The catalytic desulfurization of Wyoming fuel oil
by Oscar H Koski

A THESIS Submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree
of Master of Science in Chemical Engineering at Montana State College
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Destructive hydrogenation is the only method investigated which will continuously produce a product less than O.5 percent sulfur.

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ABSTRACT

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INTRODUCTION

Because of its deleterious effects when present in engine fuels, the removal of sulfur from petroleum distillates has received considerable attention for several decades. Primary interest has centered on the desulfurization of gasoline because of the great demand for its use as a motor fuel. However, common methods for the desulfurization of gasoline are not applicable to the heavier distillates, mainly because of the difference in the types of sulfur compounds present. In general the sulfur present in heavier distillates is more predominantly thiophenic and hence not receptive to bauxite treatment. Also, the conversion of mercaptans to disulfides is not of any interest in the production of heavier distillates since the primary problem is the reduction of sulfur to specified limits.

Because of increased utilization of the distillates heavier than gasoline, such as diesel and jet engine fuels, additional incentive is placed on the development of processes capable of producing commercially a low sulfur product. The supply of low sulfur fuel oils are of particular importance to our national defense, since at the high temperatures of jet engine operation the oxidation compounds of sulfur will combine with the engine metal producing weakness where structural strength is of prime importance.

The purpose of this investigation was to discover the contact agents and processes necessary to produce a fuel oil with a sulfur content less than 0.5% per cent.

A literature survey was conducted for the purpose of indicating successful avenues of approach to this desulfurization problem. The results

of this survey show that a preponderance of work has been directed toward the desulfurization of gasolines and napthas. Some of the contact agents used for the desulfurization are as follows: bauxite, lead alumina, boron phosphate on alumina, charcoal impregnated with alkali, aspheron clays, and a cobalt molybdate catalyst. Among the agents used for sulfur removal from heavier distillates are nickel on alumina, copper and nickel on alumina and cobalt molybdate.

It is expected that a commercially successful contact desulfurization agent will satisfy the following criteria:

1. Practical desulfurization below temperatures of incipient carbon to carbon cracking.

2. Long catalyst life.

3. Practical regeneration.

4. Reasonable cost and availability.

For analysis of the first criterion it should be pointed out that the bond energy for a carbon to carbon bond $(58.6 \frac{K \ cal}{mol})$ is only slightly higher than that for a carbon to sulfur bond $(54.5 \frac{K \ cal}{mol})$; thus it would seem evident that any thermal cracking of the carbon to sulfur bond would be accompanied by considerable carbon to carbon cracking. This fact is substantiated by data (6) on the thermal cracking of sulfur stocks where seventy-five percent of the sulfur remained in the residue. A desulfurization agent must be selective in its action in order to effect desulfurization without degradation of the hydrocarbon molecules other than the sulfur containing molecule.

There are two types of contact agents which are of interest in effecting this selective desulfurization. One is the type of contact agent which

operates through the medium of chemical reaction, e.g.: NiO(2). This type

of contact agent has the inherent disadvantage of diminishing activity with

desulfurization accomplished, and thus frequent regeneration is required.

Another class of contact agents effects desulfurization through a process

of destructive hydrogenation. Cawley and Hall (3) destructively hydrogenated

thiophene and phenyl mercaptan with a molybdenum disulfide catalyst at twenty

atmospheres of pressure to produce hydrogen sulfide and a hydrocarbon.

Byrns et al (2) reported the desulfurization of gasoline high in sulfur with

a cobalt-molybdena-alumina catalyst. The choice of contact agents to be

used in the destructive hydrogenation of high sulfur stocks must of necessity

(1) have active sulfides as hydrogenation agents (molybdenum, tung-

sten etc.)

(2) or form unstable sulfides which yield active hydrogenation agents

at the temperatures below incipient cracking.

(3) or hydrogenation agents which do not form sulfides on contact

with sulfur bearing oil.

The inherent disadvantages of this process are the operational costs associ-

ated with production and recycling of large volumes of hydrogen in comparison

with the volume of oil treated. Since the economy of any process for desul-

furization is of prime importance, it is imperative that this investigation

should begin with the cheaper contact agents at the less expensive conditions

of operation.

An initial study was made on the degree of desulfurization possible

with bauxite, acid gases with bauxite, acid gases with alumina, and metallic

compounds on alumina, all at atmospheric pressure.

Additional work under super-atmospheric conditions was done on bauxite, molybdena-alumina, and cobalt molybdate. The effects of pressure, hydrogen to oil ratio, space velocity, temperature and cycle time were briefly investigated where the results indicated fruitful study.

EQUIPMENT, METHODS, AND MATERIALS

EQUIPMENT

Three reactors were used in this investigation. Two were designed for use at atmospheric pressure and one for use at super atmospheric pressures up to nine hundred pounds per square inch.

Schematic diagrams of the reactors and their auxiliary equipment are shown in Figures 1, 2 and 3. In general design these units were identical. They were constructed from steel piping, heated electrically and insulated with layers of asbestos tape and magnesia mud. Thermowells were placed at three-inch intervals along the catalyst bed. The preheat section consisted of either iron balls or berl saddles, the former being more suitable for good temperature control, but having the disadvantage of producing poor color stability in the product. The super atmospheric reactor, as shown in Figure 1, was constructed with a particular effort for safety of operation. Crecelius (4) gives an excellent detailed description of the construction of this reactor. Auxiliary equipment consisted of a calibrated manometer, Wet test meters, water cooled copper tube condensers, hydrogen tanks with pressure regulators, receiver flasks and alkali scrubbers. Iron-constantan thermocouples were used in conjunction with a Leads and Northrup indicating potentiometer for temperature measurement.

METHODS

Control and measurement of process variables were conducted as summarized in the following paragraphs:

1. _Temperature_: Temperature was controlled by adjusting the input to the Nichrome heating elements with auto-transformers. Temperatures were measured with Iron-constantan thermocouples used in conjunction with a Leeds and Northrup indicating potentiometer. Temperatures were read at five minute intervals and the arithmetic average for every sample period recorded.

2. _Hydrogen rate_: The hydrogen rate in the atmospheric pressure runs was controlled by adjusting the regulator needle valve and measured with a calibrated manometer. In the super atmospheric runs, hydrogen rate was measured with a wet test meter. Control of the hydrogen rate was exercised by adjusting the regulator outlet pressure in conjunction with a needle valve attached to the regulator and the reactor exit valve. At the beginning of each run, the reactor was pressureized and the regulator needle valve and reactor exit valve adjusted so as to give the desired rate of flow while maintaining the reactor at operating pressure. A running record was made of the volume of exit gases (H_2S free) and the hydrogen rate over each sample period was determined from these data. Although a small amount of uncondensed hydrocarbon gases may be in the hydrogen and a portion of the hydrogen consumed in the hydrogenation, it was calculated that these compensating errors would not introduce a total error of more than 10 percent in the hydrogen rate. Because the hydrogen rate decreased after the run commenced due to the increase in resistance of the catalyst bed and the decreasing of pressure in the hydrogen tank, it was impossible to fix accurately the hydrogen rate at the beginning of the run.

3. Space velocity: Space velocity was altered by pump adjustments and determined at the end of each run from calculations involving the weight of oil charged, the catalyst charge, and the on-stream time.

4. Pressure: The reactor pressure during super-atmospheric runs was controlled by manual adjustment of the reactor exit valve in coordination with visual observation of the reactor pressure gage.

The determination of the sulfur content of the product and stock oil and the carbon laydown on the catalyst was determined in the following ways:

(1) Sulfur content: Sulfur content of the influent and effluent oil was determined by the lamp sulfur method, (1). In brief, this method involves the combustion of a weighed sample of oil and the absorption of the sulfur dioxide produced in a known amount of base. The excess base is determined by titration with a suitable acid and indicator.

(2) Carbon laydown: Carbon laydown during atmospheric pressure was determined by catalyst weight gain. This method is inherently in error due to the loss of moisture by the catalyst and the gain in weight due to adsorption of oil. Though these factors are compensating in effect, the latter is generally larger. Carbon laydown during super atmospheric runs was determined by burning the carbon off the catalyst below 600°C. The exhaust gases were metered and analyzed with an orsat for CO, O_2, and CO_2 content. Carbon laydown was calculated from the meter readings and carbon content of the burn-off gases as shown in the sample calculations. This method tends to yield higher results than actual due to the presence of adsorbed H_2S and oil on the catalyst and the oxidation of the metallic

sulfides to metallic oxides and sulfur dioxide. This error can be limited by careful blow down of the catalyst with hydrogen at the end of each run. It might be noted here that steam-stripping of the bauxite catalyst without burnoff reduced its activity presumably due to adsorbed water vapor. This phenomenon would perhaps not exhibit itself if burn-off was conducted after stripping, since it would tend to remove the adsorbed water.

MATERIALS

This study was made exclusively on a commercial grade of fuel oil available from the Husky Oil Co. of Cody, Wyoming. This particular distillate is known as Husky #3 fuel oil and has the following properties:

1. Boiling point range ($460-660^\circ F$)

2. Mean Molecular weight (Calc. of 200)

3. Specific gravity   0.8734

4. Sulfur content   2.10%

5. A.S.T.M. Distillation Table I

A list of catalysts used in this study, together with identification codes and the manufacturing concern, is given in Table II. This list includes a nickel bauxite (Porocel) with nickel nitrate and decomposing the nitrate at $440^\circ C$ in a stream of air. The nickel was then reduced with hydrogen.

SAMPLE CALCULATIONS

The calculations involved in the determination of space velocity, hydrogen to oil ratio, and carbon laydown are best demonstrated by those computed from typical runs. The following is the data recorded on one such run.

V - 1 O.K., B.M., K.G., p. 87   July 26, 1951

Run 70

Cat. 1000 grms. Harshaws Cobalt-Moly.   Bar 641.0 ^{mm}Hg.
(Same as Run 69   No Regen.)

Reactor Press. 300 #/in^2 S. V. to be calc.

Time Min.	Samp. No.	Samp. Wt.	% S	Avg. Temp. °C	Liters Exit H_2	Temp. Exit H_2
0-30	1	404	0.311	400	222	24°C
30-60	2	428	0.348	399	393	24°C
60-90	3	461	0.343	408	605	24°C
90-120	4	423	0.355	403	798	24°C
120-150	5	433	0.333	404	980	24°C
150-180	6	513	0.346	400	1131	24°C

Total effluent   2662

Oil charged   2802 grams
Oil out   2662 grams

Total losses =   140 grams

A. Calculation   % Loss on Charge

$$\frac{140 \times 100}{2802} = 5.0\%$$

B. Calculation of Space velocity

$$\frac{2802 \text{ grms. oil charged}}{3 \text{ Hrs. (1000 grams cat.)}} = 0.934 \frac{\text{grms. oil}}{\text{grm. cat. hr.}}$$

C. Calculation of average sulfur in effluent

Wt. sample	% S	Wt. Sulfur in Effluent
404	x 0.311	1.255
428	x 0.348	1.489
461	x 0.343	1.581
423	x 0.355	1.503
433	x 0.333	1.443
513	x 0.346	1.775
		9.046 grams

$$\text{Avg. Sulfur in eff.} = \frac{9.046 \text{ grams S.}}{2662 \text{ grams eff.}} = 0.340$$

D. Calculation of Hydrogen to oil ratio (avg.)

V.P. H_2O at $24^{\circ}C$ = 22.4 m.m. Hg.

