Catalyst deactivation for catalytic hydrodesulfurization
by Merrill Keith Opprecht

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

Abstract:
With the passing of time the refiner's choice of crudes has become more limited and he must now process high-sulfur crudes. This results in products containing objectionable sulfur compounds.

One of the best methods of removing the sulfur compounds is hydro-desulfurization. This method involves contacting the liquid feed with hydrogen over a cobalt molybdate oxide catalyst. The sulfur compounds in the oil are combined with the hydrogen and easily removed as hydrogen sulfide.

The catalyst activity has an effect on the desulfurization reaction. The activity of the catalyst decreases as the time it has been used increases.

For this deactivation study three feeds were used. These feeds differ ed in the aromatic content and the types of sulfur compounds in them. The other differences were of no real consequence.

This study has shown that the catalyst activity for a given on stream time was lower when a high aromatic feed was used than when a low aromatic feed was used.

A tendency for the deactivation rate to decrease as the time on stream increased was also noted.

197

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FOR
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TABLE OF CONTENTS

Page

Abstract 3

Introduction 4

Equipment and Process 10

Methods 13

Table XVII - Approximate Schedule for Profile Runs 13

Table XVIII - Approximate Schedule for Catalyst Runs 14

Discussion 20

Summary 24

Acknowledgement 25

Literature Cited 26

Appendix 27

ABSTRACT

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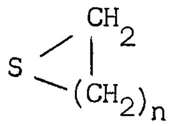
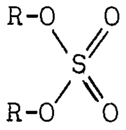
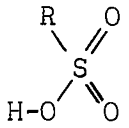
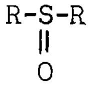
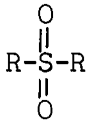
INTRODUCTION

In the early history of the petroleum industry a refiner could be selective in his choice of crudes to process, and pick one with a low sulfur content. With the passing of time and the consumption of low-sulfur curdes, the choice has become more limited and the refiner must now process crudes with a higher sulfur content.

Structural formulas for some sulfur compounds found in crudes or petroleum products are:

Hydrogen Sulfide[5*]	H-S-H
Mercaptans[5]	R-S-H
Sulfides[5]	R-S-R
Disulfides[5]	R-S-S-R
Cyclic Sulfides[5]	
Alkyl Sulfates[5]	
Sulfonic Acids[5]	
Sulfoxides[5]	 $R-\underset{\substack{\parallel \\ O}}{S}-R$
Sulfones[5]	 $R-\overset{\substack{O \\ \parallel}}{\underset{\substack{\parallel \\ O}}{S}}-R$

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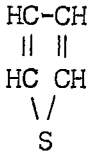
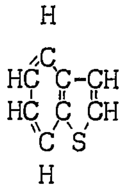
*Numbers refer to the literature cited, page 26.

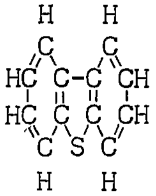
Thiophene[5]



Benzothiophene



Dibenzothiophene



With the refining of high-sulfur crudes came the problem of removing the sulfur from the products. Some of the reasons for removing sulfur are:

1. To improve the odor. The most obnoxous odors come from the low-boiling and gaseous sulfur compounds such as hydrogen sulfide, sulfur dioxide, methyl disulfide, mercaptans up to about six carbon atoms, and sulfides up to about eight carbon atoms.[5]
2. To decrease corrosion. At low temperatures hydrogen sulfide, free sulfur, low-boiling sulfides, disulfides, and mercaptans are corrosive to common metals.[5]
3. To improve color and lessen gum formation. The color stability of a product and its tendency to form gum are closely related to the sulfur concentration.[5]
4. To improve tetraethyl lead response.

> 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.[4]

5. To recover sulfur for sale. The economic feasibility of this depends upon the existing conditions and situations.
6. To decrease catalyst poisoning. The activity of many of the catalysts now in use is decreased by the presence of sulfur in the feed. Some catalysts affected by sulfur are nickel, cobalt, copper, iron, and platinum (used for dehydrogenation), and platinum and paladium (used for gasoline reforming).[7]
7. To improve lube oil life. When a high-sulfur fuel is burned in an internal combustion engine, some of the sulfur compounds produced get into the lubrication system and tend to reduce the effective life of the lube oil.[7]
8. To reduce the acrid fumes given off when burned. When exposed to air and moisture in the atmosphere, the fumes from a sulfur-containing fuel form corrosive acids and reduce the life of stacks, flues, and pipes.
9. To improve the explosion characteristics of fuels used in internal combustion engines.[5]

Before it was necessary to refine high-sulfur crudes, methods were used to convert the odoriferous sulfur compounds to those which were less objectionable. This was called "sweetening" and one such process is the Doctor process. This did not remove the sulfur, but resulted in product loss and may increase tetraethyl of lead consumption as it may add sulfur to the product.

Other methods used to reduce the sulfur content in oil products include acid treating using sulfuric acid or hydrofluoric acid; sweetening by the copper chloride process or the hypochlorite process; mercaptan removal by caustic treatment or the solutizer process; hydrogen sulfide removal by ethanolamine; glycol amine, phosphate, phenolate or alkacid scrubbing; or by one of the many catalytic treatments such as perco or Gray process, unifining, hydrofining or hydrodesulfurization.[7]

When a sulfur containing feed is passed over a cobalt molybdate oxide catalyst in an atmosphere of hydrogen, the sulfur is combined with the hydrogen and easily vented as hydrogen sulfide. This process falls under the classification of hydrodesulfurization and is the one pursued in this thesis.

A typical hydrodesulfurization reaction involving thiophene is[9]

$$C_4H_4S + 4H_2 \dashrightarrow C_4H_{10} + H_2S.$$

"The catalytic desulfurization reaction has been shown to be a pseudo-first-order reaction with respect to the concentration of the sulfur-bearing compound."[1,3,6] 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 H_2 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

$$\frac{dCa}{dt} = -kCa \qquad (1)$$

in which Ca = 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).

• • •

Equation (1) can also be written as

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

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).

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

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[9] (t = 0 to t = t, and x = 0 to x) gives

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

or

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

As mentioned previously, the catalyst activity has an effect on the velocity of the desulfurization reaction. The activity of the catalyst decreases with its use, i.e., the activity of the catalyst is reduced as the time it has been used since it was new or regenerated increases. This decrease in activity is due to the poisoning or covering up of the active sites in the catalyst. As the catalyst is used a layer of "coke" is deposited on the outer surface and prevents the sulfur molecule from coming in contact with the active sites, thus preventing the desulfurization reaction from taking place.

The extent of the "coke" deposited on the catalyst depends upon the type of catalyst used, the feed stock, and the operating conditions. There is a definite relationship in the amount of "coke" deposited on the catalyst with the time it has been used. The emperical formula of the "coke" deposited on the surface is reported to have the formula $(C_3H_4)_n$.[8]

All experimental runs were made in a small two-gallon per day bench scale unit.* For explanatory purposes, the unit has been divided into four sections. These sections are the feed section, the reactor and receiving section, the gas section, and the heating section.

The feed section consisted of the equipment necessary for stripping the feed with nitrogen, storage of the feed, and pumping the feed into the reactor. The feed was first placed in the stripping and storage tank where it was purged with nitrogen for the desired length of time. The nitrogen was bought in No. 1-A cylinders and reduced to about three pounds per square inch pressure by two pressure regulators. From the stripping and storage tank the stripped oil was transferred to the storage tank which was equipped with a graduated sight glass for measuring the space velocity. The oil was then pumped into the top of the reactor by means of a proportioning plunger pump.

The reactor and receiving section consisted of the reactor, the cooler, the level control device and the product reservoir. The reactor was fabricated from a 1-inch schedule 80 stainless steel pipe 30 inches long. The catalyst zone of the reactor was packed with the catalyst used for that particular run, and the preheat and afterheat zones of the reactor were packed with 1/8-inch alundum pellets. After the oil passed through the reactor, it proceeded down through the cooler (condenser). From the cooler the oil went into the product level control device. This device consisted of a Dynatrol Level Detector Type CL-10, purchased from Auto-

*For a schematic diagram of the unit, see Figure 1, page 45.

mation Product, Incorporated, used with a Barksdale shear seal solenoid valve and automatically controlled the level of the product. After passing from the level controller, the oil was received in the product reservoir where the hydrogen sulfide was allowed to escape into the atmosphere through a vent.

The gas section of the unit consisted of the hydrogen tank, a deoxo purifier, a drier, two rotometers and a back pressure controller. The hydrogen was purchased in No. 1-A size tanks and reduced to 300 pounds per square inch pressure before it passed into the deoxo purifier. The deoxo purifier was purchased from Baker and Company and converted oxygen in the hydrogen to water. After leaving the purifier, the gas passed through a drier containing five angstrom molecular sieves* which removed the water from the gas. The gas then passed through indicating drierite and was metered into the top of the reactor by means of one of the two calibrated rotometers. The reactor was controlled at 200 pounds per square inch gauge pressure by means of a Mason-Neilan small volume air-to-close back pressure valve in conjunction with a Fisher-Wizard proportional controller.

The heating section of the unit consisted of four powerstats, four heating coils, a thermowell containing five thermocouples, and a Leeds and Northrup indicating potentiometer. The power used for heating the

*Molecular sieves are dehydrated zeolite consisting of a network of crystals containing pores and cavities of exact uniformity, which were originally occupied by water of hydration.[10]

reactor came from a 2000 watt constant voltage transformer. From the transformer the electricity passed through four powerstats, used to control the amount of current; through four ammeters, used to indicate the amperes to each coil; and through four nichrome wire coils which were wrapped around the reactor. The coils were insulted with porcelain beads and covered with a 1-1/2-inch layer of magnesia mud insulation.

A thermowell fabricated from a piece of 3/16-inch stainless steel tubing was inserted in the middle of the reactor and contained five thermocouples. The thermocouples were of the iron-constantan type and were connected to a Leeds and Northrup indicating potentiometer.

METHODS

The data taken from this project and used for the basis of this thesis were taken from a series of runs. These runs were made in four groups, each group using a different feed.

Group one consisted of two runs using a straight Carter railroad diesel obtained from the Carter Refinery in Billings, Montana. A Nalco Esso Cobalt Molybdate 1/16-inch extruded catalyst was used. This is a mixture of cobalt and molybdenum oxides on an alumina support. These two runs were made at a reactor pressure of 200 pounds per square inch gauge, and used a gas rate of 1000 standard cubic feet of hydrogen per barrel of feed. The first run was made at a temperature of 700°F. with a varying space velocity between two and ten grams of oil per hour per gram of catalyst and was designated run Carter-six-profile (C-6-P). This run was made to determine the effect of space velocity on the conversion of sulfur in the feed to hydrogen sulfide. This run followed the schedule outlined below.

TABLE XVII

APPROXIMATE SCHEDULE FOR PROFILE RUNS

Temperature (°F.)	Time (hrs.)	Space Velocity (gm./hr./gm.)	Feed
400	4	4	Aramco*
500	4	4	Aramco
600	16	4	Aramco
700	24	4	Aramco**

(cont.)

Temperature (°F.)	Time (hrs.)	Space Velocity (gm./hr./gm.)	Feed
700	24	4	Carter
700	4	10	Carter
700	14	4	Carter
700	10	6	Carter
700	20	2	Carter
700	20	4	Carter
700	15	3	Carter
700	14	4	Carter

*Aramco light waxy distillate was used as a break in feed for this run.

**The procedure up to this point is duplicated for each run to condition the catalyst the same for each run.

The second run of group one was made at a space velocity of 4 gm./hr./gm. and at temperatures of 700 and 775°F. This run was designated Carter-six-catalyst (C- 6-C) and was made to determine the catalyst life and deactivation rate under these conditions and using this feed. This run was made according to the schedule outlined below.

TABLE XVIII

APPROXIMATE SCHEDULE FOR CATALYST RUNS

Temperature (°F.)	Time	Feed
400	4 hrs.	Aramco
500	4 hrs.	Aramco

(cont.)

Temperature (°F.)	Time	Feed
600	16 hrs.	Aramco
700	24 hrs.	Aramco
700	24 hrs.	Carter
775	8 days	Carter
700	24 hrs.	Carter
775	7 days	Carter
700	24 hrs.	Carter
775	2 days	Carter
700	24 hrs.	Carter

Group two consisted of runs Carter-seven-profile (C-7-P) and Carter-seven-catalyst (C-7-C). These two runs were made using the same catalyst as group one (100 gms. of Nalco Esso 1/16-inch Extruded Cobalt Molybdate). A gas rate of 1000 SCF of hydrogen was used and the reactor pressure was 200 p.s.i.g. These runs also approximated the preceding schedules. These runs, however, used a feed of 75 weight percent Carter railroad diesel and 25 weight percent Carter medium cycle oil. The MCO was also obtained from the Carter Refinery in Billings, Montana.

