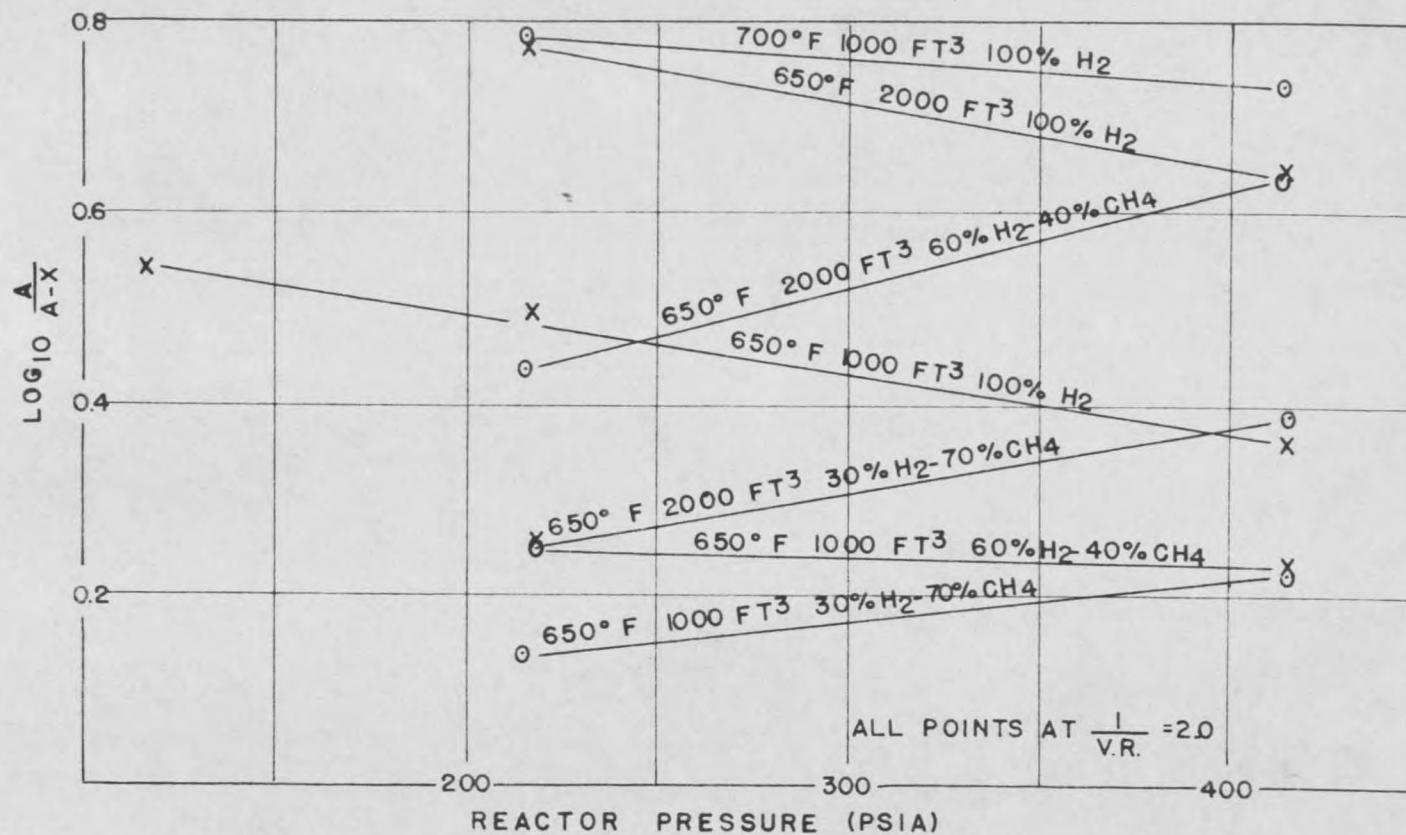


Figure 16. Effect of Reactor Pressure on Desulfurization.