P.P. dry H_2 = 641.0 - 22.4 = 618.6 m.m. Hg.

$$\frac{618.6}{760} \times \frac{(273)}{273 + 24} \times \frac{1131.1}{2802 \text{ grms. oil}} = 0.302 \frac{\text{Liters } H_2 \text{ S.T.P.}}{\text{grm. oil}}$$

E. Calculation of Burn-off

Since regeneration of the catalyst on the run from which the preceeding data were taken is not warranted, the following data were substituted from another run.

Data: (Plotted Fig. 1A)

Time Minutes	5	15	30	60	90	120
Liters Effluent	12.5	37.5	75	150	225	300
by Analysis						
CO_2	10.0	14.7	15.1	13.2	6.0	1.5
CO	3.4	2.3	2.4	2.5	1.0	0
O_2	0.2	0.5	0.5	1.1	10.0	15.2
Total CO + CO_2	13.4	17.0	17.6	15.7	7.0	1.5

(Total Vol. Effluent in Liters $(CO_2 + CO)$ by) = 36.1 liters
(graphical integration of Fig. 1A)

Temperature = $24^{\circ}C$ $V.P.H_2O = 22.4$ Press. = 639

$$\text{Wt. Carbon Burned off} = \frac{(639-22.4)^{*}}{760} \times \frac{273}{273 + 24} \times 36.1 = 14.4 \text{ grms. Cbn}$$

* Correction for V.P. of H_2O necessary since gases are metered with wet test meter.
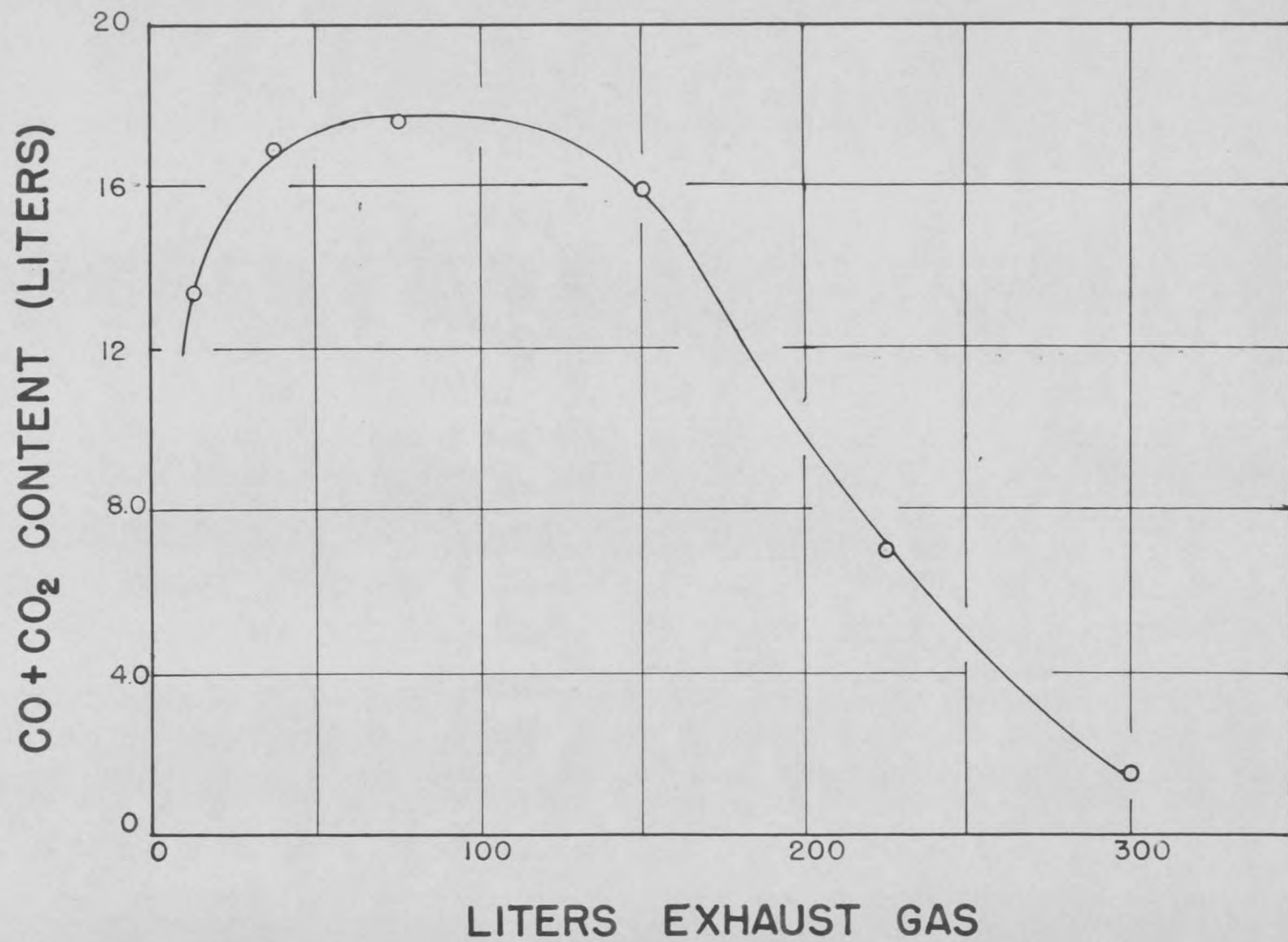
Fig. 1A Plot of Burn-off Data

RESULTS AND DISCUSSION

Desulfurization characteristics of various catalysts at atmospheric
pressure.

Table III and Figures 4, 5, and 6 present the desulfurization char-
acteristics of acid activated bauxite, acid activated alumina, chrome-
alumina, molybdena-alumina, Harshaws cobalt molybdate and Union Oil Co.
cobalt molybdate. These tests were conducted at atmospheric pressure, a
space velocity of 1.083 grams of oil per gram of catalyst per hour, average
run temperatures from 407 to 422°C, a hydrogen rate of 1.74 ft^3 S.T.P. per
hour, and an on stream time of two hours on five hundred gram samples of the
catalysts as identified in Table II. A schematic diagram of the apparatus
is found in Figure 3. The charged oil, which is standard throughout this
study, contains 2.10% sulfur. It may be noted that the metal oxide-alumina
catalysts (Fig. 6) exhibit a characteristic decline in activity with on-
stream time. As with the work of Haas (5), this is apparently due to the
formation of metallic sulfides. The best desulfurization was obtained with
molybdena-alumina which gave an average effluent of 1.08 per cent sulfur.

The acid activated alumina catalyst exhibits low initial activity with
the HCL activated alumina yielding the best results. (Fig. 5). The acid
activated bauxite catalysts (Fig. 4) yield about the same overall result
with the HF activated bauxite exhibiting the highest initial activity and
the HCL activated bauxite the highest final activity. BF$_3$ activated bauxite
gave a product of good color stability while the others did not. The maxi-
mum overall desulfurization for this group was obtained with acid activated
bauxite, with the effluent oil containing an average of 1.01 per cent sulfur
for the two-hour period.

<u>The relationship of pressure, hydrogen rate, temperature and space</u>

<u>velocity to desulfurization with bauxite.</u>

The data relative to the effect of hydrogen rate on the desulfurization

of this oil at atmoshperic pressure may be found in Table IV. For a plot

of the results of these six runs, refer to Fig. 7. This plot shows no dis-

cernable effect of hydrogen rate from rates of zero to 1.74 ft^3 S.T.P. per

hour.

The relationships existing between temperature and desulfurization with

bauxite catalyst at space velocities of 4.1 and 1 gram of oil per gram of

catalyst per hour are presented in Table V and Fig. 8. This plot indicates

that the same desulfurization can be obtained at both space velocities in

the vicinity of 440°C. Since temperature and contact time may be considered

as a composite variable, it is odd that at the same temperature two values

of contact time should yield the same result unless the reaction went to

completion. Thus, it is indicated that about half the sulfur present in

the oil is receptive to bauxite treatment. The maximum desulfurization ob-

tained was such as to yield a product slightly over one per cent sulfur.

The effect of space velocity on desulfurization with a HF activated

bauxite and with bauxite alone is given in Tables VI and VII. Fig. 9 gra-

phically presents this relationship. It may be noted, by inspection of this

plot, that convergence of both space velocity curves to yield a product of

slightly less than one per cent sulfur at zero space velocity is indicated.

The space velocities range from 8.2 to 0.25 grams of oil per gram of cat-

alyst per hour. In theory, the discussion of the preceding applies here also.

Maximum desulfurization should be obtained at the longest contact times or lowest space velocities. This is substantiated by the results.

The effect of pressure on desulfurization can be determined from the results of two runs on fresh bauxite catalyst at atmospheric and 500 psig as recorded in Table VIII. The effect of pressure is shown to be only slightly negative. The implication drawn from this fact is that the portion of the desulfurization taking place under bauxite treatment is primarily of an irreversible nature. The parent hydrocarbon molecule containing sulfur yields a condensible product in the boiling point range of $196°F$ to $660°F$ and hydrogen sulfide and other gaseous products not liquefied in a water cooled condenser.

It might be added that recycle of the oil reduced the sulfur content to a minimum of slightly less than one per cent. This substantiates the data on space velocity versus desulfurization (Fig. 9) where the effect of infinite contact time or zero space velocity showed a minimum of slightly less than one percent sulfur in the effluent. Recycle oil with a sulfur content of 1.1 per cent was treated with a nickel impregnated bauxite (8% Nickel) with the result of only 0.022 grams of sulfur removed per gram of nickel. Regeneration of this catalyst by successive air oxidation and reduction with hydrogen failed. Desulfurization was then equal to that obtained by recycling over bauxite.

A correlation between desulfurization and per cent total loss on oil charged was compiled from the results of 17 runs on bauxite, acid activated bauxites, and alumina catalysts. (Table IX, Fig. 10). The runs were conducted at atmospheric pressure over a range of space velocities of 0.5 to 8.2 grams of oil per gram of catalyst per hour, and temperature ranging

from 350° to 450°C. It can be deduced that desulfurization to a product
of slightly over one percent sulfur will involve a total loss of slightly
over 5 per cent for bauxite and from 6 to 9 per cent for acid activated
bauxites. These losses include carbon laydown and uncondensed gases.
Bauxite in several two-hour runs shows no catalyst weight gain which was
a measure of carbon laydown.

Desulfurization through destructive hydrogenation with molybdena-alumina and cobalt molybdate catalysts.