The runs in group three were also made at a reactor pressure of 200 p.s.i.g. and used a gas rate of 1000 SCF of hydrogen per barrel of feed. The catalyst was the same as used previously (100 gms. of Nalco Esso 1/16-inch extruded Cobalt Molybdate) and the runs approximated the schedules for the runs of group one. The feed for these runs was a blend of 50 weight percent Carter railroad diesel and 50 weight percent Carter medium cycle oil. This group had three runs--run Carter-eight-profile (C-8-P), the first catalyst run (A-C-8-C) and the second catalyst run (B-C-8-C). The A and B catalyst runs were the same and were both of short duration because the catalyst deactivated very rapidly.

For the first three groups the feed was not purged with nitrogen and no particular care was taken to remove or protect the feeds from the atmosphere. These runs were also prior to the installation of the deoxo purifier and drier and no attempt was made to remove the oxygen from the treat gas.

Group four consisted of only one run, Aramco-sixteen (Ar-16). The object of this run was to check the equipment and methods with those used in the pilot plant laboratory of Esso Research and Engineering Company. This run was made at a temperature of 725°F. and a treat gas rate of 500 SCF per barrel. The treat gas for this run was a mixture of 70% hydrogen and 30% methane. This run was made after the installation of the deoxo purifier and drier. The feed was Aramco light waxy distillate and was purged with nitrogen to remove all traces of oxygen in the feed and kept under an atmosphere of nitrogen at all times. This was done to eliminate all possible oxygen and obtain a product that was color stable. One hundred grams of Peter Spence cobalt molybdate catalyst were used. This catalyst was calcined for 12 hours at a temperature of 1200°F. under an atmosphere of nitrogen prior to its use in the reactor. This run was made at a reactor pressure of 200 p.s.i.g. and a space velocity of one volume of oil per hour per volume of catalyst. A different startup procedure was used for this run. It was as follows:

> Four hours at 400°F. with Aramco feed containing 0.6 wt.% CS_2; liquid feed rate of 4 v./hr./v.; 200 p.s.i.g. reactor pressure; no gas flow.
>
> Sixteen hours at 600°F. with Aramco feed containing 0.6 wt.% CS_2; liquid feed rate of 1 v./hr./v.; 200 p.s.i.g. reactor pressure; treat gas rate of 1,000 SCF per barrel.

After the startup procedure, the unit was set to the run conditions and operated for 676 hours.

Two methods of determining the catalyst activity were used. The first method was based on the idea that the total rate equation for the reaction contained two multiplying factors; namely, space velocity and catalyst activity. For the same rate equation to apply for all catalyst activities, it is apparent that the space velocity must change as the catalyst activity changes. Therefore, if a comparison of the space velocity is made, this must be a comparison of the catalyst activities if all other conditions have been kept constant.[2] The profile runs of the first three groups, i.e., runs C-6-P, C-7-P, and C-8-P, were made to obtain the percent conversion for a given space velocity, using a fresh catalyst. The data obtained from these runs are found in Tables II, III, and IV, pages 30, 31 and 32. These data are plotted in Figures 2, 3, and 4 on pages 46, 47 and 48.

The catalyst runs, i.e., C-6-C, C-7-C, A-C-8-C and B-C-8-C, were made to determine the catalyst deactivation rate for each of the three feeds used. These data are tabulated (Tables V through XV) on pages 33 through 43.

As an example of the first method of determining the catalyst activity, here are some actual data and the method used. From the C-6-P run the samples were collected and analyzed for their sulfur content (A-x). By knowing the initial sulfur content of the feed (A) and using the sample sulfur content, the conversion (x/A) was calculated according to the following equation:

$$\frac{x}{A} \doteq 1 - \frac{A-x}{A} \qquad (6)$$

The conversion was plotted against the reciprocal space velocity (hrs.). This curve is shown in Figure 2, page 46. From sample C-6-C/5, run C-6-C, the sulfur content was 0.442 weight percent sulfur and the percent conversion was 66.5 (Table VI, page 34). Using this value of percent conversion and the space velocity at which the sample was run, ($S.V._{act.}$), a point was established on Figure 2, Point M. From point M a horizontal line was drawn to the curve, point O. From point O a vertical line was drawn down to point R, which is the equivalent reciprocal space velocity ($1/S.V._{equiv.}$). The values along the abscissa were then compared to obtain the percent activity according to the following equation:

$$\%\ \text{Activity} = \frac{RS}{QS} = \frac{1/S.V._{equiv.}}{1/S.V._{act.}}100 = \frac{S.V._{act.}}{S.V._{equiv.}}100 \qquad (7)$$

The percent activity obtained was plotted versus the hours on stream. (See Figures 5 through 7, pages 49 through 51.) .

The second method used for determining the catalyst activity was one of comparing directly the percent conversions (100 x/A = C). A conversion near the first of the run was picked as the initial conversion (C_0) and all other conversions for that run were referred to it. This comparison was called the percent conversion activity (100 C/C_0). This percent conversion activity was plotted versus the hours on stream as was the percent activity. For these plots, see Figures 8 and 9 on pages 52 and 53.

Both methods of determining the catalyst activity were applied for the runs using a Carter feed. For the run Aramco-16, only the second method was employed as no profile run was made using this feed. The data collected from this run are found in Table XV, page 43, and the plots are found in Figures 11 and 12 on pages 55 and 56.

Figures 10 and 12, pages 54 and 56, are plots of loss in conversion activity versus on stream time (hrs.). The conversion (C) is defined as (x/A). The initial conversion (C_0) was taken at the point of the first sample.

DISCUSSION

The runs made in the first three groups outlined in the Methods section differed only in the feeds used:

Run	Feed
C-6-P C-6-C	100 Wt. % R.R.D.
C-7-P C-7-C	75 Wt. % R.R.D. 25 Wt. % M.C.O.
C-8-P C-8-C	50 Wt. % R.R.D. 50 Wt. % M.C.O.

Both the R.R.D. and the M.C.O. were obtained from the same place and from the same crude. The main differences between the feeds used for these runs were density, ASTM distillation, weight percent sulfur, and percent aromatics. For a comparison of feeds, see Table I, page 29.

The graphs from Figures 2, 3, and 4 show that at a reciprocal space velocity of 0.2 hours, the following percent conversions were obtained:

Run	Percent Conversion
C-6-P	80.5
C-7-P	85.0
C-8-P	88.5

This indicates that the higher the percent of M.C.O. in the feed, the higher the percent conversion. An analysis as to the types of compounds in the R.R.D. and the M.C.O. shows that the R.R.D. has about 7.5 percent benzothiophene and 2.5 percent dibenzothiophene in the aromatic fraction and the M.C.O. contains about 12.5 percent benzothiophene and no dibenzothiophene in its aromatic fraction. Waterman showed that benzothiophene is easier to remove than dibenzothiophene.[6] The addition of M. C. O. to the feeds used in runs C-7-P and C-8-P, in effect, diluted the amount of the harder-to-remove dibenzothiophene in the feed and allowed a higher conversion, using the same conditions.

The profile runs were all made at a temperature of 700°F. This temperature was used to lessen the effect of time on the catalyst activity; at higher temperatures the time has a marked effect on catalyst deactivation. The catalyst runs were made at 775°F. for the opposite reason. During the catalyst runs the temperature was periodically dropped to 700°F. so that the conversion at that time could be compared to the profile run, on the same temperature basis. Figure 5, page 49, shows the curves that resulted from this comparison using the first method outlined previously. Figure 6, page 50, shows the percent activity is effected by hours on stream at 775°F. This comparison of conversions to obtain the activity was made using the profile runs at 700°F. and the 775°F. portions of the catalyst runs. As the conversion increased, with an increase in temperature, the activity resulting from this type of a comparison was high. Although this gave an apparent activity which was higher than the actual activity, it showed the tendency of the catalyst to deactivate.

In runs C-7-C and A-C-8-C, during the 24-hour period between 74 and 96 hours, a sample was taken every two hours in order to get a closer look at the deactivation immediately after the temperature was raised to 775°F. The data are shown in Tables IX through XII on pages 37 through 40. Figure 7, page 51, shows the curve of percent activity versus hours on stream for this period and indicates a large drop in activity.

Figures 5, 6 and 7, pages 49 through 51, show that the deactivation at a given time was greater for run C-7-C than for run C-6-C and that it was greater for run C-8-C than for either of the other two runs. This may be for one or both of the following reasons:

1. The higher aromatic content of the feeds used in runs C-7-C and C-8-C.
2. The higher conversions obtained using the feed that desulfurized easier.

The aromatic content of the three feeds was as follows:

Feed	Aromatic Content
100 Wt. % R. R. D.	24.5 Wt. %
75 Wt. % R. R. D. 25 Wt. % M. C. O.	26.7 Wt. %
50 Wt. % R. R. D. 50 Wt. % M. C. O.	29.0 Wt. %

Tables VI, VIII, X, and XII show the precent conversion activity for runs C-6-C, C-7-C and C-8-C. This is the second method outlined in the methods section and involves a comparison of the conversions obtained. These data are plotted in Figures 8 and 9, pages 52 and 53. The curves show the same tendency as shown in Figures 5, 6 and 7 explained above.

Figure 10, page 54, shows the loss in conversion activity versus hours on stream at 775^{O}F. This curve indicates that the loss in conversion activity per hour is the greatest at the first part of the run and decreases as the run proceeds.

Run Ar-16 was made using the break-in procedure outlined previously.

The temperature was then set at 725°F. and maintained at that temperature throughout the run. The curves on Figures 11 and 12, pages 55 and 56 were made from this run which is tabulated in Table XV, page 43. These curves also showed the tendency for the deactivation rate to decrease as the on stream time increased. Because this run was made at a different temperature and a different treat gas was used, no direct comparison between the runs can be made.

Table XVI on page 44 shows some figures taken from plots made from runs C-6-C, C-7-C and C-8-C (A and B). This table helps to show the effect of percent aromatics in the feed. As the percent aromatics in the feed increased, the percent activity and percent conversion activity decreased for any on stream time. The rate of deactivation also increased with an increase in aromatic content of the feed. When making this comparison it must be remembered that slightly higher conversions are obtained with feeds containing higher proportions of M. C. O.

SUMMARY

The effect of aromatic content in the feed on catalyst activity and deactivation was studied under the following conditions.

Catalyst: 100 grams Nalco Esso 1/16-inch extruded Cobalt Molybdate

Reactor Pressure: 200 p.s.i.g.

Temperature: 775°F.

Gas Rate: 1000 SCF of hydrogen per barrel of feed.

Feed:
Run C-6-C - 100 Wt. % Carter R.R.D.
Run C-7-C - 75 Wt. % Carter R.R.D. + 25 Wt. % Carter M.C.O.
Run C-8-C - 50 Wt. % Carter R.R.D. + 50 Wt. % Carter M.C.O.

As the weight percent M.C.O. in the feed increased, the aromatic content increased and the weight percent of dibenzothiophene decreased. As the aromatic content of the feed increased the activity of the catalyst for a given on stream time decreased. A decrease in dibenzothiophene content caused an increase in conversion which also caused a decrease in catalyst activity for any given on stream time.

The deactivation rate decreased as the on stream time at 775°F. increased.