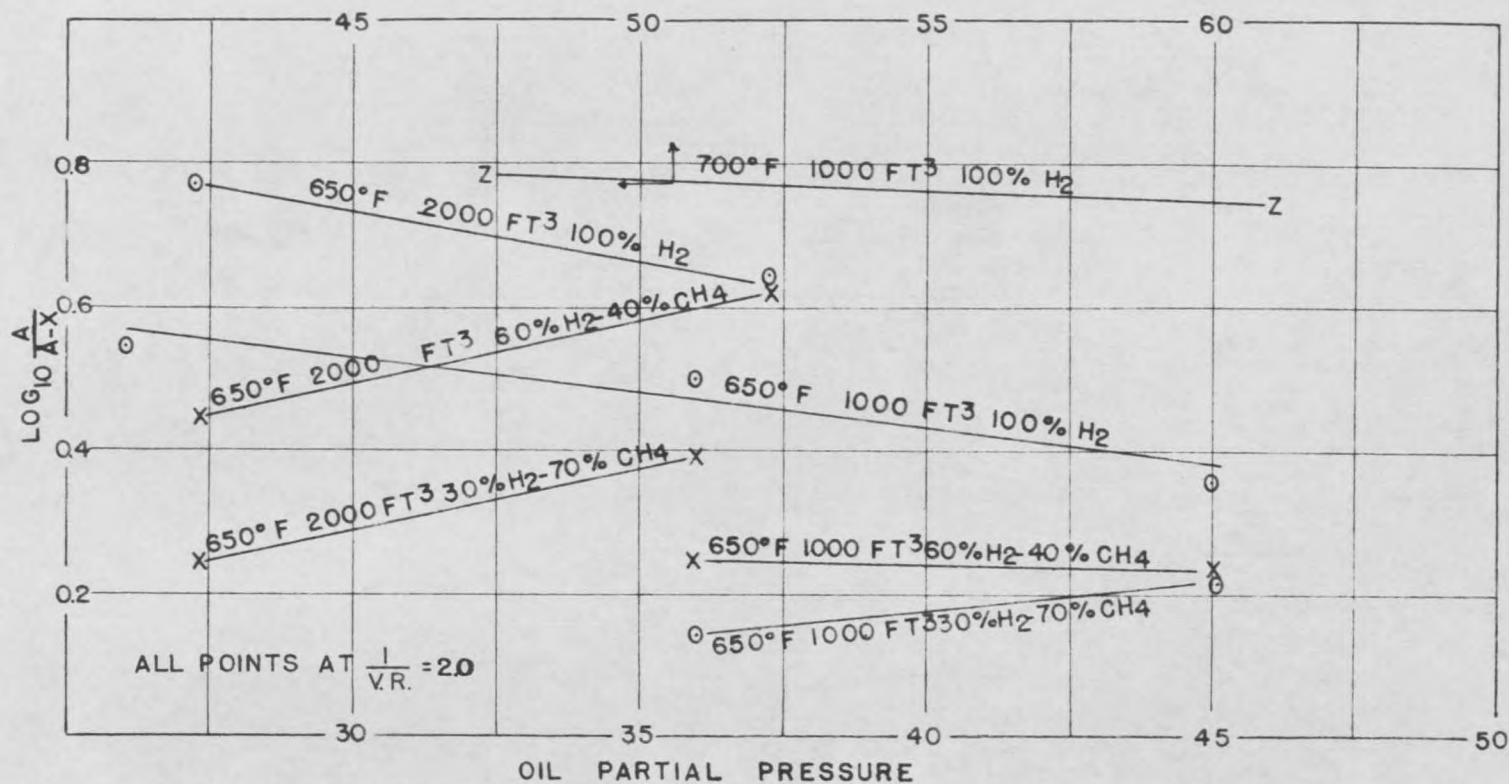


Figure 17. Effect of Oil Partial Pressure on Desulfurization.