The mechanism of the elimination of the sulfur compounds not receptive
to bauxite treatment may be proved to be one of hydrogenation. Through the
exclusion of hydrogen or the hydrogenation catalyst desulfurization is
markedly decreased. (See Table VIII)

The relationship existing between desulfurization and temperature was
obtained from the data of three runs on molybdena alumina catalyst and
plotted in Fig. 11 from the information in Table X. These were subject to
limitations in practical use as a reference because of the numerous factors
affecting results. These factors will be discussed later. This curve was
found useful, however, in the decision to investigate the effects of other
process variables in the neighborhood of 400°C, since a large increase in
desulfurization is not indicated with increasing temperatures. From general
considerations, a minima should be obtained in the plot of desulfurization
vs. temperature on an overall average of long period runs, since the carbon
laydown and consequent deactivation of the catalyst would, at some point,
be greater than the increased desulfurization obtained by raising the tem-
perature. Since temperature and hydrogen to oil ratio both affect carbon

laydown as shown in Table 11, higher temperatures may be used in conjunction with higher hydrogen to oil ratios without prohibitive carbon laydown.

An indication of the effect of pressure on the desulfurization effected with a molybdena-alumina catalyst is shown in Table XII and in Figure 12. The data was selected from runs after five and six regenerations to limit the effect of regeneration. Inspection of Fig. 13 (Runs 80, 81, and 82, Table XIII) substantiate the results of Fig. 12, since a greater increase in desulfurization is realized than can be expected from the difference in hydrogen to oil ratio. Also, the deduction that the mechanism is one of hydrogenation is in part substantiated by the fact that increased pressures give increased desulfurization. However, from general considerations, the effect of pressure increase should also tend to reverse the elimination of hydrogen sulfide unless the reaction is of an irreversible nature. The effect of higher hydrogen to oil ratios should tend to minimize this negative effect of pressure.

The effect of hydrogen to oil ratios upon desulfurization with a molybdena-alumina and a cobalt molybdate catalyst is indicated in Fig. 13, which was plotted from the data obtained from 14 runs at temperatures in the vicinity of $400^{\circ}C$ and space velocities from 0.764 to 1.011 grams of oil per gram of catalyst per hour, as presented in Table XIII. Lines are drawn through those points which are best suited for comparison with respect to the number of regenerations on the catalyst preceding the run, and the history of the catalyst. "Wild" results were obtained from runs 80, 81, 82 (Table XIII) using high hydrogen to oil ratios. This is apparently caused by the difference in the history of the catalyst. In elucidation of this

remark, it must be pointed out that the catalyst which produced these results
(Runs 80, 81, and 82, Table XIII) was never exposed to low hydrogen to oil
ratios or temperatures in excess of 410°C. It may be theorized that in the
runs at low hydrogen to oil ratios (Run #51 etc.) the formation of a more
active molybdenum sulphide took place. Since both hydrogen to oil ratios
and temperatures were different for the two tests on fresh molybdena-alum-
ina catalyst at 300 psig (Runs 57 and 86) Table XIII, the precise reason for
the variance in activity is not known. From the data on runs 60, 70, and 71
Table XIII, it should be noted that the cobalt molybdate catalyst exhibited
a period of increased activity during the second three hour run. This also
may be attributed to the formation of a highly active molybdenum sulfide.
If this is true, it would lend credence to the assumption that an active
molybdenum sulphide is formed at about 400°C and at low hydrogen to oil ratios.

In theory, the hydrogenation should be determined by hydrogen pressure
alone. One may then wonder at the increased desulfurization effected with
higher hydrogen to oil ratios. This fact is best explained by the deduction
that the hydrogenation and elimination of hydrogen sulfide from the parent
hydro-carbon molecule is reversible reaction and thus, the higher hydrogen
to oil ratios tend to shift the equilibrium toward the production of the
hydrocarbon and hydrogen sulfide by removing and diluting the hydrogen sul-
fide. Since bauxite will remove that portion of the sulfur, it might be
found feasible to bauxite treat the oil previous to hydrogenation to reduce
the sulfur compound concentration and, consquently reduce the hydrogen to
oil ratios necessary for a given desulfurization. Also, the efficiency of
the hydrogenation might be improved by concentrating the sulfur bearing

portion of the oil through solvent extraction followed by bauxite treatment and hydrogenation.

The effect of regeneration by air oxidation can be deduced from a study of Fig. 13. Cobalt molybdate, after one regeneration, though vastly more active in a fresh condition, approaches the activity of molybdena-alumina. The effect of regeneration on molybdena-alumina can be ascertained by following the code given on Fig. 13. In general, regeneration decreases the activity of the catalyst.

The total loss on oil charged for both molybdena-alumina and cobalt molybdate is in the range of from 4.5 to 8 per cent. However, in review, the losses with bauxite alone, are also in this range.

The laboratory data from which the previous figures and tables were compiled is presented in Table XIV.

SUMMARY

One may justly criticize some of the deductions and discussion presented in the results as not being supported by a sufficient bulk of data. These were included, however, with the hope that they may be of assistance to those who continue the work upon this desulfurization problem.

Of the tests at atmospheric pressure on acid activated alumina, chrome-alumina, molybdena-alumina, cobalt molybdate and acid treated bauxites, the acid treated bauxites gave the lowest overall desulfurization for the two-hour period and were unique in the fact that activity was fairly uniform throughout the test.

Desulfurization with bauxite or HF activated bauxite reaches a maximum where the effluent oil contains approximately one percent sulfur. Attendant losses are 5.2 percent with bauxite and 6 to 9 percent for HF and bauxite. Continuous desulfurization through destructive hydrogenation to a product lower than 0.5 percent sulfur for periods in excess of nine hours at space velocities of one is possible with both cobalt molybdate and molybdena-alumina. The respective hydrogen to oil ratios and pressures are (8.3 liters H_2 S.T.P. per gram of oil and 300 psig for cobalt molybdate) and (0.63 liters H_2 S.T.P. per gram of oil and 500 psig for molybdena-alumina). The effect of the following factors on the sulfur content of the effluent product for a molybdena-alumina catalyst is summarized as follows:

pressures — decreasing through 500 psig

temperatures — decreasing through 430°C.

Hydrogen to oil ration — decreasing through 0.76 $\dfrac{\text{liters } H_2 S.T.P.}{\text{gram of oil}}$

regeneration by an oxidation -- increases

sulfiding of catalyst -- decreases

The total losses on oil charged are all in the range of from 4.5 to

8 per cent.

. In conclusion, destructive hydrogenation is the only process investi-

gated which will continuously produce an oil with a sulfur content less than

0.5 percent.

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APPENDIX

TABLE I

A.S.T.M. Distillation Data

Percent	Feed Oil	Bauxite Treated	HF + Bauxite Treatment	Molybdena Alumina	Cobalt Molybdate
First drop	460°F	196°F	180°F	196°F	216°F
5%	500	348	340	365	406
10	518	450	442	438	460
20	534	500	496	492	506
30	546	526	522	513	518
40	556	540	538	538	540
50	566	552	550	548	551
60	576	564	562	562	564
70	586	576	574	576	579
80	600	590	588	592	591
90	621	614	610	616	616
Final Temp.	660	662	660	658	661
% Recovery	98	98	98	97	98.5
% Sulfur	2.04	1.055	1.025	0.465	0.399

TABLE II

CATALYSTS

Catalyst	Identification Code	Producer
Bauxite (Porocel)	SB - 2446 - 51	Porocel Corp.
Alumina	Al - 0104 . T 1/8 "	Harshaw Chemical Co.
Chrome-alumina	Cr - 0202T 1/8 "	Harshaw Chemical Co.
Molybdena-alumina	Mo - 0602T 1/8 "	Harshaw Chemical Co.
Cobalt-molybdate (H)	Co - Mo - 0201T 1/8 "	Harshaw Chemical Co.
Cobalt-molybdate (U)		Union Oil Co.
Nickel-Bauxite		Made in Laboratory

TABLE III

DESULFURIZATION CHARACTERISTICS OF VARIOUS
CATALYSTS AT ATMOSPHERIC PRESSURE

S.V. = 1.083 $\dfrac{\text{grams oil}}{\text{gram cat. hr.}}$ H_2 Rate = 1.74 $\dfrac{\text{ft}^3 \text{ S.T.P.}}{\text{HR.}}$

Catalyst 500 Grams	On-Stream Time (Min)	Avg. % Sulfur in Effluent	Avg. Temp. °C	Data From Run
Bauxite + HF	0 - 30	0.92	427	
	30 - 60	0.99	410	#34
	60 - 90	1.05	412	
	90 - 120	1.08	412	
Bauxite + HCL	0 - 30	1.03	425	
	30 - 60	1.03	408	#36
	60 - 90	0.951	404	
	90 - 120	0.95	405	
Bauxite + BF_3	0 - 30	1.00	420	
	30 - 60	1.01	418	#51
	60 - 90	1.01	409	
	90 - 120	1.01	404	
Molybdena-Alumina	0 - 30	0.83	411	
	30 - 60	1.01	414	#48
	90 - 120	1.16	416	
HCL + Alumina	0 - 30	1.13	415	
	30 - 60	1.09	433	#37
	60 - 90	1.14	427	
	90 - 120	1.18	412	
Alumina + HF	0 - 30	1.36	425	
	30 - 60	1.23	427	#38
	60 - 90	1.25	417	
	90 - 120	1.23	420	
Chrome-Alumina	0 - 15	1.12	405	
	15 - 30	1.19	413	#49
	30 - 60	1.24	414	
	90 - 120	1.315	407	

TABLE III (CONTINUED)

DESULFURIZATION CHARACTERISTICS OF VARIOUS CATALYSTS AT ATMOSPHERIC PRESSURE

S.V. = 1.083 $\frac{\text{grams oil}}{\text{gram Cat. hr.}}$ $\qquad\qquad$ H_2 Rate = 1.74 $\frac{\text{ft}^3 \text{S.T.P.}}{\text{HR.}}$

Catalyst 500 Grams	On-Stream Time (Min)	Avg. % Sulfur in Effluent	Avg. Temp. °C	Data From Run
Harshaws	0 - 15	0.975	403	
Cobalt	15 - 30	1.054	417	#56
Molybdate	30 - 60	1.102	415	
	60 - 90	1.115	412	
	90 - 120	1.282	416	
Union Oil	0 - 15	0.813	391	
Cobalt	15 - 30	0.892	398	#55
Molybdate	30 - 60	1.174	412	
	60 - 90	1.197	418	
	90 - 120	1.307	418	

TABLE IV

DESULFURIZATION VS. HYDROGEN RATE (BAUXITE)

% Sulfur In Effluent	H_2 Rate Ft3 S. T. P. Hr.	Temp. °C	Space Velocity Grams Oil Grams Catalyst Hr.	Data From Run Sample
1.06	0	412	1.08	40-2
1.04	1.74	404	1.08	43-2
1.046	0.35	412	0.989	53-2
1.089	0.70	412	0.991	54-2
1.01	0	406	1.08	41-1
1.04	1.74	404	1.08	43-2