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APPENDIX

Page

TABLE I Charge Oil Inspection Data 29

TABLE II Tabulated Data from Run Carter-Six-Profile 30

TABLE III Tabulated Data from Run Carter-Seven-Profile 31

TABLE IV Tabulated Data from Run Carter-Eight-Profile 32

TABLE V Tabulated Data from Run Carter-Six-Catalyst 33

TABLE VI Tabulated Data from Run Carter-Six-Catalyst 34

TABLE VII Tabulated Data from Run Carter-Seven-Catalyst 35

TABLE VIII Tabulated Data from Run Carter-Seven-Catalyst 36

TABLE IX Tabulated Data from Run Carter-Seven-Catalyst 37

TABLE X Tabulated Data from Run Carter-Seven-Catalyst 38

TABLE XI Tabulated Data from Run A-Carter-Eight-Catalyst 39

TABLE XII Tabulated Data from Run A-Carter-Eight-Catalyst 40

TABLE XIII Tabulated Data from Run B-Carter-Eight-Catalyst 41

TABLE XIV Tabulated Data from Run B-Carter-Eight-Catalyst 42

TABLE XV Tabulated Data from Run Aramco-Sixteen Comparison Run . . 43

TABLE XVI Tabulated Data from Runs Carter-Six-Catalyst, Carter-Seven-Catalyst, A-Carter-Eight-Catalyst, and B-Carter-Eight-Catalyst 44

FIGURE 1 Schematic Flow Diagram of the Desulfurization System . . . 45

FIGURE 2 Percentage Conversion Versus Reciprocal Space Velocity . . 46

FIGURE 3 Percentage Conversion Versus Reciprocal Space Velocity . . 47

FIGURE 4 Percentage Conversion Versus Reciprocal Space Velocity . . 48

FIGURE 5 Percentage Activity Versus On Stream Time 49

FIGURE 6 Percentage Activity Versus On Stream Time at 775°F. . . . 50

APPENDIX
(continued)

Page

FIGURE 7 Percentage Activity Versus On Stream Time 51

FIGURE 8 Percentage Conversion Activity Versus On Stream Time at 775°F. 52

FIGURE 9 Percentage Conversion Activity Versus On Stream Time . . 53

FIGURE 10 Loss in Conversion Activity Versus On Stream Time at 775°F. 54

FIGURE 11 Percentage Conversion Activity Versus On Stream Time for Aramco-Sixteen 55

FIGURE 12 Loss in Conversion Activity Versus On Stream Time for Run Aramco-Sixteen 56

TABLE I

CHARGE OIL INSPECTION DATA

Charge Oil	Aramco Light Waxy Distillate	100 Wt.% Carter R.R. Diesel	75 Wt.% Carter R.R. Diesel 25 Wt.% Carter Medium Cycle Oil	50 Wt.% Carter R.R. Diesel 50 Wt.% Carter Medium Cycle Oil
Gravity °A.P.I.	34.1	31.2	32.7	28.9
Volume % Distilled at °F.				
I. B. P.	334	361	391	420
5	425	466	480	483
10	456	497	500	499
20	495	524	519	516
30	522	540	530	524
40	548	551	539	533
50	567	562	548	540
60	588	573	557	546
70	606	583	569	555
80	625	597	583	570
90	647	612	605	591
95	662	626	621	611
E. P.	672	640	631	627
Wt. % Sulfur	1.33	1.32	1.65	2.01
% Aromatics		24.5	26.7	29.0

TABLE II

TABULATED DATA FROM RUN CARTER-SIX-PROFILE

Sample No.	Hrs. on Stream	Temp. °F.	Space Velocity (gm./hr./gm.)	1/Space Velocity (hrs.)	Avg. Wt.%* S in Product (A-x)	$100 (\frac{x}{A}) = \%$ Conversion
C-6-P/A-1	44	705	4.00	0.250	0.162	87.0
C-6-P/A-2	48	702	4.00	0.250	0.162	87.0
C-6-P/3	70	701	4.00	0.250	0.214	83.8
C-6-P/4	72	704	4.00	0.250	0.200	84.6
C-6-P/7	75	696	10.00	0.100	0.468	64.4
C-6-P/8	76	700	10.00	0.100	0.453	75.6
C-6-P/12	88	706	3.96	0.252	0.187	85.8
C-6-P/13	90	703	4.00	0.250	0.187	85.8
C-6-P/17	98	693	6.06	0.165	0.300	77.2
C-6-P/18	100	701	6.01	0.165	0.269	79.7
C-6-P/21	115	698	2.06	0.485	0.108	91.8
C-6-P/22	120	703	2.02	0.495	0.131	90.0
C-6-P/31	138	714	4.00	0.250	0.183	86.1
C-6-P/32	140	706	4.06	0.246	0.202	84.7
C-6-P/36	152	702	3.00	0.333	0.142	85.8
C-6-P/37	155	699	3.02	0.331	0.162	87.3
C-6-P/43	167	702	4.00	0.250	0.211	84.0
C-6-P/44	169	703	4.04	0.248	0.205	84.4

*A_a = 1.25 Wt. % S (Aramco Feed)

A_c = 1.32 Wt. % S (Carter R. R. Diesel)

Gas Rate: 1000 SCF Pure Hydrogen Per Barrel Feed
Catalyst: 100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE III

TABULATED DATA FOR RUN CARTER-SEVEN-PROFILE

Sample No.	Hrs. on Stream	Temp. °F.	Space Velocity (gm./hr./gm.)	1/Space Velocity (hrs.)	Avg. Wt.%* S in Product (A-x)	$100 (\frac{x}{A}) = \%$ Conversion
C-7-P/A-1	46	705	4	0.25	0.165	87.6
C-7-P/A-2	48	709	4	0.25	0.164	87.7
C-7-P/4	72	712	4.04	0.248	0.190	88.5
C-7-P/9	77	718	10.00	0.100	0.375	77.3
C-7-P/14	88	732	6.07	0.165	0.283	82.8
C-7-P/19	103	706	3.97	0.252	0.214	87.0
C-7-P/24	123	702	2.98	0.336	0.232	85.9
C-7-P/28	153	703	1.98	0.502	0.092	94.4
C-7-P/34	172	703	4.00	0.250	0.232	85.9

*A_a = 1.25 Wt. % S (Aramco Feed)

A_c = 1.65 Wt. % S (75 Wt. % Carter R. R. Diesel)
(25 Wt. % Carter Medium Cycle Oil)

Gas Rate: 1000 SCF Pure Hydrogen per Barrel Feed
Catalyst: 100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE IV

TABULATED DATA FOR RUN CARTER-EIGHT-PROFILE

Sample No.	Hrs. on Stream	Temp. °F.	Space Velocity (gm./hr./gm.)	1/Space Velocity (hrs.)	Avg. Wt.%* S in Product (A-x)	$100\,(\frac{x}{A}) = \%$ Conversion
C-8-P/A-1	46	701	4.01	0.249	0.162	
C-8-P/A-2	48	700	4.01	0.249	0.169	
C-8-P/3	70	709	3.95	0.253	0.193	90.4
C-8-P/4	72	708	4.04	0.248	0.204	89.8
C-8-P/5	83	709	10.00	0.100	0.471	76.6
C-8-P/6	84	712	10.00	0.100	0.462	77.0
C-8-P/7	92	732	6.00	0.167	0.265	86.8
C-8-P/8	94	721	6.00	0.167	0.304	84.8
C-8-P/9	106	701	3.94	0.254	0.232	88.4
C-8-P/10	109	709	3.96	0.252	0.193	94.5
C-8-P/11	125	705	2.95	0.339	0.161	92.0
C-8-P/12	129	708	3.00	0.333	0.139	93.1
C-8-P/13	165	703	1.90	0.526	0.056	97.2
C-8-P/14	169	703	1.99	0.502	0.079	96.1
C-8-P/15	184	704	3.98	0.251	0.257	87.2
C-8-P/16	186	703	4.00	0.250	0.255	87.3

*A_a = 1.33 Wt. % S (Aramco Feed)

A_c = 2.01 Wt. % S (50 Wt. % Carter R. R. Diesel)
(50 Wt. % Carter Medium Cycle Oil)

Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE V

TABULATED DATA FROM RUN CARTER-SIX-CATALYST

Sample No.	Temp. °F.	Hrs. on Stream	Space Velocity	1/S.V. act.	1/S.V. equiv.	% Activity = $\frac{\text{S.V. act.}}{\text{S.V. equiv.}}$ (100)
C-6-A/1	702	48	4.08	0.245	--	--
C-6-C/2	705	72	3.92	0.255	0.255	100
12/31	775	96	4.00	0.250	0.295	118
1/1	775	120	3.97	0.252	0.275	109
1/2	775	144	4.00	0.250	0.245	98.0
1/3	777	168	3.96	0.252	0.228	89.4
C-6-C/3	781	192	4.06	0.246	0.210	85.2
1/5	775	216	3.96	0.252	0.197	79.1
1/6	777	240	4.01	0.249	0.183	73.5
C-6-C/4	777	264	4.00	0.250	0.170	67.9
C-6-C/5	707	288	3.97	0.252	0.130	40.8
1/9	773	312	4.02	0.249	0.165	62.2
1/10	775	336	3.98	0.251	0.183	73.0
1/11	775	360	4.00	0.250	0.163	65.2
C-6-C/6	775	384	4.00	0.250	0.162	64.8
1/13	777	408	4.01	0.249	0.159	63.8
1/14	775	432	4.00	0.250	0.148	59.3
C-6-C/7	775	456	4.00	0.250	0.149	59.6
C-6-C/8	702	480	3.97	0.252	0.085	34.5
1/17	775	504	4.01	0.249	0.150	60.2
1/18	779	528	4.02	0.249	0.137	55.0
C-6-C/9	702	552	4.08	0.245	0.075	30.6

Break-in Feed:	Aramco Light Waxy Distillate
Run Feed:	Carter R. R. Diesel
Gas Rate:	1000 SCF of Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE VI

TABULATED DATA FROM RUN CARTER-SIX-CATALYST

Sample No.	Hrs. on Stream	Avg. Wt. % S in Product (A-x)	$\frac{A-x}{A}$*	100 $(\frac{x}{A})$ = % Conversion = C	%Conversion Activity = C/C_o (100)	Loss in Conversion Activity = $\frac{C_o-C}{C_o}$
C-6-A/1	48	0.177				
C-6-C/2	72	0.200	0.152	84.8		
12/31	96	0.184	0.138	86.2 = C_o	100	
1/1	120	0.191	0.145	85.5	99.1	0.008
1/2	144	0.207	0.157	84.3	97.8	0.022
1/3	168	0.220	0.168	83.2	96.4	0.035
C-6-C/3	192	0.238	0.181	81.9	95.0	0.050
1/5	216	0.251	0.191	80.9	93.9	0.062
1/6	240	0.268	0.203	79.7	92.5	0.075
C-6-C/4	264	0.285	0.216	78.4	91.0	0.090
C-6-C/5	288	0.442	0.335	66.5		
1/9	312	0.285	0.216	78.4	91.0	0.090
1/10	336	0.267	0.203	79.7	92.5	0.075
1/11	360	0.296	0.224	77.6	90.0	0.100
C-6-C/6	384	0.298	0.226	77.4	89.6	0.102
1/13	408	0.302	0.229	77.1	89.4	0.106
1/14	432	0.320	0.243	75.7	87.8	0.122
C-6-C/7	456	0.318	0.242	75.8	87.9	0.121
C-6-C/8	480	0.516	0.391	60.9		
1/17	504	0.316	0.240	76.0	88.1	0.118
1/18	528	0.340	0.258	74.2	86.0	0.139
C-6-C/9	552	0.547	0.415	58.5		

*A_{Aramco} = 1.25 Wt. % S

A_{Carter} = 1.32 Wt. % S (100 Wt.% R.R.D.)

Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE VII

TABULATED DATA FOR RUN CARTER-SEVEN-CATALYST

Sample No.	Temp. °F.	Hrs. on Stream	Space Velocity	1/S.V. act.	1/S.V. equiv.	% Activity = $\frac{S.V._{act.}}{S.V._{equiv.}}(100)$
C-7-C/A-1	700	46	4.03	0.248		
C-7-C/A-2	712	48	4.00	0.250		
C-7-C/3	707	70	4.00	0.250	0.295	118
C-7-C/4	705	72	4.00	0.250	0.293	117
C-7-C/5	786	96	3.96	0.254	0.245	96.5
C-7-C/6	783	120	4.00	0.250	0.220	88.0
C-7-C/7	786	144	4.00	0.250	0.176	70.3
C-7-C/8	783	168	4.02	0.249	0.129	51.8
C-7-C/9	779	192	4.00	0.250	0.136	54.4
C-7-C/10	784	216	4.00	0.250	0.113	45.2
C-7-C/11	783	240	3.98	0.251	0.123	49.0
C-7-C/A-12	712	264	3.90	0.256		
C-7-C/13	703	288	3.93	0.254	0.052	20.4
C-7-C/14	784	312	4.00	0.250	0.110	44.0
C-7-C/15	781	336	3.98	0.251	0.100	39.8
C-7-C/16	783	360	3.97	0.252	0.105	39.7
C-7-C/17	786	384	3.96	0.254	0.097	38.2
C-7-C/18	783	408	3.96	0.254	0.088	34.6
C-7-C/19	783	432	3.96	0.254	0.080	31.5
C-7-C/20	779	456	4.07	0.246	0.075	30.5
C-7-C/A-21	707	480	4.05	0.247		
C-7-C/22	702	504	4.03	0.248	0.034	13.7
C-7-C/23	775	528	4.07	0.246	0.080	32.5
C-7-C/24	783	552	4.08	0.245	0.072	29.4
C-7-C/25	779	576	4.10	0.244	0.061	25.0
C-7-C/26	777	600	3.96	0.254	0.067	26.4
C-7-C/A-27	705	624	4.03	0.248		
C-7-C/28	705	648	4.00	0.250	0.028	11.2
C-7-C/29	702	650	4.06	0.246	0.026	10.6

Break-in Feed: Aramco Light Waxy Distillate
Run Feed: 75 Wt. % Carter R.R.D. + 25 Wt. % Carter M.C.O.
Gas Rate: 1000 SCF Pure Hydrogen per Barrel Feed
Catalyst: 100 gms Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE VIII