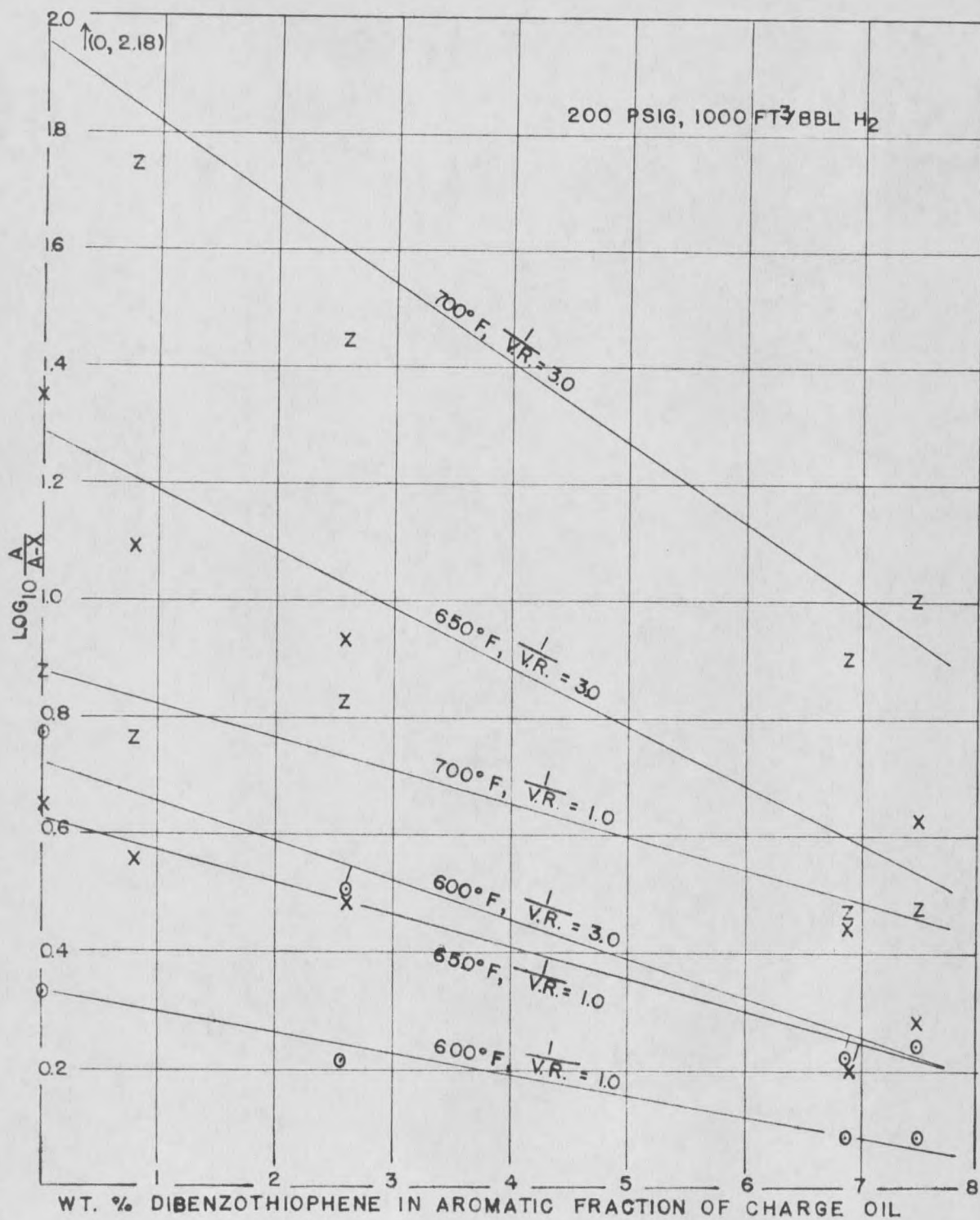


Figure 18. Effect of Dibenzothiophene on Desulfurization.

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