TABLE V

DESULFURIZATION VS. TEMP. (BAUXITE)

% Sulfur In Effluent	Temp. °C.	H_2 Rate Ft3 S. T. P. Hr.	Space Velocity	Data From Run Sample
1.11	360	0	1.083	40-3
1.07	400	1.74	1.083	43-avg.
1.075	412	0.35	0.989	53-avg.
1.11	417	0.70	0.991	54-avg.
1.455	362	0.70	4.1	61-2
1.182	416	0.70	4.1	61-3

TABLE VI

DESULFURIZATION VS. SPACE VELOCITY (BAUXITE)

% Sulfur In Effluent	Space Velocity Grams Oil Gram Catalyst Hr.	Temp. °C.	H₂ Rate Ft³ S.T.P. Hr.	Average of Run Sample
0.975	1.07	416	1.74	#31-1,2,3
1.075	0.989	407	0.35	53-avg
1.11	0.991	417	0.70	54-avg
1.122	4.1	416	0.70	#61-1,3
1.33	8.2	407	0.70	#62-avg

TABLE VII

DESULFURIZATION VS. SPACE VELOCITY (BAUXITE + HF)

% Sulfur In Effluent	Space Velicity Grams Oil Grams Catalyst Hr.	Temp. °C	H₂ Rate Ft³ S.T.P. Hr.	Average of Run Sample
1.05	0.221	393	1.1	#30-avg
1.11	1.07	407	1.74	#31-4,5,6
1.01	1.083	415	1.74	#34-avg
1.296	3.95	466	2.5	#28-1,2,3
1.59	6.98	451	2.5	#28-4,5
1.61	6.77	394	2.5	#27-avg

TABLE VIII

DATA ON DETERMINATION OF MECHANISM OF DESULFURIZATION

CATALYST	GAS USED	GAS OIL	LITERS S.T.P. GRAM OIL	% SULFUR IN EFFLUENT	REACTOR PRESSURE PSIG	SPACE VEL. GRAMS OIL GRAMS CAT. HR.	AVG. TEMP. °C	AVG. OF RUN
Cobalt	CH_4		0.312	1.452	300	0.805	403	#76
Molybdate	H_2		0.302	0.340	300	0.934	402	#70
Bauxite	H_2		0.268	1.220	500	1.156	399	#67
	H_2		0.0927	1.08	ATM	1.08	399	# 43
Molybdena	H_2		0.346	0.465	300	0.949	392	#58
Alumina	None		xxxxx	1.06	300	0.950	383	#60

TABLE IX

DESULFURIZATION VS. % LOSS ON CHARGE

% SULFUR IN EFFLUENT	% LOSS ON CHARGE	CATALYST	RUN NUMBER
1.07	5.25	Bauxite	#43
1.11	4.5	Bauxite	#54
1.16	2.49	Bauxite	#41
1.2	3.62	Bauxite	#44
1.21	3.72	Bauxite	#61
1.31	2.87	Bauxite	#42
1.33	3.32	Bauxite	#62
1.01	5.92	Bauxite + HF	#34
1.04	7.83	Bauxite + HF	#31
1.05	8.38	Bauxite + HF	#30
1.443	3.81	Bauxite + HF	#28
1.01	6.83	Bauxite + BF_3	#52
1.01	7.66	Bauxite + BF_3	#51
1.13	7.7	HCl + Alumina	#37
1.27	1.85	HF + Alumina	#38
1.02	8.45	Molybdena Alumina	#48
1.23	3.15	Chrome-Alumina	#49

TABLE X

DESULFURIZATION VS. TEMPERATURE
MOLYBDENA-ALUMINA CATALYST

Temp. °C	% Sulfur In Effluent	$\frac{H_2}{O}$ Liters S.T.P. Gram Oil	Reactor Press.	Space Vel. $\frac{Grams\ Oil}{Gram\ Catalyst\ Hr.}$	Data of Run Sample
322	1.379	0.168	300	0.945	59-4
333	1.304	0.201	300	0.945	59-1
340	1.337	0.1715	300	0.945	59-2
383	0.756	0.307	300	0.926	63-2
393	0.709	0.281	300	0.926	63-3
397	0.665	0.280	300	0.926	63-4
404	0.656	0.271	300	0.926	63-5
432	0.568	0.198	300	0.927	57-avg
427	0.573	0.206	300	0.927	57-2
435	0.594	0.177	300	0.927	57-3

TABLE XI

DATA ON CARBON LAYDOWN VS. TEMP.
HYDROGEN OIL RATIO

%Carbon Laydown On Charge	Temperature °C	$\frac{H_2}{O}$ Liters S.T.P. Gram Oil	Run Number
8.3	432	0.198	#57
1.915	330	0.1775	#59
4.37	383	0	#60
0.957	399	0.778	#64

TABLE XII

DESULFURIZATION VS. PRESSURE MOLYBDENA ALUMINA

Pressure P.S.I.A.	% Sulfur In Effluent	H_2 Liters S.T.P. Gram Oil	Reactor Press. P.S.I.G.	Space Vel. Grams Oil Grams Cat. Hr.	Data Of Run Sample
12.2	1.08	0.108	0	1.083	#60
312.	0.734	0.278	300	0.924	#64
512.	0.583	0.244	500	1.011	#66

TABLE XIII

CORRELATION OF DESULFURIZATION WITH HYDROGEN TO OIL RATIO AND E. T. C.

CATALYST	H_2 LITERS STP / O GRAM OIL	% SULFUR IN EFFLUENT	TEMP °C	SPACE VELOCITY GRAMS OIL / GRAM CATALYST HR.	REACTOR PRESS PSIG	NUMBER OF REGENERATIONS ON CATALYST	TEST PERIOD HRS	NUMBER OF 3 HR. RUNS PREVIOUS WITHOUT REGENERATION	RUN NO.
Molybdena Alumina	0.198	0.568	432	0.927	300	0	1	0	#57
	0.346	0.465	392	0.949	300	1	1	0	#58
	0.294	0.683	395	0.926	300	4	3	0	#63
	0.284	0.734	399	0.924	300	5	3	0	#64
	0.441	0.583	399	0.947	300	0	3	0	#80
	0.433	0.472	402	0.764	500	6	3	0	#65
	0.244	0.583	399	1.011	500	6	3	1	#66
	0.633	0.387	397	0.991	500	0	3	1	#82
	0.760	0.328	398	0.812	500	0	3	0	#81
Harshaws Cobalt Molybdate	0.312	0.396	409	1.01	300	0	3	0	#69
	0.302	0.340	402	0.934	300	0	3	1	#70
	0.326	0.398	404	0.954	300	0	3	2	#71
	0.517	0.363	405	0.943	300	1	3	0	#79
	0.192	0.530	405	0.951	300	1	3	1	#78

TABLE XIV

TABULATED RESULTS FOR RUNS

Run No.	TIME INTERVAL MINUTES	SAMPLE NO.	SAMPLE WEIGHT IN GRAMS	% SULFUR	°C AVG. TEMP.	H_2 RATE FT3 STP HR.	OIL CHARGE	% LOSS OF CHARGE	CATALYST 500 GRAMS	ACTIVATED WITH	SPACE VEL. GR. OIL GR. CAT. HR.	REMARKS
27	0-15	1	796.0	1.61	399	2.5	847	6.2	Cyclocel	HF Gas	6.77	Run discontinued. Incomplete condensation "Undersized" condensor
28	0-20	1	611.2	1.31	448.5	2.5	3332	3.81	Cyclocel	HF	3.95	Catalyst same as
	20-40	2	622	1.28	481	2.5					3.95	Run 27.
	40-60	3	629.4		470	2.5					3.95	No cracking
	60-73	4	703.7	1.51	468	2.5					6.98	evident at 470°C
	73-83	5	638.7	1.67	435	2.5					6.98	
29	0-20	1	422	1.095	410	1.74			Cyclocel	HF Gas	1.08	Cat. check
30	0-30	1	25.5	1.055	401	1.1	361.0	8.38	Cyclocel	HF Gas	0.221	Eff. of high H_2 rate checked
	30-60	2	35.9	1.055	389	1.1	361.0					
	60-110	3	68.0	1.04	383	1.1	361.0					
	110-160	4	66.5	1.04	991	1.1	361.0					
	160-200	5	59.0	1.045	387	1.1	361.0					
	200-250	6	78.2	1.105	394	2.5	361.0					

TABLE XIV (CONTINUED)

TABULATED RESULTS FOR RUNS

Run No.	TIME INTERVAL MINUTES	SAMPLE NO.	SAMPLE WEIGHT IN GRAMS	% SULFUR	°C AV. TEMP.	H_2 RATE FT^3 STP HR.	OIL CHARGE	% LOSS OF CHARGE	CATALYST 500 GRAMS	ACTIVATED WITH	SPACE VEL. GR. OIL GR. CAT. HR.	REMARKS
31	0-30	1	194.2	0.93	413	1.74	1512	7.83	Cyclocel	None	1.07	Fresh Cat
	30-60	2	232	0.94	422	1.74				None		10-30 mesh
	60-90	3	249.1	1.055	413	1.74				None		
	90-120	4	233.2	1.12	404	1.74				HF		
	120-150	5	254.9	1.10	410	1.74				Gas		
	150-175	6	229.2	1.10	415	1.74				Same		
32	0-30	1	191.5	1.02	407	1.74			Cyclocel same as 31	HF	1.038	
	30-60	2	172.2	1.025	407							Gasket leakage run discontinued
33	0-30	1		0.84	396	1.74			10-30 mesh cyclocel	HF Gas	1.038	Run discontinued
34	0-30	1	243.1	0.92	427	1.74	1120	5.92	10-30 mesh cyclocel	HF Gas	1.083	Cat. same as Run 33
	30-60	2	261.9	0.99	410	1.74						
	60-90	3	271.9	1.05	412	1.74						
	90-120	4	276.5	1.08	412	1.74						
35	0-25	1	200	1.00	427	1.74	362.9	5.75	10-30 mesh Cyclocel	HF Gas	1.083	Recycle oil of 1.1% sulfur used for feed oil
	25-40	2	142	0.96	423	1.74						

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TABLE XIV (CONTINUED)