TABULATED DATA FROM RUN CARTER-SEVEN-CATALYST

Sample No.	Hrs. on Stream	Avg. Wt.% S in Product (A-x)	$\frac{A-x}{A}$*	$100 (\frac{x}{A})$ = % Conversion= C	%Conversion Activity = $C/C_0(100)$	Loss in Conversion Activity = $\frac{C_0-C}{C_0}$
C-7-C/A-1	46	0.162				
C-7-C/A-2	48	0.205				
C-7-C/3	70	0.166	0.100	90.0		
C-7-C/4	72	0.174	0.105	89.5		
C-7-C/5	96	0.204	0.124	87.6 = C_0	100	
C-7-C/6	120	0.226	0.137	86.3	98.4	0.015
C-7-C/7	144	0.272	0.165	83.5	95.2	0.047
C-7-C/8	168	0.329	0.200	80.0	91.2	0.087
C-7-C/9	192	0.319	0.193	80.7	91.8	0.080
C-7-C/10	216	0.353	0.214	78.6	89.5	0.103
C-7-C/11	240	0.340	0.206	79.4	90.5	0.094
C-7-C/A-12	264	0.488				
C-7-C/13	288	0.582	0.352	64.1		
C-7-C/14	312	0.363	0.220	78.0	89.0	0.110
C-7-C/15	336	0.395	0.239	76.1	86.6	0.132
C-7-C/16	360	0.381	0.231	76.9	87.7	0.122
C-7-C/17	384	0.398	0.241	75.9	86.5	0.133
C-7-C/18	408	0.429	0.260	74.0	84.4	0.155
C-7-C/19	432	0.458	0.278	72.2	82.3	0.176
C-7-C/20	456	0.476	0.289	71.1	81.4	0.186
C-7-C/A-21	480	0.745				
C-7-C/22	504	0.718	0.435	56.5		
C-7-C/23	528	0.462	0.281	72.0	82.1	0.178
C-7-C/24	552	0.485	0.294	70.6	80.5	0.194
C-7-C/25	576	0.538	0.326	67.4	76.8	0.230
C-7-C/26	600	0.511	0.308	69.1	80.5	0.211
C-7-C/A-27	624	0.755				
C-7-C/28	648	0.784	0.475	52.5		
C-7-C/29	650	0.788	0.478	52.2		

*A_{Aramco} = 1.25 Wt.% S

A_{Carter} = 1.65 Wt.% S (75 Wt.% R.R.D. ≠ 25 Wt.% M.C.O.)

Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE IX

TABULATED DATA FROM RUN CARTER-SEVEN-CATALYST

Sample No.	Temp. °F.	Hrs. on Stream	Space Velocity	1/S.V. act.	1/S.V. equiv.	% Activity = $\frac{\text{S.V.act.}}{\text{S.V.equiv.}}(100)$
C-7-C/3	707	70	4.00	0.250	0.295	118
C-7-C/4	705	72	4.00	0.250	0.293	117
3:30	756	74	3.98	0.251	0.425	168
5:30	770	76	3.97	0.252	0.400	158
7:30	772	78	3.99	0.250	0.371	148
9:30	774	80	4.03	0.248	0.327	132
11:30	781	82	3.98	0.251	0.330	131
13:30	786	84	3.98	0.251	0.305	120
15:30	786	86	3.98	0.251	0.320	128
17:30	784	88	3.88	0.258	0.286	111
19:30	781	90	4.00	0.250	0.272	109
21:30	781	92	4.00	0.250	0.252	101
23:30	779	94	3.99	0.250	0.257	106
C-7-C/5	786	96	3.96	0.254	0.245	96.5

Break-in Feed:	Aramco Light Waxy Distillate
Run Feed:	75 Wt.% R.R.D. + 25 Wt.% M.C.O.
Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE X

TABULATED DATA FROM RUN CARTER-SEVEN-CATALYST

Sample No.	Hrs. on Stream	Avg. Wt. % S in Product (A-x)	$\frac{A-x^*}{A}$	$100 (\frac{x}{A}) = \%$ Conversion = C	%Conversion Activity = C/C_o (100)
C-7-C/3	70	0.166	0.100	90.0	
C-7-C/4	72	0.174	0.106	89.4	
3:30	74	0.105	0.064	93.6 = C_o	100
5:30	76	0.114	0.069	93.1	99.5
7:30	78	0.126	0.076	92.4	98.5
9:30	80	0.147	0.089	91.1	97.3
11:30	82	0.146	0.088	91.2	97.4
13:30	84	0.160	0.097	90.3	96.5
15:30	86	0.150	0.091	90.9	97.0
17:30	88	0.172	0.104	89.6	95.6
19:30	90	0.183	0.111	88.9	94.9
21:30	92	0.198	0.120	88.0	93.9
23:30	94	0.191	0.118	88.2	94.1
C-7-C/5	96	0.204	0.124	87.6	93.5

*A_{Aramco} = 1.25 Wt.% S

A_{Carter} = 1.65 Wt.% S (75 Wt.% R.R.D. + 25 Wt.% M.C.O.)

Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE XI

TABULATED DATA FROM RUN A-CARTER-EIGHT-CATALYST

Sample No.	Temp. °F.	Hrs. on Stream	Space Velocity	$1/S.V._{act.}$	$1/S.V._{equiv.}$	% Activity = $\frac{S.V._{act.}}{S.V._{equiv.}}(100)$
C-8-C/A-1	700	46	4.06	0.247		
C-8-C/A-2	699	48	4.05	0.247		
C-8-C/3	702	72	4.02	0.249	0.290	116.5
C-8-C/4	793	96	4.05	0.247	0.210	85.2
#1	766	74	4.05	0.247	0.400	162.0
#2	772	76	4.06	0.247	0.350	141.8
#3	772	78	4.02	0.249	0.330	132.5
#4	774	80	4.02	0.249	0.306	123.0
#5	783	82	4.02	0.249	0.290	116.5
#6	789	84	4.02	0.249	0.253	101.5
#7	792	86	4.03	0.248	0.252	101.5
#8	793	88	4.04	0.248	0.251	101.3
#9	789	90	4.05	0.247	0.210	85.7
#10	789	92	4.05	0.247	0.230	93.2
#11	788	94	4.06	0.247	0.220	89.2
C-8-C/5	789	120	4.00	0.250	0.180	72.0
C-8-C/6	784	144	4.00	0.250	0.120	48.0
C-8-C/7	783	168	4.00	0.250	0.120	48.0
C-8-C/8	784	192	4.01	0.249	0.115	46.2
C-8-C/9	783	216	3.98	0.251	0.103	41.2
C-8-C/10	789	240	4.10	0.244	0.100	41.0
C-8-C/A-11	702	264	3.98	0.251		

Break-in Feed: Aramco Light Waxy Distillate
Run Feed: 50 Wt.% R.R.D. + 50 Wt.% M.C.O.
Gas Rate: 1000 SCF Pure Hydrogen per Barrel Feed
Catalyst: 100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE XII

TABULATED DATA FROM RUN A-CARTER-EIGHT-CATALYST

Sample No.	Hrs. on Stream	Avg. Wt.% S in Product (A-x)	$\frac{A-x}{A}$*	100 ($\frac{x}{A}$) = % Conversion = C	%Conversion Activity = $C/C_o(100)$	Loss in Conversion Activity = $\frac{C_o-C}{C_o}$
C-8-C/A-1	46	0.174				
C-8-C/A-2	48	0.169				
C-8-C/3	72	0.171	0.085	91.5		
C-8-C/4	96	0.240	0.119	88.1 = C_o	100	
#1	74	0.098	0.049	95.1 = C_o	100	
#2	76	0.125	0.062	93.8	98.5	
#3	78	0.140	0.069	93.1	97.8	
#4	80	0.160	0.079	92.1	96.7	
#5	82	0.171	0.085	91.5	96.1	
#6	84	0.195	0.097	90.3	94.9	
#7	86	0.200	0.100	90.0	94.5	
#8	88	0.202	0.101	89.9	94.4	
#9	90	0.241	0.120	88.0	92.5	
#10	92	0.224	0.112	88.8	93.3	
#11	94	0.233	0.116	88.4	92.9	
C-8-C/5	120	0.274	0.136	86.4	98.0	0.019
C-8-C/6	144	0.388	0.193	80.7	91.5	0.084
C-8-C/7	168	0.391	0.195	80.5	91.3	0.086
C-8-C/8	192	0.409	0.203	79.7	90.4	0.095
C-8-C/9	216	0.458	0.228	77.2	87.5	0.124
C-8-C/10	240	0.467	0.232	76.8	87.1	0.128
C-8-C/A-11	264	0.743				

*A_{Aramco} = 1.33 Wt.% S

A_{Carter} = 2.01 Wt.% S (50 Wt.% R.R.D. + 50 Wt.% M.C.O.)

Gas Rate: 1000 SCF Pure Hydrogen per Barrel Feed
Catalyst: 100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE XIII

TABULATED DATA FROM RUN B-CARTER-EIGHT-CATALYST

Sample No.	Temp. °F.	Hrs. on Stream	Space Velocity	1/S.V. act.	1/S.V. equiv.	% Activity = $\frac{S.V._{act.}}{S.V._{equiv.}}(100)$
C-8-C/A-1	704	56	4.05	0.247		
C-8-C/A-2	705	58	4.05	0.247		
C-8-C/3	712	72	3.94	0.254	0.297	117.0
C-8-C/4	786	96	3.98	0.251	0.220	87.8
C-8-C/5	787	120	3.96	0.253	0.165	65.3
C-8-C/6	784	144	3.93	0.255	0.125	48.0
C-8-C/7	779	194	4.08	0.245	0.118	48.2
C-8-C/8	784	216	4.04	0.248	0.105	42.4
C-8-C/9	784	240	4.08	0.245	0.100	40.9
C-8-C/A-10	711	273	3.99	0.251		
C-8-C/11	712	297	3.96	0.253	0.043	17.0

Break-in Feed: Aramco Light Waxy Distillate
Run Feed: 50 Wt.% R.R.D. + 50 Wt.% M.C.O.
Gas Rate: 1000 SCF Pure Hydrogen per Barrel Feed
Catalyst: 100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure: 200 p.s.i.g.

TABLE XIV

TABULATED DATA FROM RUN B-CARTER-EIGHT-CATALYST

Sample No.	Hrs. on Stream	Avg. Wt.% S in Product (A-x)	$\frac{A-x}{A}$*	$100 (\frac{x}{A})$ = % Conversion = C	%Conversion Activity = $C/C_o(100)$	Loss in Conversion Activity = $\frac{C_o-C}{C_o}$
C-8-C/A-1	56	0.189				
C-8-C/A-2	58	0.183				
C-8-C/3	72	0.164	0.092	91.8		
C-8-C/4	96	0.230	0.115	88.5 = C_o	100	
C-8-C/5	120	0.301	0.150	85.0	96.0	0.040
C-8-C/6	144	0.373	0.186	81.4	91.8	0.080
C-8-C/7	194	0.402	0.200	80.0	90.4	0.096
C-8-C/8	216	0.447	0.222	77.8	88.0	0.121
C-8-C/9	240	0.469	0.233	76.7	86.6	0.133
C-8-C/A-10	273	0.710				
C-8-C/11	297	0.887	0.441	55.9		

*A_{Aramco} = 1.33 Wt.% S

A_{Carter} = 2.01 Wt.% S (50 Wt.% R.R.D. ⌿ 50 Wt.% M.C.O.)

Gas Rate:	1000 SCF Pure Hydrogen per Barrel Feed
Catalyst:	100 gms. Nalco Esso 1/16-inch Extruded Cobalt Molybdate
Reactor Pressure:	200 p.s.i.g.