TABULATED RESULTS FOR RUNS

Run No.	TIME INTERVAL MINUTES	SAMPLE NO.	SAMPLE WEIGHT IN GRAMS	% SULFUR	°C AVG. TEMP.	H₂ RATE FT3 STP HR.	OIL CHARGE	% LOSS OF CHARGE	CATALYST 500 GRAMS	ACTIVATED WITH	SPACE VEL. GR. OIL GR. CAT. HR.	REMARKS
36	0–30	1	204.7	1.03	425	1.74	1083	17.9	10–30	HCL	1.083	Fresh cat.
	30–60	2	200.2	1.03	408	1.74			mesh	Gas		
	60–90	3	230.5	0.90	404	1.74			Cyclocel			
	90–120	4	253.5	0.95	405	1.74						
37	0–30	1	216.5	1.13	415	1.74	1083	7.7	Alumina	HCL	1.083	No coke on cat.
	30–60	2	249.5	1.09	433							
	60–90	3	252.7		427							No cracking evident as high as 434°C
	90–120	4	281.0	1.18	412							
38	0–30	1	239.5	1.36	425	1.74	1078	1.85	Alumina	HF	1.083	
	30–60	2	265	1.23	427	1.74						
	60–90	3	232.5	1.25	417	1.74						
	90–120	4	301	1.23	420	1.74						
39	0–30	1	245	1.95	426	None	879	0	None	None		Steel balls of pre-heat section alone 542 grs. oil/hr
	30–60	2	264.8	1.88	431	1.74				None		
	60–100	3	368.9	1.99	410					HF		
40	0–60	1	444.5	0.89	410	None	1421	11.2	Cyclocel	None	1.083	Run discontined due to blow out Cause of high loss
	60–120	2	454.5	1.06	412							
	120–160	3	278.0	1.11	360							

TABLE XIV (CONTINUED)
TABULATED RESULTS FOR RUNS

Run No.	Time Interval Minutes	Sample No.	Sample Weight In grams	% Sulfur	°C Avg. Temp.	H_2 Rate Ft^3 STP Hr.	Oil Charge	% Loss of Charge	Catalyst 500 grams	Activated With	Space Vel. Gr. Oil Gr. Cat. Hr.	Remarks
41	0-30	1	228.5	1.01	406	None	1068	2.49	Cyclocel	None	1.083	
	30-60	2	271.5	1.15	409	1.74						
	60-120	3	542.5	1.33	398	1.74						
42	0-30	1	218	1.125	408	1.74	1620	2.87	Same	None	1.083	
	30-60	2	280	1.32	408	1.74						
	60-120	3	530.5	1.39	408	1.74						
	120-180	4	555.0	1.41	404	None						587 gm of catalyst & coke removed
43	0-30	1	222	1.08	396	1.74	1344	5.25	Cyclocel	None	1.083	
	30-60	2	250.5	1.04	404	1.74						Fresh cat.
	60-120	3	518.5		400	1.74						
	120-150	4	282.7	1.09	400	1.74						
44	0-60	1	466.5	1.23	405	1.74	1574	3.62	Same	None	1.083	Cat. removed Wt. 527 gm.
	60-120	2	542.0	1.19	401	1.74						
	120-180	3	510.5	1.17	402	1.74						
45	0-10	1	42	0.30	393	1.74	721	9.9	$NiNO_3$ on Cyclocel	None	1.083	Cat. was 0.69 mols of $NiNO_3$ absorbed in 500 gm of cyclocel. Cat. then heated 2 hrs. at 440°C in air stream, then reduced with H_2 1.10% S in feed.
	10-20	2	75	0.61	394							
	20-30	3	84	0.79	396							
	30-40	4	82	0.84	398							
	40-50	5	80		394							
	50-60	6	83		393							
	60-80	7	204	0.95	391							

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TABLE XIV (CONTINUED

TABULATED RESULTS FOR RUNS

Run No.	Time Interval Minutes	Sample No.	Sample Weight In Grams	% Sulfur	oC Avg. Temp.	H₂ Rate Ft3 STP Hr	Oil Charge	% Loss of Charge	Catalyst 500 Grams	Activated With	Space Vel. Gr. Oil Gr. Cat Hr.	Remarks
46	0-10	1	49	0.79	370	1.74	735	4.74	500		1.083	Recycle oil in at
	10-30	2	202	0.97	395				cyclocel			1.1% Sulfur
	30-55	3	223		433				Nickel impreg.			
	55-78	4	226.5	0.90	415				cyclocel			
47	0-20	1	114	0.81	412	1.74	847.5	9.45	Same			
	20-40	2	172.5	0.97	415				(Run 45)			
	40-60	3	170.0		410						1.083	Cat. regenerated
	60-90	4	311.0	1.01	398							from Run 46 by burning off and reduction with hydrogen. Recycle oil in at 1.1% S.
48	0-30	1	213	0.83	411	1.74	1100	8.47	500		1.083	
	30-60	2	255	1.01	414				moly-alumina			Cat. wt. grm
	60-90	3	253		415							= 20 gm.
	90-120	4	286	1.16	416							
49	0-15	1	96	1.12	405	1.74	1016	3.15	500		1.083	No coke on cat.
	15-30	2	123	1.19	413				chrome			No cat. wt. gain
	30-60	3	247	1.24	419				alumina			
	60-90	4	250		412							
	90-120	5	268	1.315	407							

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TABLE XIV (CONTINUED)

TABULATED RESULTS FOR RUNS

Run No.	Time Interval Minutes	Sample No.	Sample Weight in Grams	% Sulfur	°C Avg. Temp.	H₂ Rate Ft.³ STP Hr.	Oil Charge	% Loss of Charge	Catalyst 500 Grams	Activated With	Space Vel. Gr. Oil / Gr. Cat. Hr.	Remarks
50	0-15	1	97	1.79	413	1.74	1011	1.8	500 gr.		1.083	No cat. wt. gain
	15-30	2	123		421				John Manville			
	30-60	3	230	1.88	420				Cat.			
	60-90	4	248	1.90	418							
	90-120	5	275		414							
51	0-30	1	200	1.0	420	1.74	993	7.66	500 gr.	BF₃	1.08	Good color
	30-60	2	229		418				Cyclocel			stability of product
	60-90	3	236	1.01	409				fresh			
	90-120	4	252	1.01	404							
52	0-30	1	158	0.97	413	1.74	542	6.83	500 gr.		0.720	BF₃ treated oil in. Resin formed was filtered out. Good color stability of product
	30-60	2	179		413				cyclocel			
	60-90	3	168	1.04	418				fresh			
53	0-30	1	38.2	1.036	402	0.35	197.7	10.1	100 gr.		0.989	No catalyst wt. gain. Preheat sect. gained is berl saddles
	30-60	2	43.6	1.046	412				cyclocel			
	60-90	3	46.1	1.105	408							
	90-120	4	51.9	1.112	407							
54	0-30	1	79.2	1.076	423	0.70	396.2	4.5	200 gr.		0.991	Cat. lost 3.5 gr. in wt. Preheat sect. gained 0.5 gr. Water off cat. est. 2-5 grms.
	30-55	2	81.2	1.089	412				fresh			
	55-90	3	109.6	1.104	421				cyclocel			
	90-120	4	108.4	1.17	412							

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TABLE IV (CONTINUED)

TABULATED RESULTS FOR RUNS

Run No.	Time Interval Minutes	Sample No.	Sample Weight in Grams	% Sulfur	°C Avg. Temp.	H₂ Rate Ft.³ STP Hr.	Oil Charge	% Loss of Charge	Catalyst 500 Grams Activated With	Space Vel. Gr. Oil Gr. Cat. Hr.	Remarks
55	0-15	1	78.2	0.813	391	1.74	1045	11.05	500 gr.	1.046	Cat. wt. gain
	15-30	2	117	0.892	398				3/16" cobalt		= 55 gm.
	30-60	3	235.3	1.174	412				molyb.		
	60-90	4	263	1.197	418				" Union Oil Co"		
	90-120	5	235.7	1.307	418						
56	0-15	1	100	0.975	403	1.74	1051	8.2	500 gr.	1.05	
	15-30	2	114	1.054	417				Cobalt		
	30-60	3	238.5	1.102	415				molyb.		
	60-90	4	246	1.115	412				(Harshaw)		
	90-120	5	266	1.282	416						

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TABLE XIV (CONTINUED)

CATALYTIC DESULFURIZATION OF #3 FUEL OIL

Run No.	Time Interval Minutes	Sample No.	Sample Weight in Grams	% Sulfur	°C Avg. Temp.	H$_2$ Rate l./min.	Total % Loss on Charge	% Carbon Laydown on Charge	Catalyst 1000 gms	Space Vel.	Reactor Pressure lb./in.^{2}	Baro. Pressure mm./Hg.	Remarks
57	0-15	1	124.5	0.357	427	3.80		18.9	1000 gr. molyb. Alumina	0.927	300	633.7	76.8 gr. carbon
	15-30	2	209.8	0.573	427	3.19							
	30-45	3	176.0	0.594	435	2.73							by burn-off
	45-60	4	241.1	0.653	440	2.13							calc.
58	0-15	1	126.5	0.368	382	5.78	9.6	2.65	Molyb. Alumina	0.949	300	639.6	
	15-30	2	227.5	0.545	377	5.38							
	30-45	3	224	0.420	401	5.22							
	45-60	4	208	0.486	406	5.53							
59	0-15	1	110	1.304	333	3.16	3.81	1.915	Molyb. Alumina	0.945	300	636.7	
	15-30	2	214	1.337	340	2.70							
	30-45	3	225	1.498	326	2.65							
	45-60	4	360	1.379	322	2.65							
60	0-15	1	68	0.916	377	0	7.8	4.37	Molyb. Alumina	0.95	300	635.2	
	15-30	2	164	1.014	391	0							
	30-45	3	204	1.189	382	0							
	45-60	4	440	1.129	383	0							
61	0-15	1	169	0.992	417	0.33	3.72		Cyclocel 200 gms.	4.1	Atm.	631.6	
	15-30	2	222	1.455	362	0.33							
	30-60	3	399	1.182	416	0.33							

TABLE XIV (CONTINUED)

CATALYTIC DESULFURIZATION OF #3 FUEL OIL

Run No.	Time Interval Minutes	Sample No.	Sample Weight in Grams	% Sulfur	°C Avg. Temp.	H_2 Rate l./min.	Total % Loss on Charge	% Carbon Laydown on Charge	Catalyst 1000 gms.	Space Vel.	Reactor Pressure lb./in.2	Baro. Pressure mm. Hg.	Remarks
62	0–15	1	190	1.259	413	0.165	3.32		Cyclocel 100 gms	8.27	Atm.	636	
	15–30	2	211	1.393	400	0.165							
	30–60	3	399	1.352	411	0.165							
63	0–30	1	366	0.424	404	5.50	0.665	N. D.	Molyb. Alumina	0.926	300	639.6	
	30–60	2	418	0.756	383	4.73							
	60–90	3	412	0.709	393	4.34							
	90–120	4	436	0.665	397	4.32							
	120–150	5	446	0.656	404	4.17							
	150–180	6	589	0.812	393	4.20							
64	0–30	1	353	0.765	400	4.50	5.87	0.957	Molyb. Alumina	0.924	300	640.3	
	30–60	2	468	0.653	398	4.50							
	60–90	3	424	0.772	392	4.80							
	90–120	4	446	0.724	402	4.43							
	120–150	5	430	0.730	401	4.80							
	150–180	6	490	0.768	400	2.63							
65	0–30	1	287	0.401	404	5.41	4.81	No Regen.	Molyb. Alumina	0.764	500	640.9	
	30–60	2	232	0.309	406	5.63							
	60–90	3	354	0.448	401	5.98							
	90–120	4	378	0.485	399	4.83							
	120–150	5	413	0.581	401	5.73							
	150–180	6	519	0.503	404	5.43							

TABLE XIV (CONTINUED)
CATALYTIC DESULFURIZATION OF #3 FUEL OIL

Run No.	Time Interval Minutes	Sample No.	Sample Wt. in Grams	% Sulfur	°C Avg. Temp.	H$_2$ Rate l./min.	Total % Loss on Charge	% Carbon Laydown on chg.	Catalyst 1000 gms.	Space vel.	Reactor Pressure lb./in.^{2}	Baro. Pressure mm. Hg.	Remarks
66	0-30	1	413	0.614	399	3.62	4.4	No	Molyb.	1.011	500	637.1	
	30-60	2	464	0.524	406	3.36		Regen.	Alumina				
	60-90	3	409	0.649	393	4.26							
	90-120	4	647	0.548	398	4.72							
67	0-30	1	335	1.122	368	2.98	9.51	No					
	30-60	2	600	1.319	335	2.98		Regen.	Cyclocel	1.033	500	639.1	
68	0-30	1	413	1.167	407	5.83	5.7	No	Cyclocel	1.156	500	637.1	
	30-60	2	524	1.219	402	6.17		Regen.					
	60-90	3	508	1.272	396	6.68							
	90-120	4	585	1.640	395	5.33							
	120-150	5	699	1.462	397	5.42							
69	0-30	1	517	0.553	416	6.48	7.43	No	Cobalt				
	30-60	2	647	0.603	404	5.52		Regen.	Molyb.	1.01	300	638.2	Space Vel.
	60-90	3	318	0.241	415	4.90							during this
	90-120	4	372	0.228	404	4.97							run varied due
	120-150	5	444	0.241	413	5.03							to pump. See sample wt.
	150-180	6	508	0.330	402	4.60							
70	0-30	1	404	0.311	400	5.53	5.0	No	Cobalt	0.934	300	641	
	30-60	2	428	0.348	399	4.27		Regen.	Molyb.				
	60-90	3	461	0.343	408	5.28							
	90-120	4	423	0.355	403	4.81							
	120-150	5	433	0.333	404	4.53							
	150-180	6	513	0.346	400	3.77							

TABLE XIV (CONTINUED)
CATALYTIC DESULFURIZATION OF #3 FUEL OIL

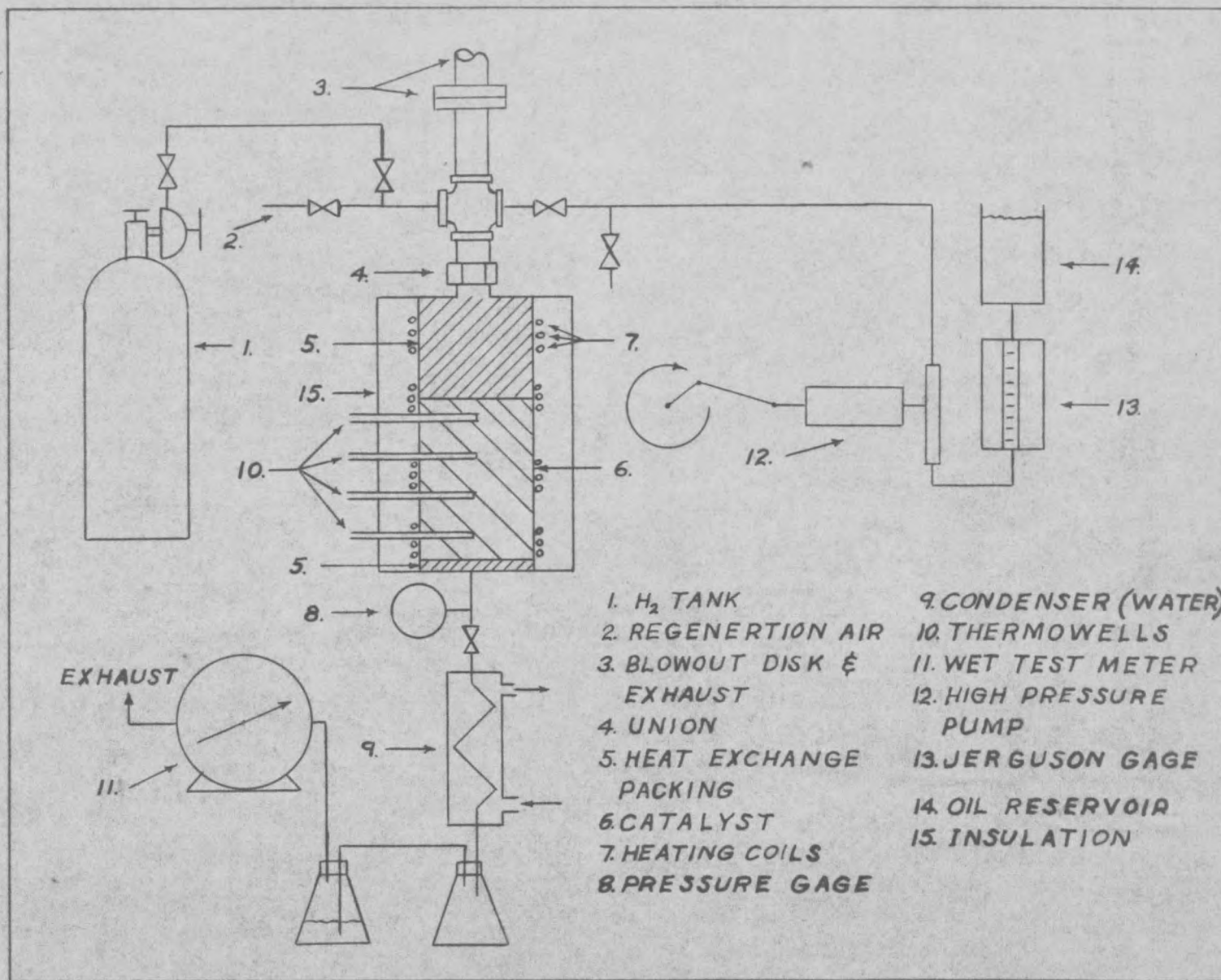| Run No.	Time Interval Minutes	Sample No.	Sample Wt. in Grams	% Sulfur	°C Avg. Temp.	H2 Rate l./min.	Total % Loss on Charge	% Carbon Laydown on chg.	Catalyst 1000 gms.	Space vel.	Reactor Pressure lb./in.2	Baro. Pressure mm. Hg.	Remarks
71	0-30	1	379	0.332	407	4.93	5.73	No	Cobalt	0.954	300	640	
	30-60	2	407	0.477	403	3.73		Regen.	Molyb.				
	60-90	3	488	0.462	404	3.82							
	90-120	4	472	0.339	404	6.63							
	120-150	5	363	0.439	405	1.96							
	150-180	6	590	0.356	403	10.1							
72	0-30	1	341.0	0.0355	417	4.7	5.34		Cobalt	0.849	300	642.7	#1 oil
	30-60	2	414.0	0.053	401	4.42			Molyb.				
	60-90	3	387.0	0.0289	404	4.32			No				
	90-120	4	424.5	0.0186	399	4.52			Regen.				
	120-150	5	390.5	0.046	402	4.07							
	150-180	6	452.5	-	401	4.2							
			2409.5										
73	0-30	1	444	0.0661	406	4.87			Cobalt	1.058	300	638.1	#1 oil
	30-60	2	504	0.0442	404	4.87			Molyb.				
	60-90	3	468.5	0.0322	407	4.45			No				
	90-120	4	498	0.0296	403	4.65			Regen.				
	120-150	5	493	0.0300	412	6.52							
	150-180	6	Lost	-	395	5.1							
74	0-30	1	489.5	0.0544	412	5.1	8.72		Cobalt	1.133	300	640.8	#1 oil
	30-60	2	503.0	0.0511	421	5.02			Molyb.				
	60-90	3	558	0.043	406	4.36			No				
	90-120	4	521	-	396	3.78			Regen.				
	120-150	5	540.5	-	405	4.3							
	150-180	6	489.5	0.0453	404	3.52							
			3101.5										

TABLE XIV (CONTINUED)
CATALYTIC DESULFURIZATION OF #3 FUEL OIL

Run No.	Time Interval Minutes	Sample No.	Sample Wt. in Grams	% Sulfur	°C Avg. Temp.	H₂ Rate l./min.	Total % Loss on Charge	% Carbon Laydown on chg.	Catalyst 1000 gms.	Space Vel.	Reactor Pressure lb./in.²	Baro. Pressure mm. Hg.	Remarks
75	0-30	1	450.5	0.265	389	5.85*	7.63		Cobalt 1.068		300	636.5	#1 oil CH₄
	30-60	2	510.0	0.261	397	6.76			Molyb.				sub'd for H₂
	60-90	3	489.0	0.271	405	5.82			No.				
	90-120	4	522.5	0.370	402	6.48			Regen.				
	120-150	5	531.0	-	401	6.3			CH₄ gas				
	150-180	6	456.7	0.382	403	5.92							
			2959.7										
76	0-30	1	248	1.147	424	4.55*	7.28		Cobalt 0.805		300	638.4	#3 Oil
	30-60	2	346.5	1.442	396	4.50			Molyb.				
	60-90	3	381.5	-	398	4.12			No				
	90-120	4	403.5	1.602	400	3.92			Regen.				
	120-150	5	388.5	-	402	3.33			CH₄ Gas				
	150-180	6	472.0	1.619	400	3.60							
			2240.0										
77	0-30	1	368.5	1.196	404	3.36*	2.87		Cobalt 0.942		300	639.2	Regen. for
	30-60	2	469.5	1.282	401	3.04			Molyb.				20 hrs. to
	60-90	3	468.0	1.198	401	2.96			No Regen.				give a calculated
	90-120	4	521.0	1.196	404	2.57			CH₄ gas				213.5 gm. C
			1827.0										
78	0-30	1	348.0	0.534	409	3.77	5.97		Cobalt 0.951		300	638.6	#3 Oil
	30-60	2	411.5	0.716	404	1.57			Molyb.				
	60-90	3	456.0	0.627	404	2.53			Regenerated				
	90-120	4	496.5	0.464	405	4.14							
	120-150	5	453.0	0.476	405	4.30							
	150-180	6	521.5	0.427	404	3.38							
			2686.5										

TABLE XIV (CONTINUED)
CATALYTIC DESULFURIZATION OF #3 FUEL OIL.