TABLE XV

TABULATED DATA FROM RUN ARAMCO-SIXTEEN COMPARISON RUN

Sample No.	Hrs. on Stream	Temp. ^oF.	Space Velocity (v./hr./v.)	Avg. Wt.% S in Product (A-x)	$\frac{A-x}{A}$*	100 $(\frac{x}{A})$ = % Conversion = C	%Conversion Activity = C/C_o (100)	Loss in Conversion Activity = $\frac{C_o-C}{C_o}$
Ar-16/1	52	725	1.028	0.168	0.126	87.4 = C_o	100	
2	76	720	1.005	0.219	0.165	83.5	95.6	.044
3	100	727	1.000	0.222	0.165	83.5	95.6	.044
4	124	720	1.004	0.232	0.199	80.1	91.7	.072
5	148	722	1.002	0.224	0.168	83.2	95.2	.048
6	172	723	1.001	0.240	0.181	81.9	93.8	.063
7	196	725	0.995	0.282	0.212	78.8	90.2	.098
8	220	725	1.038	0.300	0.226	77.4	88.7	.126
9	244	725	1.000	0.302	0.227	77.3	88.4	.127
10	268	723	1.003	0.295	0.222	77.8	89.2	.110
11	292	726	1.000	0.302	0.227	77.3	88.4	.127
12	316	727	1.000	0.309	0.232	76.8	88.0	.121
13	340	725	1.000	0.311	0.234	76.6	87.7	.123
14	364	724	1.000	0.322	0.243	75.7	86.7	.134
15	388	723	1.000	0.378	0.284	71.6	82.0	.181
16	412	725	1.000	0.324	0.243	75.7	86.7	.134
17	436	726	1.000	0.310	0.233	76.7	87.8	.122
18	464	725	1.000	0.326	0.243	75.7	86.7	.134
19	484	724	1.000	0.358	0.276	72.4	82.8	.172
20	508	725	1.000	0.349	0.262	73.8	84.4	.155
21	532	724	1.000	0.356	0.270	73.0	83.6	.165
22	556	725	1.000	0.354	0.268	73.2	83.8	.162
23	580	725	1.000	0.344	0.259	74.1	84.8	.152
24	604	725	1.000	0.345	0.260	74.0	84.7	.154
25	628	724	1.000	0.355	0.267	73.3	83.9	.162
26	652	725	1.000	0.349	0.262	73.7	84.4	.156
27	676	725	1.000	0.365	0.274	72.6	83.1	.170

$^*A_{Aramco}$ = 1.33 Wt.% S

Gas Rate: 500 SCF of 30% Methane + 70% Hydrogen per Barrel Feed

Catalyst: 100gms. Peter Spence Cobalt Molybdate   Reactor Pressure: 200 p.s.i.g.

TABLE XVI

TABULATED DATA FROM RUNS CARTER-SIX-CATALYST, CARTER-SEVEN-CATALYST, A-CARTER-EIGHT-CATALYST AND B-CARTER-EIGHT-CATALYST

Run Carter-Six-Catalyst
(24.5% Aromatics in the feed)

Hrs. on Stream	$\frac{S.V._{act.}}{S.V._{equiv.}}(100)$	$\frac{A}{A-x}$	$100\frac{C}{C_o}$	$\frac{C_o - C}{C_o}$
96	80	7.15	100	
192	55	5.54	95.0	0.050
264	44	4.62	91.0	0.090
312	39.5	4.62	91.0	0.090
384	36.5	4.42	89.6	0.102
456	33.0	4.14	87.9	0.121

Run Carter-Seven-Catalyst
(26.7% Aromatics in the feed)

Hrs. on Stream	$\frac{S.V._{act.}}{S.V._{equiv.}}(100)$	$\frac{A}{A-x}$	$100\frac{C}{C_o}$	$\frac{C_o - C}{C_o}$
96	83	8.09	100	
192	38.5	5.17	91.8	0.080
240	27.5	4.85	90.5	0.094
312	19.0	4.55	89.0	0.110
384	15.0	4.15	86.5	0.133
456	12.5	3.46	81.4	0.186

Run Carter-Eight-Catalyst
(29.0% Aromatics in the feed)

Hrs. on Stream	$\frac{S.V.\ act.}{S.V.\ equiv.}(100)$	$\frac{A}{A-x}$	$100\frac{C}{C_o}$	$\frac{C_o - C}{C_o}$
96	66.0	8.55	100	
192	33.0	4.96	90.4	0.095
240	25.0	4.30	86.8	0.130