Run No.	Time Interval Minutes	Sample No.	Sample Wt. in Grams	% Sulfur	⁰C Avg. Temp.	H₂ Rate l./min.	Total % Loss on Charge	% Carbon Laydown on chg.	Catalyst 1000 gms.	Space Vel.	Reactor Pressure lb./in.²	Baro Pressure mm. Hg.	Remarks
79	0-30	1	414.5	0.317	410	9.67	4.18		Cobalt 0.943	300		639.6	#3 Oil
	30-60	2	443.5	0.382	404	8.95			Molyb.				
	60-90	3	439.0	-	403	7.00			No Regen.				
	90-120	4	541.7	0.309	407	7.65							
	120-150	5	442.0	0.454	401	7.85							
	150-180	6	515.5	0.372	405	11.7							
			2706.2										
80	0-30	1	409.0	0.508	406	5.13	6.03		Molyb. 0.945	300		641.1	#3 Oil
	30-60	2	461.0	0.580	406	6.1			Alumina				
	60-90	3	406.5	0.616	392	9.05							
	90-120	4	432.5	0.544	401	7.46							
	120-150	5	474.0	0.660	389	8.70							
	150-180	6	485.5	0.590	399	8.25							
			2668.5										
81	0-30	1	339	0.496	399	14.2	6.8		Molyb. 0.812	500		637.4	#3 Oil
	30-60	2	363	0.202	411	6.1			Alumina				
	60-90	3	377.5	0.391	398	11.9			No. Regen.				
	90-120	4	379	0.239	403	14.6							
	120-150	5	366	0.412	387	8.2							
	150-180	6	443	0.257	394	11.9							
			2267.5										
82	0-30	1	381	0.461	395	8.55	5.88		Molyb. 0.991	500		640.1	#3 Oil
	30-60	2	440.5	0.284	406	9.35			Alumina				
	60-90	3	466.5	0.474	389	10.70			No Regen.				
	90-120	4	490	0.350	401	8.16							
	120-150	5	483	0.435	392	13.85							
	150-180	6	541	0.336	398	12.10							
			2802.0										

Fig. 1 Diagram of Hydrogenation Equipment for Super-atmospheric Work

1. H_2 TANK
2. REGENERTION AIR
3. BLOWOUT DISK & EXHAUST
4. UNION
5. HEAT EXCHANGE PACKING
6. CATALYST
7. HEATING COILS
8. PRESSURE GAGE
9. CONDENSER (WATER)
10. THERMOWELLS
11. WET TEST METER
12. HIGH PRESSURE PUMP
13. JERGUSON GAGE
14. OIL RESERVOIR
15. INSULATION

EXHAUST
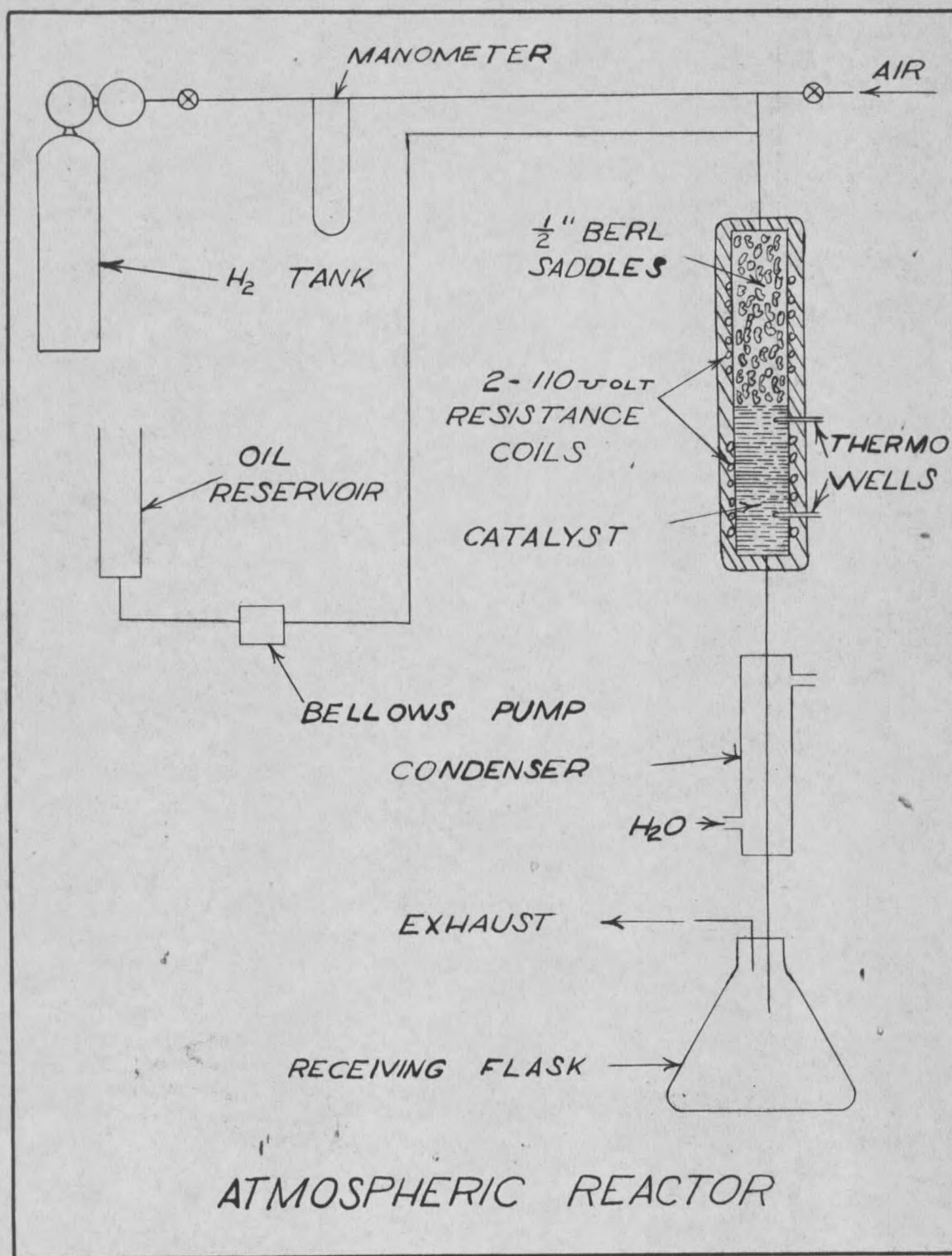
Fig. 2 Diagram of Atmospheric System for Catalytic Desulfurization
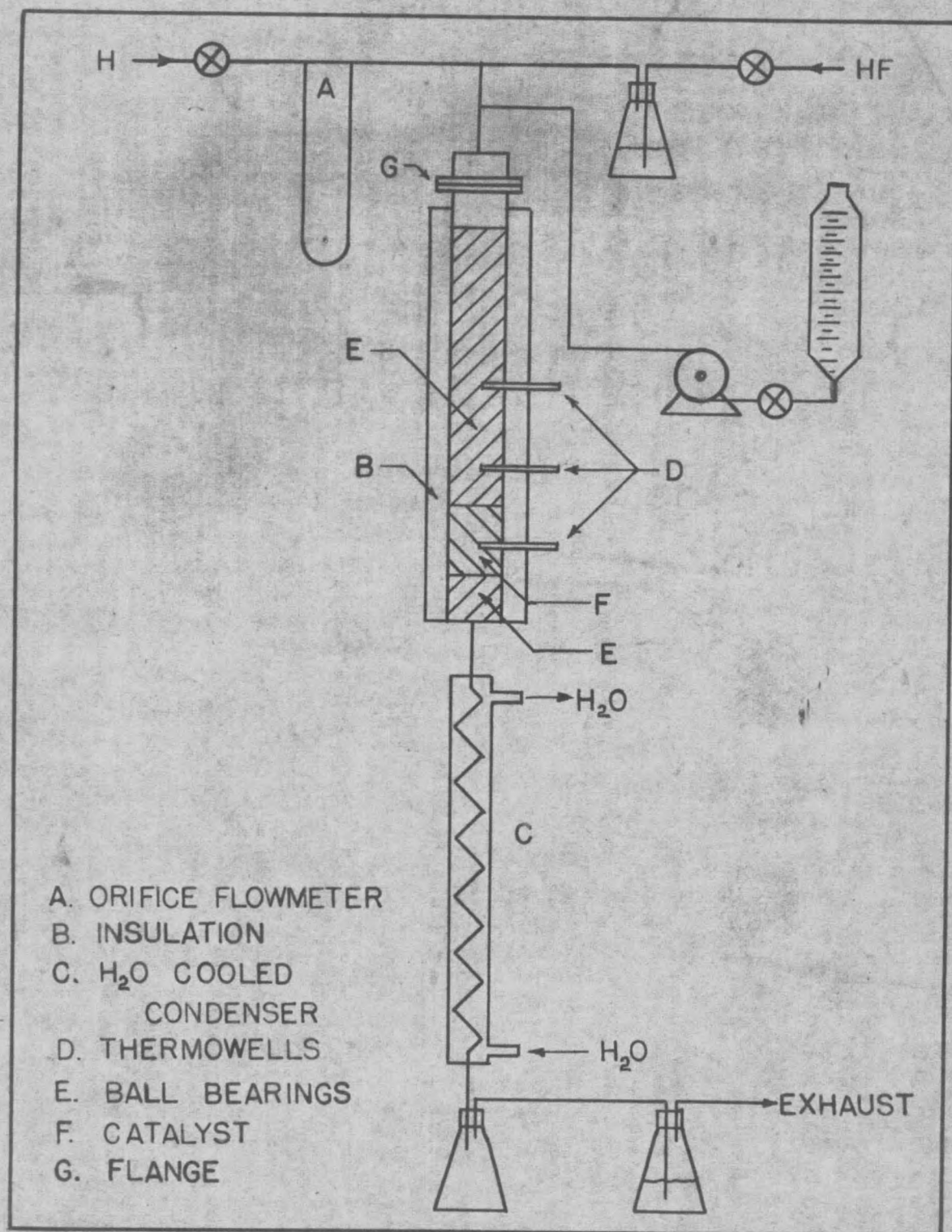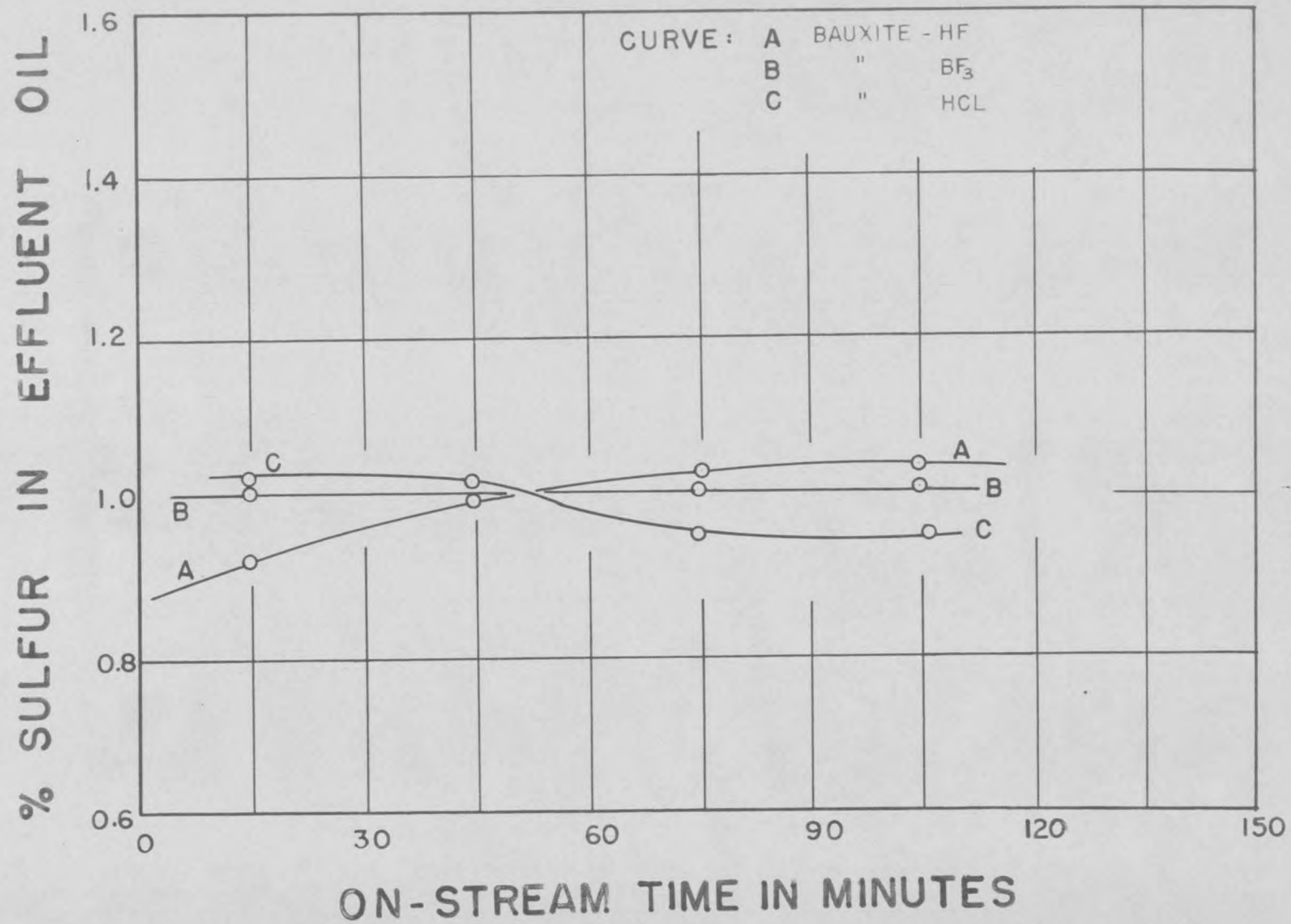
FIGURE 3.   REACTOR SYSTEM FOR HF ACTIVATED CATALYST

Fig. 4 Plot of Desulfurization vs. On-Stream Time For
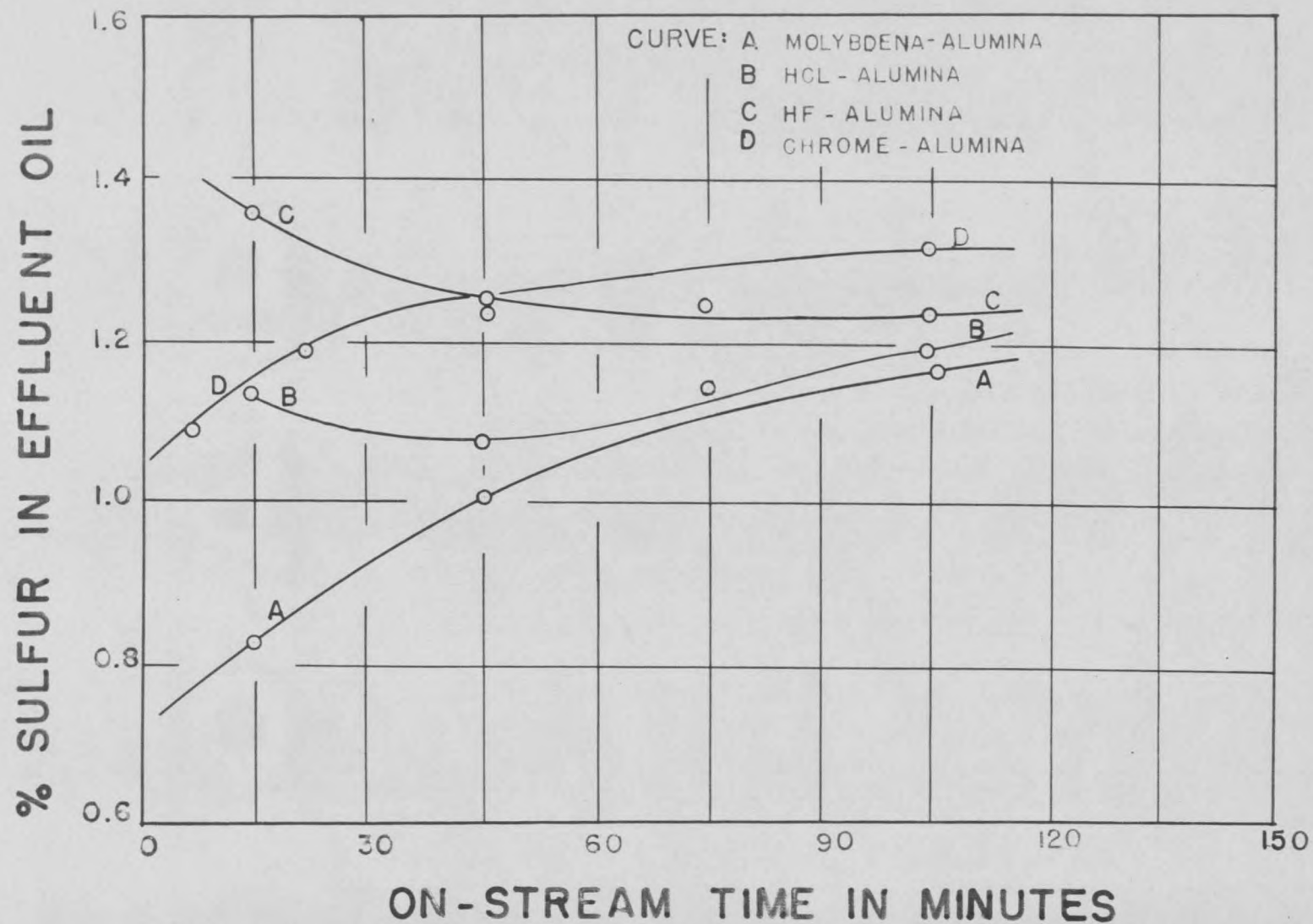Acid Activated Bauxite Catalysts

% SULFUR IN EFFLUENT OIL

ON-STREAM TIME IN MINUTES

CURVE: A   MOLYBDENA-ALUMINA
B   HCL - ALUMINA
C   HF - ALUMINA
D   CHROME - ALUMINA

Fig. 5 Plot of Desulfurization vs. On-stream Time For
Metallic-oxide-alumina Catalysts and Acid
Activated Alumina Catalysts

CURVE: A - MOLYBDENA ALUMINA
       B - UNION COBALT MOLYBDATE
       C - HARSHAW'S " "
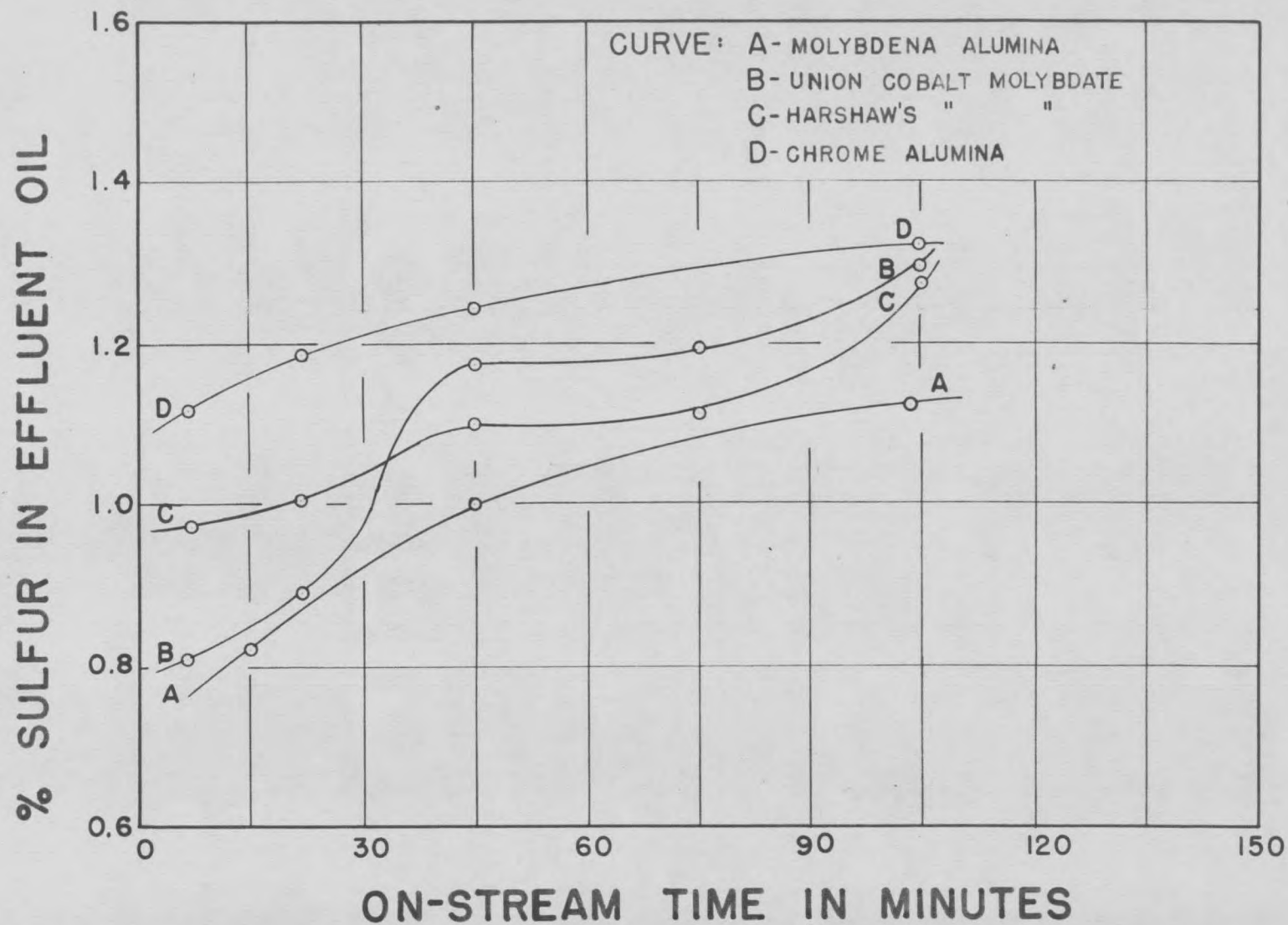   D - CHROME ALUMINA

Fig. 6 Plot of Desulfurization vs. On-stream Time for
         Metallic-oxide alumina catalysts and
         Cobalt Molybdate Catalysts