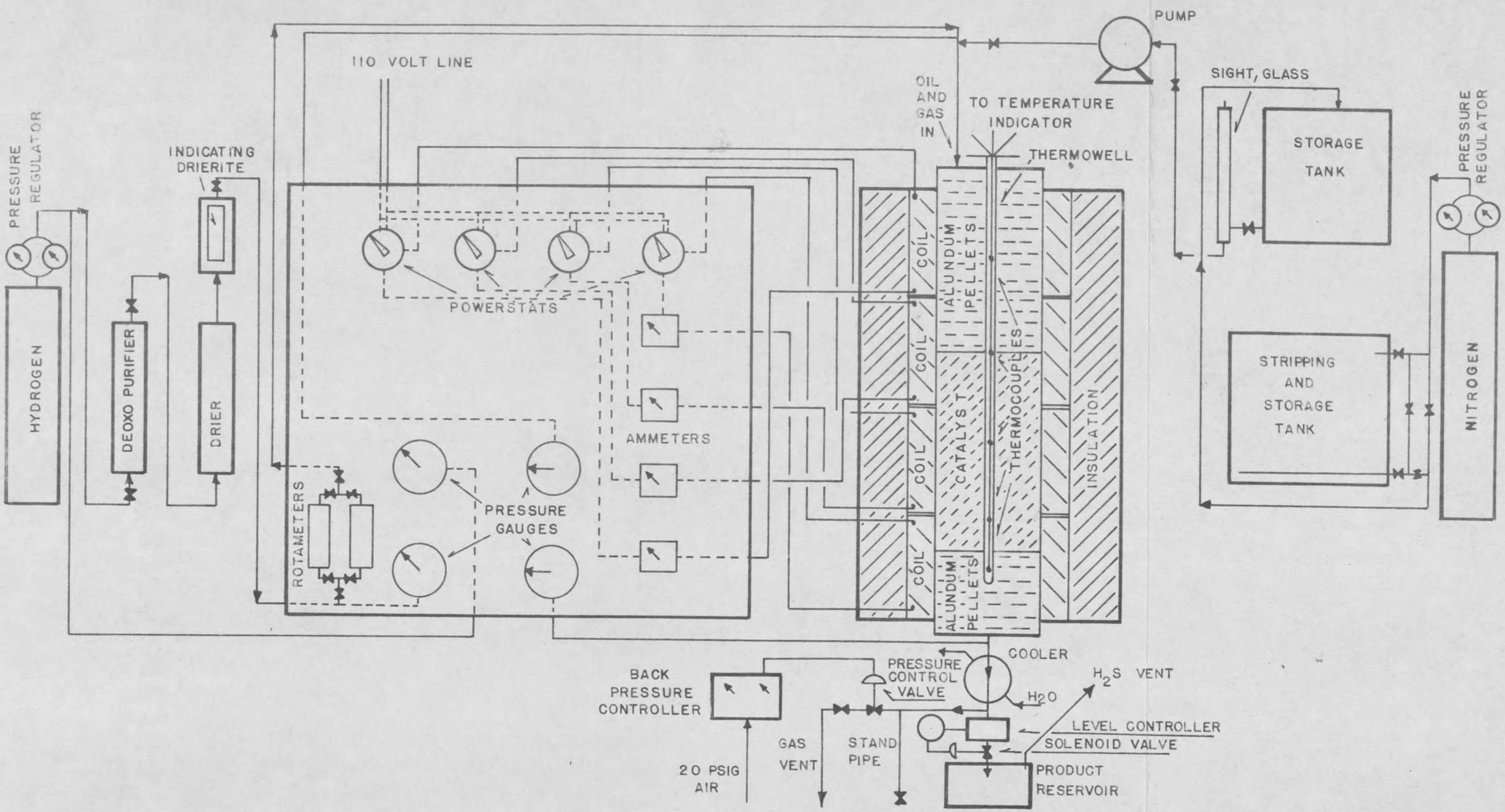

FIGURE 1 SCHEMATIC FLOW DIAGRAM OF THE DESULFURIZATION SYSTEM

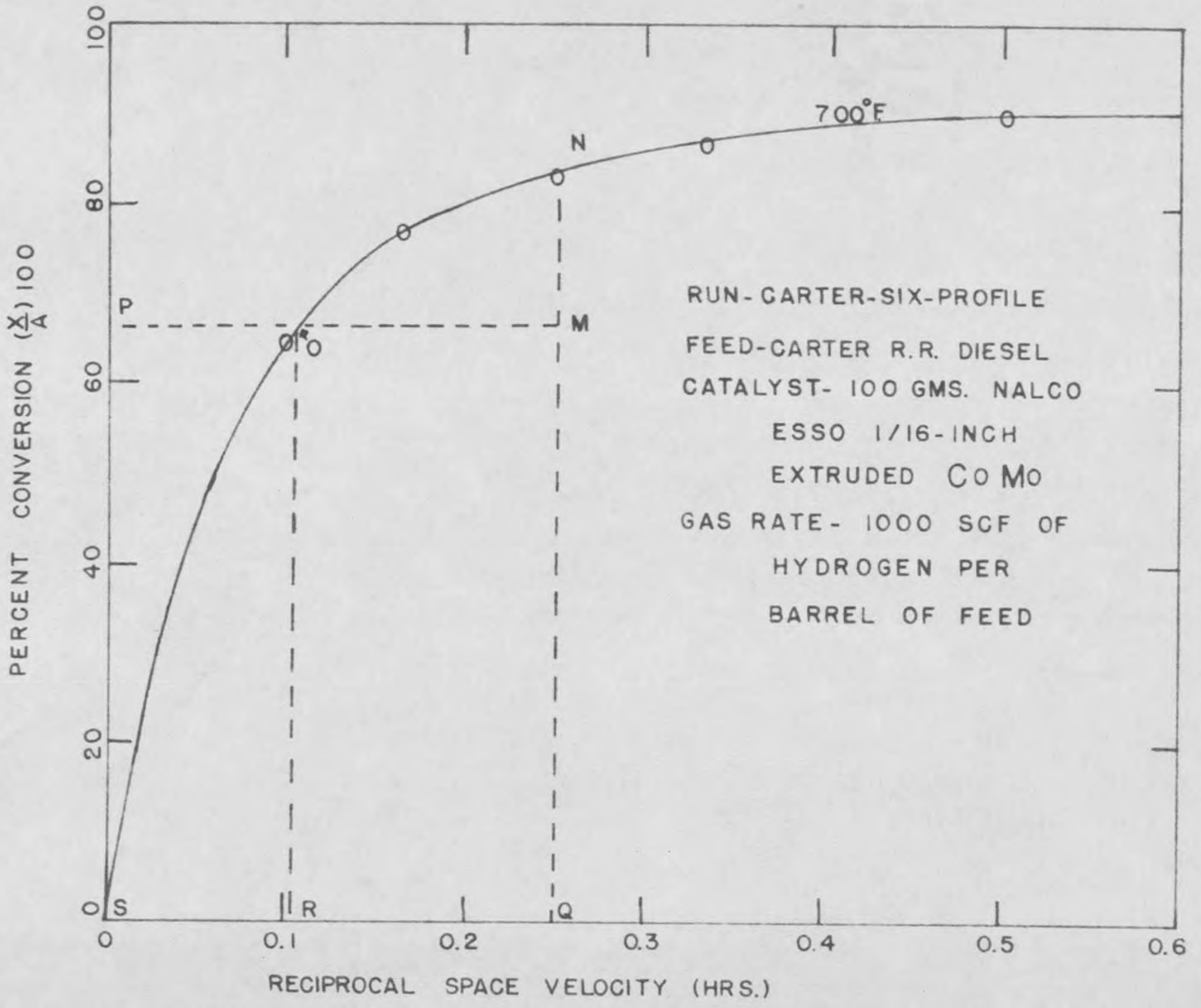

FIGURE 2 PERCENTAGE CONVERSION VERSUS RECIPROCAL SPACE VELOCITY

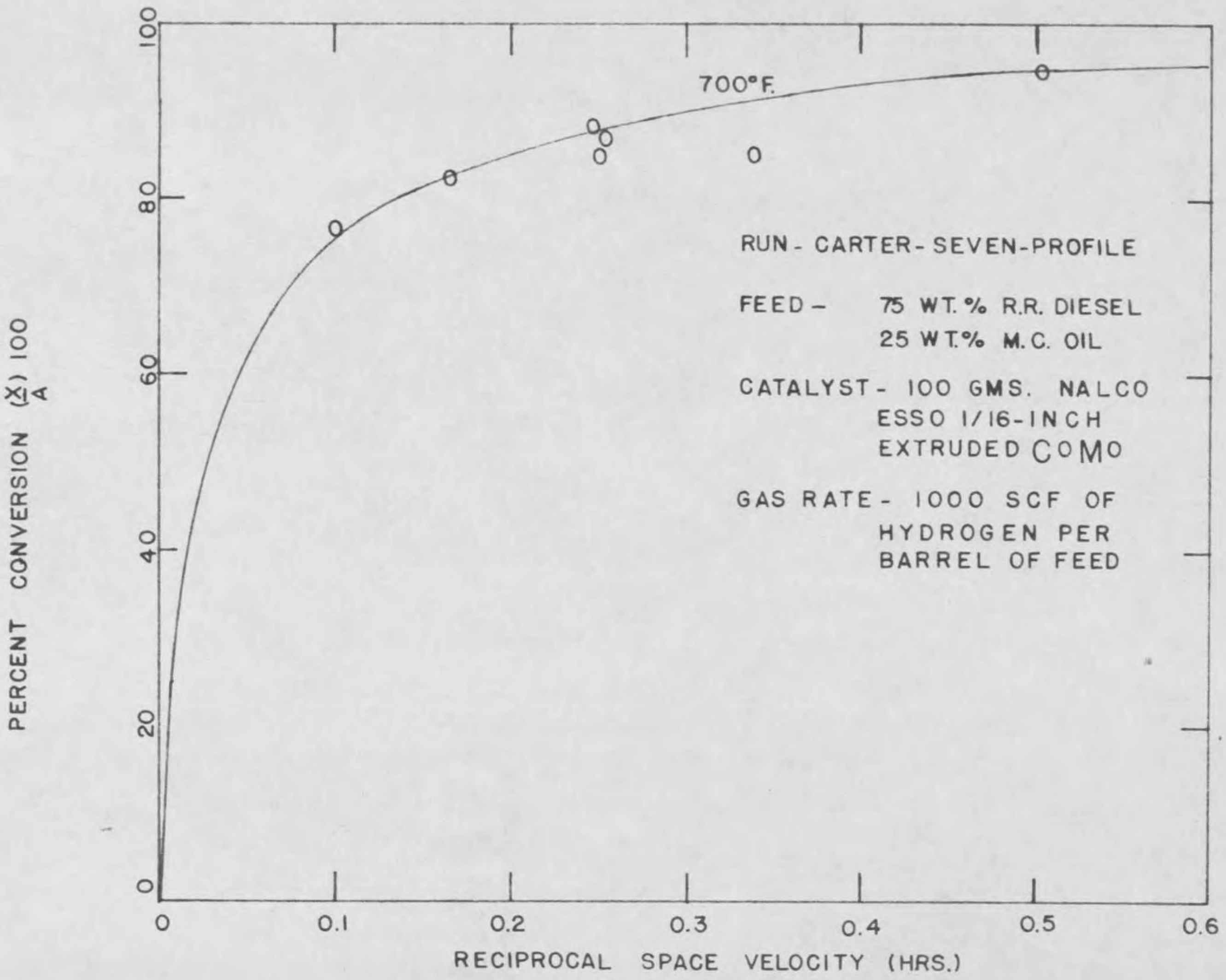

FIGURE 3 PERCENTAGE CONVERSION VERSUS RECIPROCAL SPACE VELOCITY

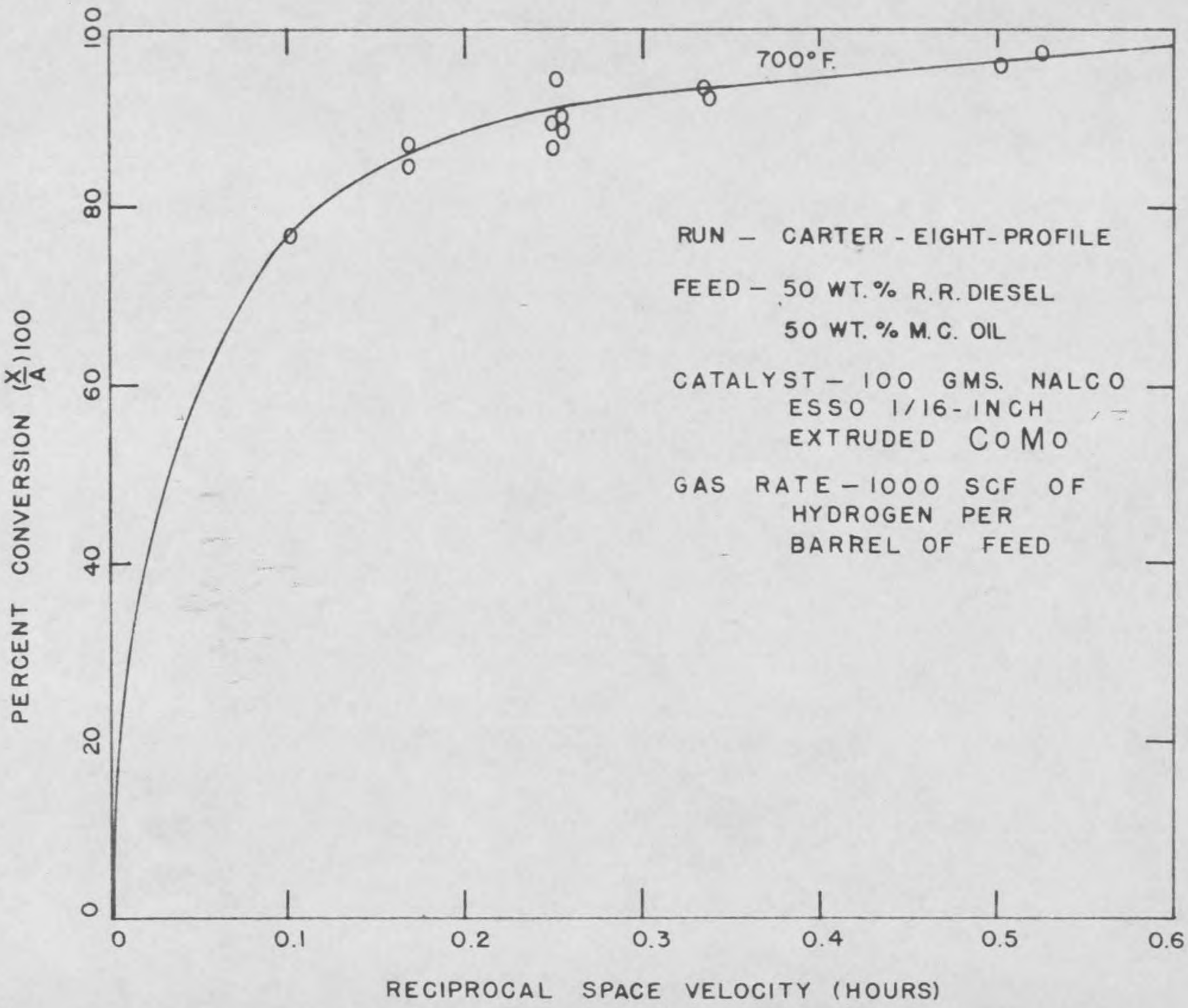

FIGURE 4 PERCENTAGE CONVERSION VERSUS RECIPROCAL SPACE VELOCITY

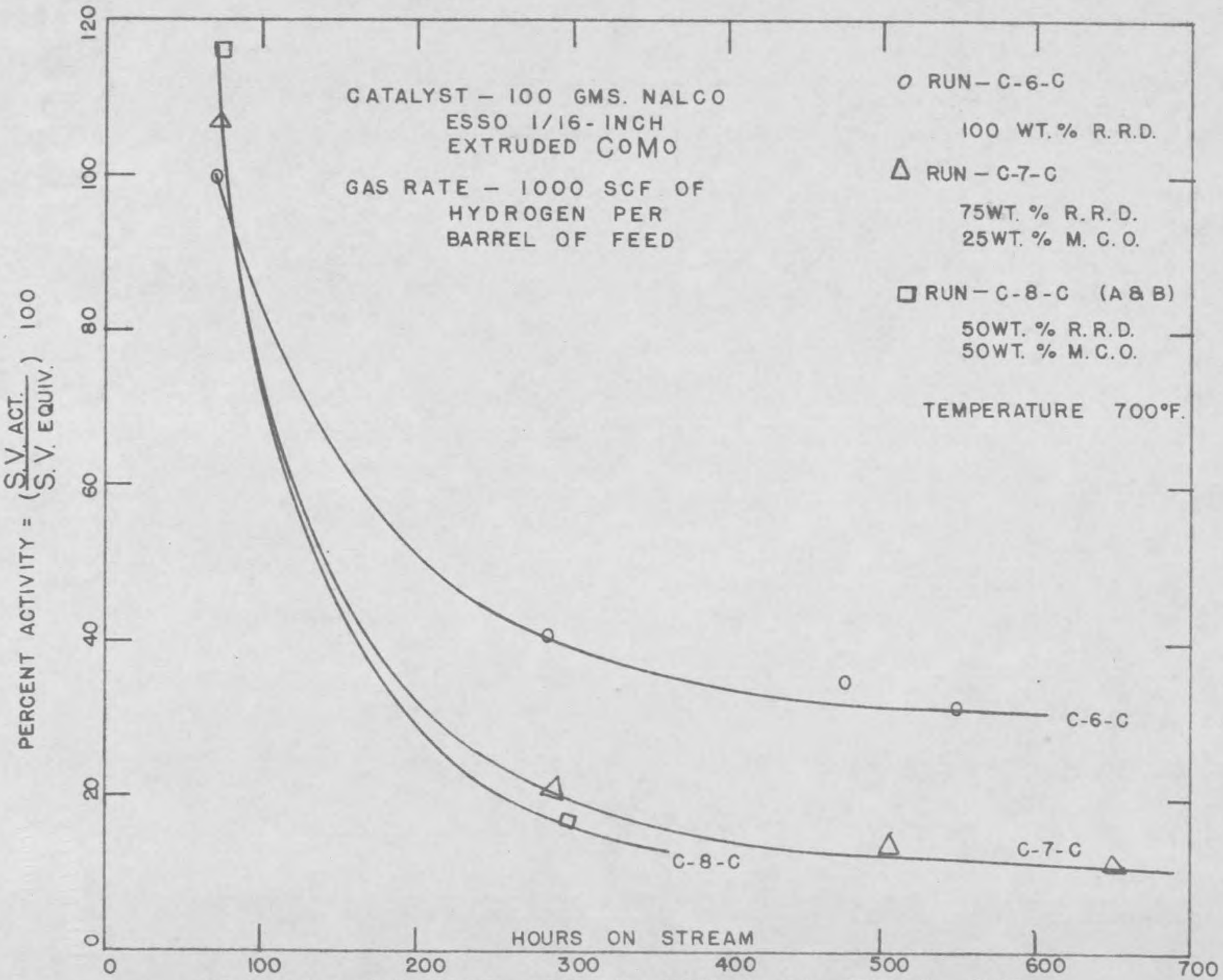

FIGURE 5 PERCENTAGE ACTIVITY VERSUS ON STREAM TIME

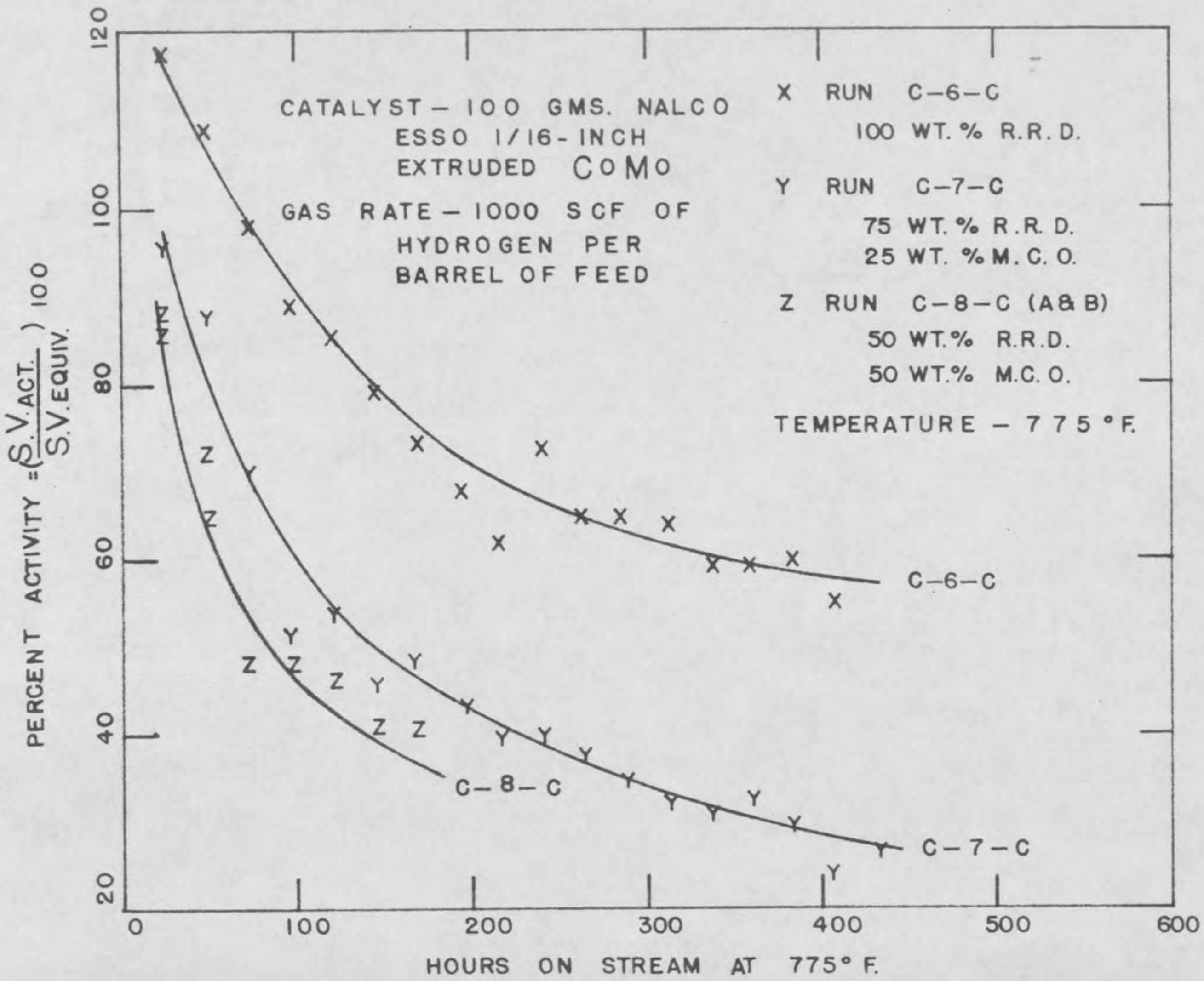

FIGURE 6 PERCENTAGE ACTIVITY VERSUS ON STREAM TIME AT 775° F.

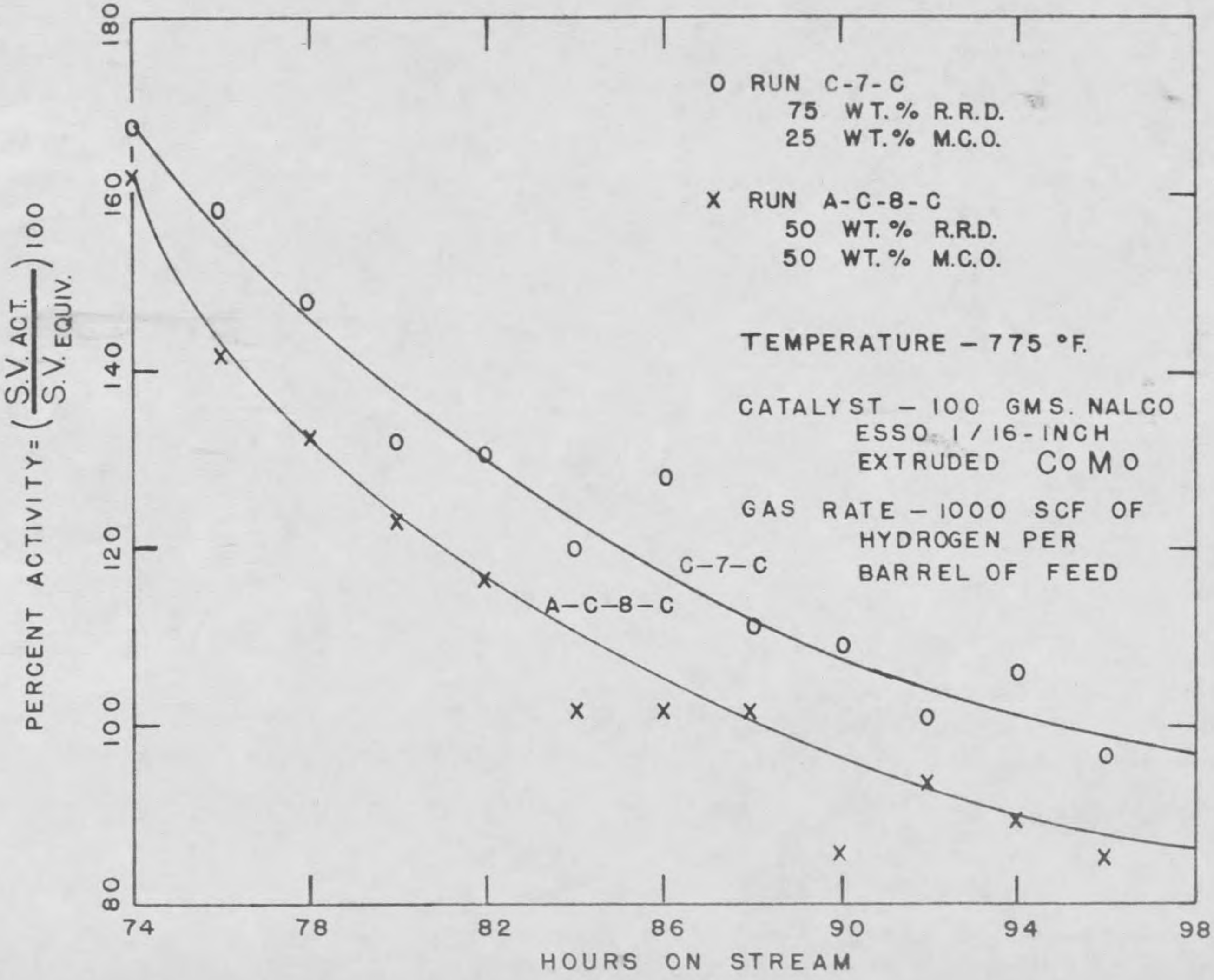

FIGURE 7 PERCENTAGE ACTIVITY VERSUS ON STREAM TIME

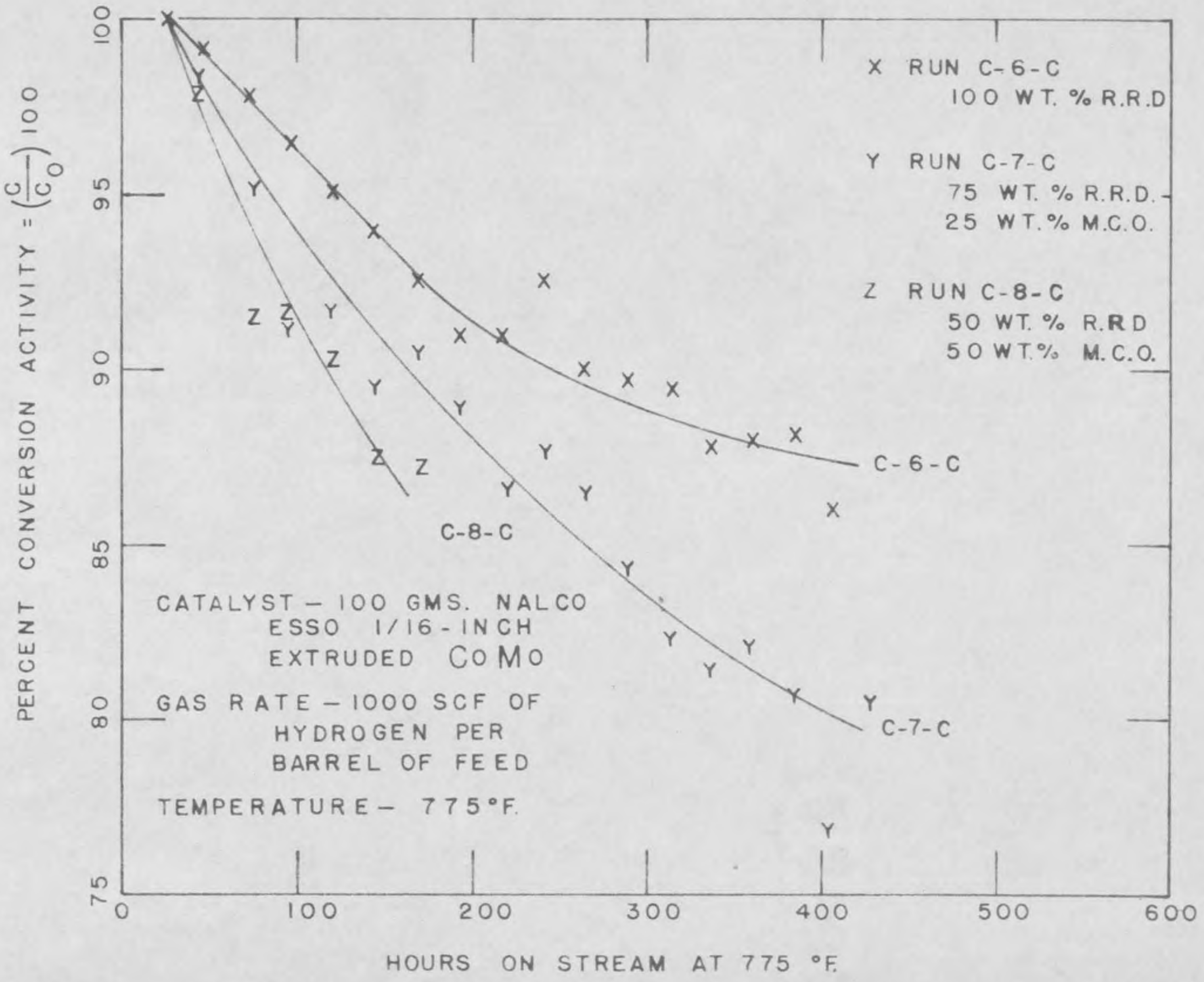

FIGURE 8 PERCENTAGE CONVERSION ACTIVITY VERSUS ON STREAM TIME AT 775°F.

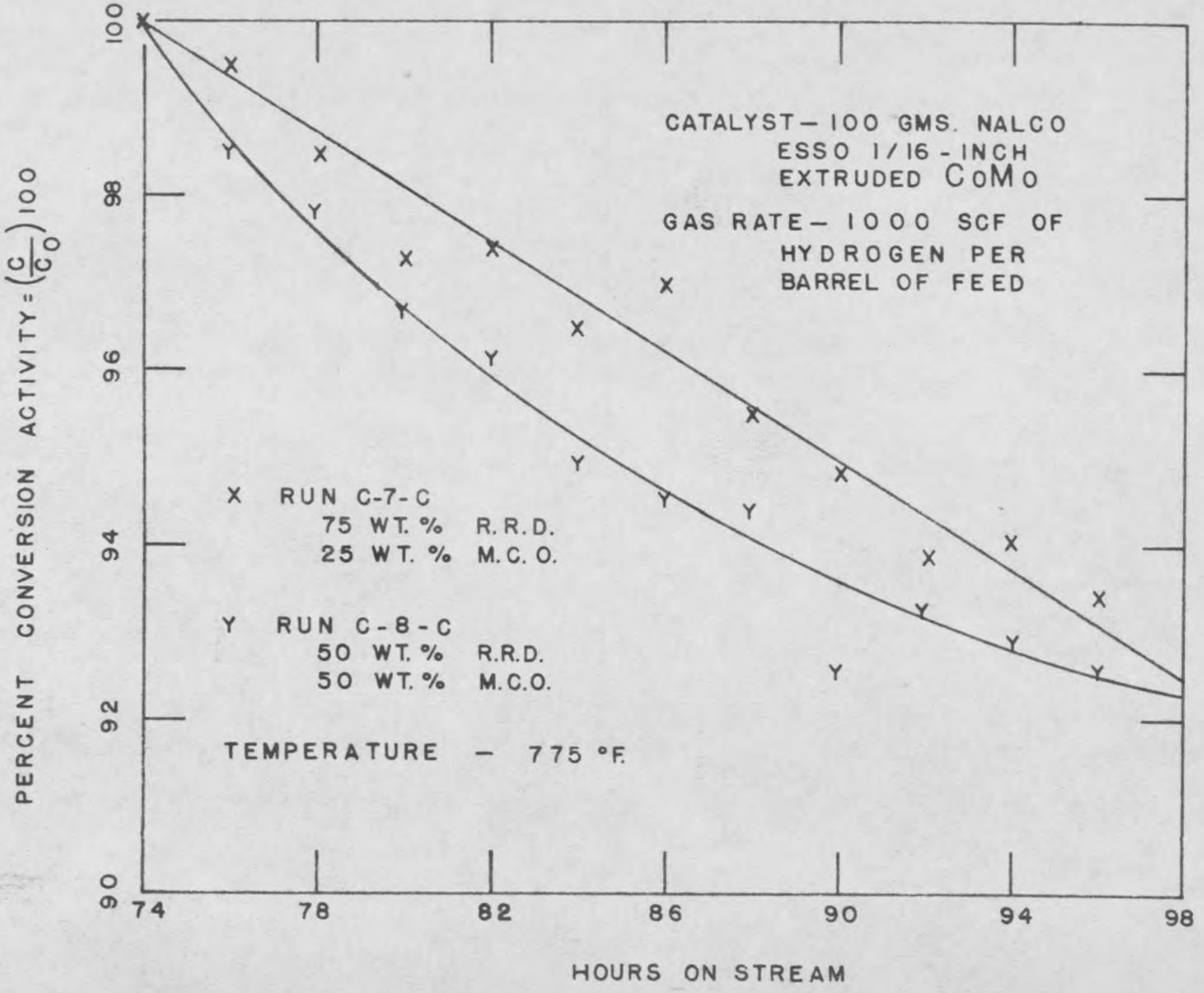

FIGURE 9 PERCENTAGE CONVERSION ACTIVITY VERSUS ON STREAM TIME

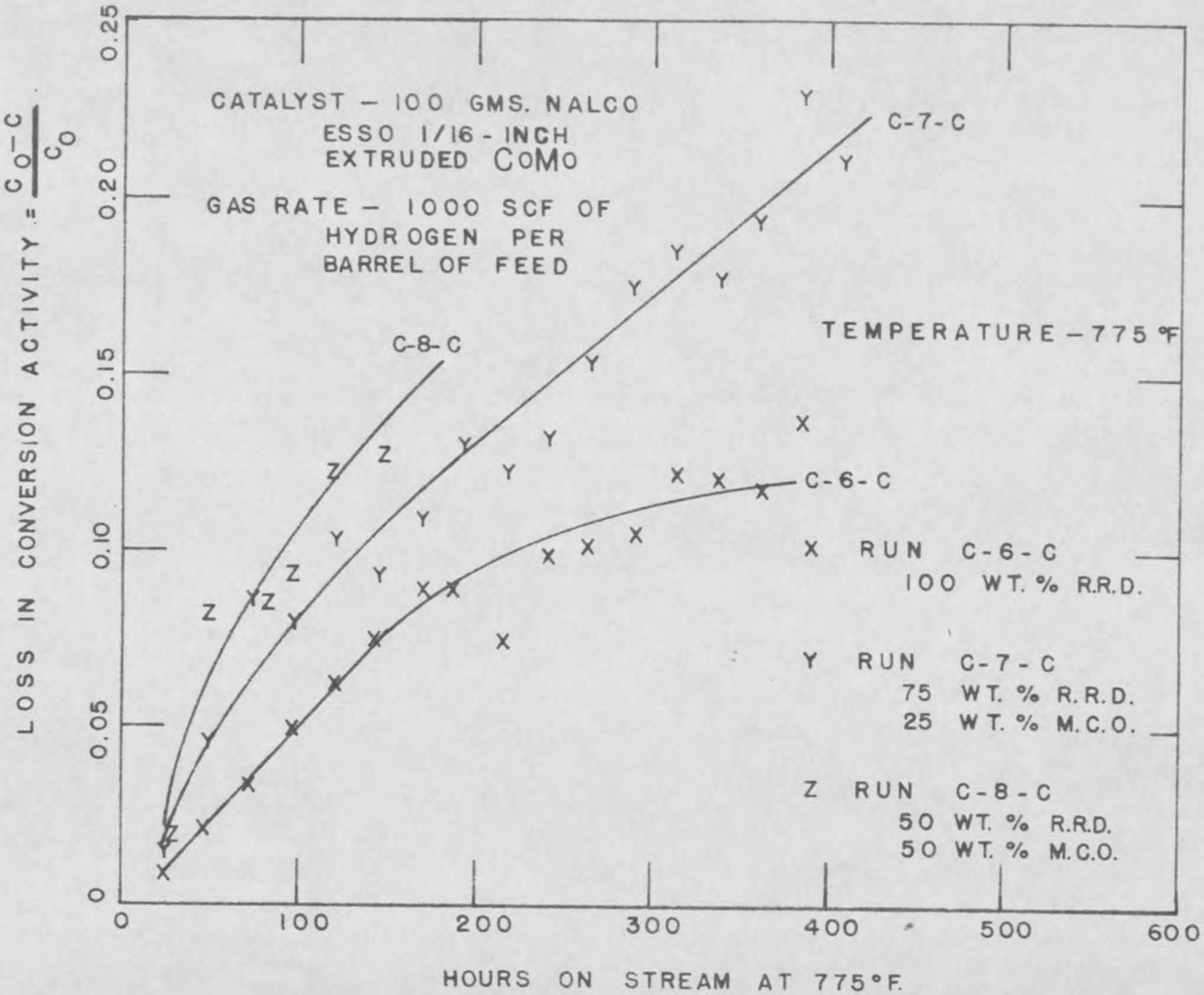

FIGURE 10 LOSS IN CONVERSION ACTIVITY VERSUS ON STREAM TIME AT 775 °F.

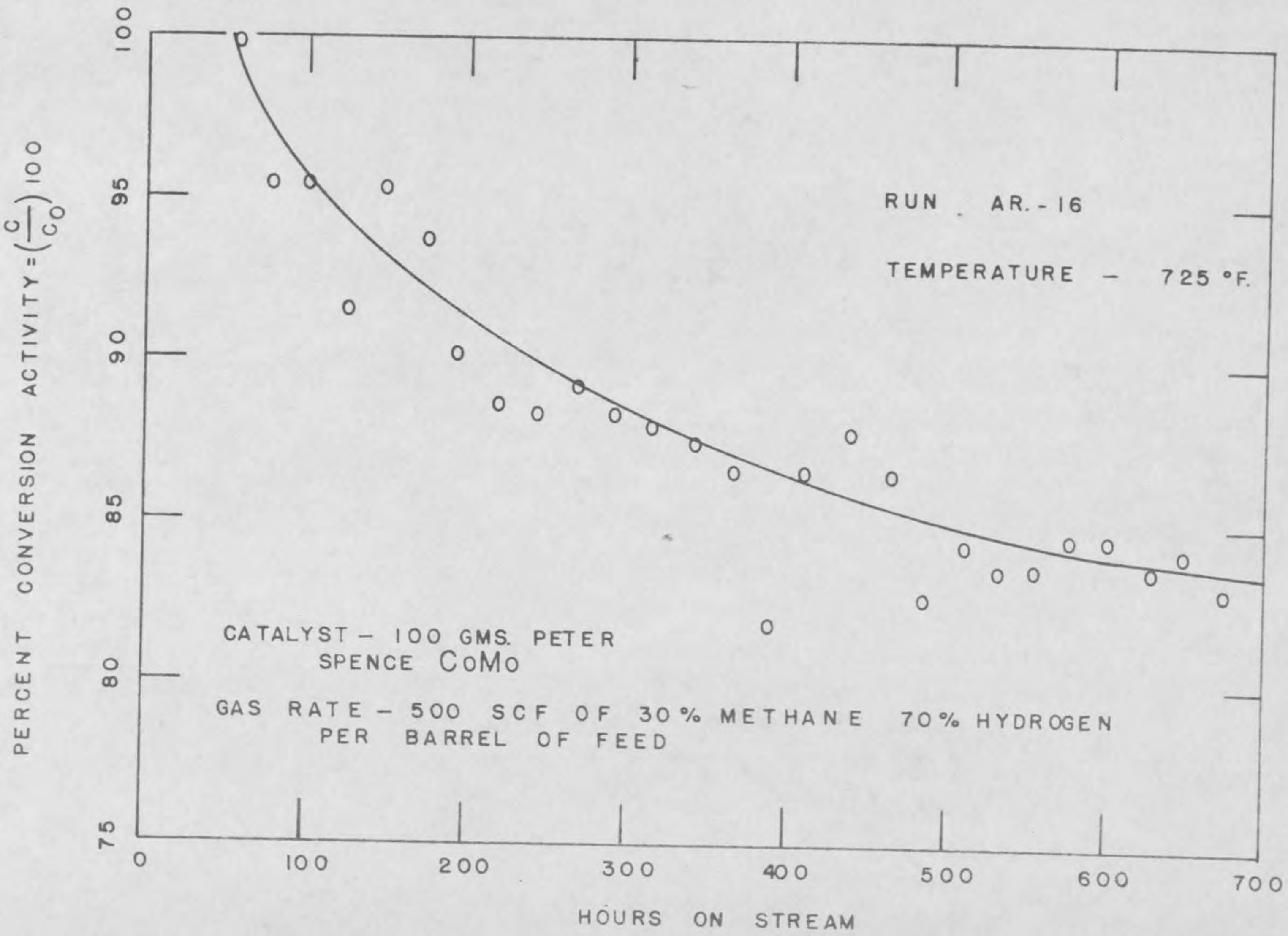

FIGURE 11 PERCENTAGE CONVERSION ACTIVITY VERSUS ON STREAM TIME FOR AR-16

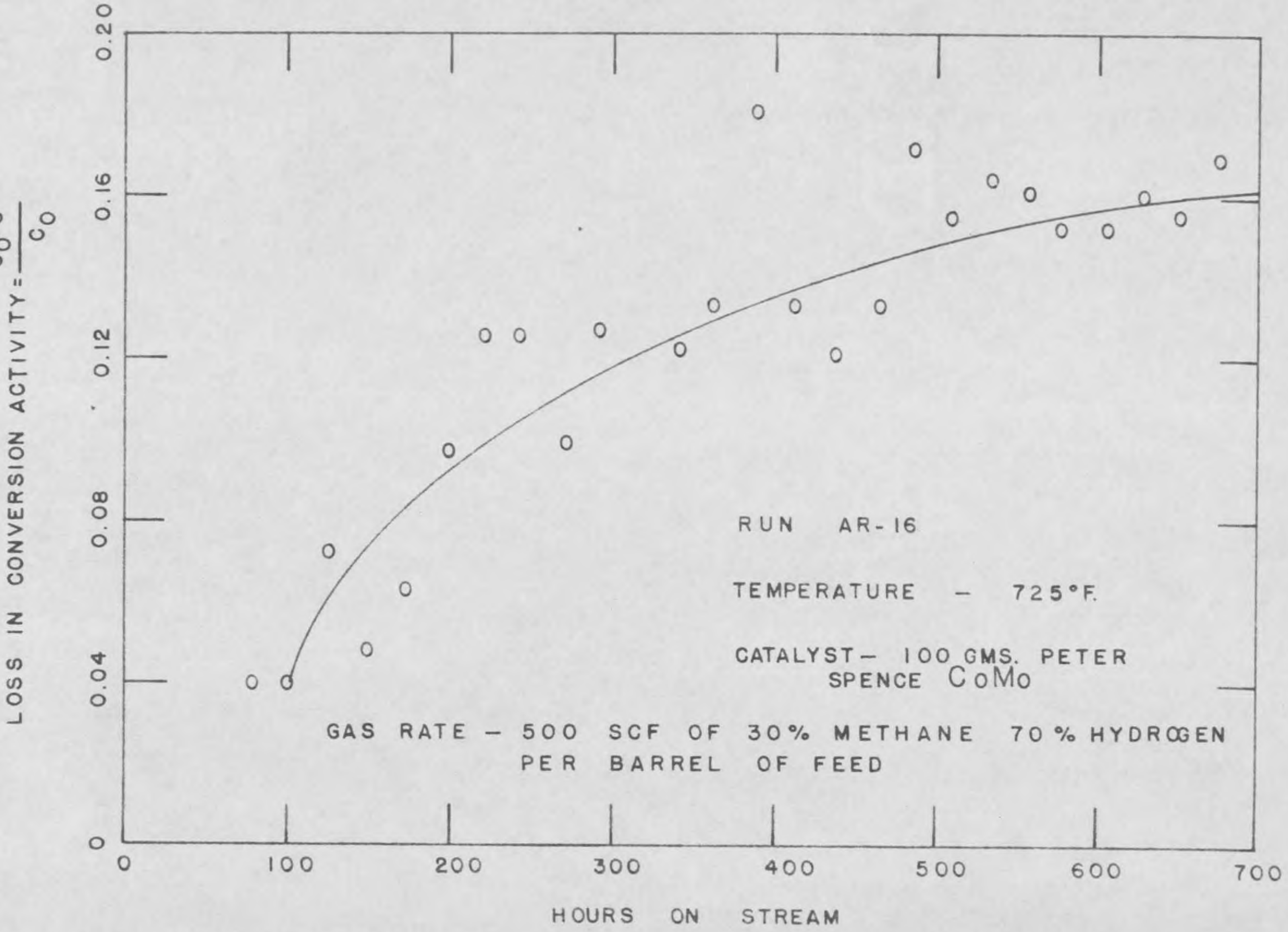

FIGURE 12 LOSS IN CONVERSION ACTIVITY VERSUS ON STREAM TIME FOR AR-16

131442

Opprecht, M. K.
Catalyst deactivation for catalytic hydrode-sulfurization.

	NAME AND ADDRESS
FEB 1 6 '61	INTERLIBRARY LOAN
AP 13 '61	Mary [illegible] [redacted]
DEC 22 '62 (S) MR	Jack [illegible]
11-29-67	[illegible]
[illegible]	Andr
" "	
2 weeks 4/10/	

131442