Nickel oxide as a desulfurizing agent
by John W Coykendall

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
Montana State University

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This investigation studied the desulfurization activity of a spent nickel oxide catalyst which was regenerated by dissolving it in sulfuric acid, precipitating the nickel carbonate, and calcining the precipitate- in the neighborhood of 800°F The effect of calcining atmosphere and temperature on catalyst activity was also investigated.

The results of this investigation show that: (l) it is possible to re- generate spent nickel oxide catalysts by a wet chemical method, (2) the activity of fresh Harshaw #1 and Gwynn #1 catalysts decreases upon calcining at temperatures in excess of 1000°F, (3) from the standpoint of economy of operation and catalyst activity, a low calcine temperature is indicated, (4) nickel oxide acts as both a catalyst and a chemical reagent in desulfurizing fuel oil. . ' ^

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Approved:

Lloyd Berg

Head, Major Department

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Chairman, Examining Committee

Dean, Graduate Division

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ABSTRACT

This investigation studied the desulfurization activity of a spent nickel oxide catalyst which was regenerated by dissolving it in sulfuric acid, precipitating the nickel carbonate, and calcining the precipitate in the neighborhood of 800°F. The effect of calcining atmosphere and temperature on catalyst activity was also investigated.

The results of this investigation show that: (1) it is possible to regenerate spent nickel oxide catalysts by a wet chemical method, (2) the activity of fresh Harshaw #1 and Gwynn #1 catalysts decreases upon calcining at temperatures in excess of 1000°F, (3) from the standpoint of economy of operation and catalyst activity, a low calcine temperature is indicated, (4) nickel oxide acts as both a catalyst and a chemical reagent in desulfurizing fuel oil.

INTRODUCTION

All crude petroleums contain sulfur compounds, the types and amounts depending on the source of the oil (7). In the United States, crudes particularly high in sulfur come from fields in California, West Texas, and from certain fields in the Rocky Mountain Area. The sulfur may be present as elemental sulfur, hydrogen sulfide, mercaptans, thioethers, sulfides, disulfides, thiophenes, and thiophanes. Although there are exceptions, usually the greater percentage of the sulfur appears as thiophenic compounds which are chemically stable and inert (3) (11).

Many processes are available for the removal of sulfur from gasoline fractions, however with one exception (3) (5), most of the processes are not satisfactory for the desulfurization of heavier distillates. According to Berg et al (3), "Sulfur in kerosene and gas oil stocks gives rise to objectionable odor, corrosion, poor color stability, and is responsible for acrid fumes on burning."

Destructive hydrogenation results in partial or almost complete desulfurization (13), however, this is an expensive process and results in cracking and production of lower molecular weight products. Non-destructive hydrogenation, resulting in desulfurization, can be performed at temperatures below those giving destructive hydrogenation by using active catalysts, however, the active catalysts such as platinum, palladium, nickel, nickel oxides etc., as well as being expensive, are poisoned by sulfur compounds. Nickel sulfide is an active hydrogenation catalyst, but not at temperatures below 400°C. (13). Gwynn (8) (9) has patents on the use of nickel and nickel oxides for the hydrofining of petroleum distillates. He claims nickel oxide

functions both as a catalyst and reagent in desulfurizing:

$Ni_3O_4 \cdot 4H_2O + 3RS + nR + (7 + n)H_2 \longrightarrow 3NiS + (3 + n)RH_2 + 8H_2O$

Work by the Husky Oil Company has shown that it is possible to use nickel oxide to lower the sulfur content of a fuel oil fraction from over 2% to as low as 0.1%. Haas (10) studied the effect of temperature, space velocity, and hydrogen rate on the desulfurization of fuel oil with nickel oxide and the regeneration of spent catalyst. He concluded that:

1. Between 600 and 675°F. the desulfurization was independent of temperature.
2. Desulfurization was dependent on contact time.
3. Hydrogen rate was not a critical factor except that high rates reduced the effective contact time.
4. Free nickel may have been the active desulfurizing agent.
5. Active nickel oxide could not be prepared by decomposition of nickel hydroxide or nickel carbonate prepared from spent catalyst.

If desulfurization using nickel oxide catalysts is to be a commercially feasible process, a method must be developed to regenerate the spent catalyst at a low cost. This investigation was concerned with this developement and some of the factors contributing to high catalyst activity. The effect of calcine atmosphere and temperature on catalyst activity was studied as well as the activity of nickel oxide catalyst regenerated by various methods.

EQUIPMENT, METHODS, MATERIALS

EQUIPMENT

The equipment used in this investigation, called the comparison unit, is shown in Figure 2. It consisted essentially of: a glass reactor, a condenser system, a reservoir and pump system, and a hydrogen supply system.

Reactor

The reactor consisted of a piece of 25 mm glass tubing 17 inches long, with a glass thermowell, which was mounted in a 1½ inch standard steel pipe 11 inches long. The pipe was wrapped with asbestos tape over which was wrapped a heating coil. Another layer of asbestos tape and asbestos mud was placed over the coil. A Variac controlled the coil voltage thus controlling the reactor temperature. An iron-constantan thermocouple was inserted into the thermowell and connected to a potentiometer calibrated to read in degrees Centigrade.

Condenser System

The reactor was connected directly to a glass water cooled condenser, which was in turn connected to a condenser with an ice finger. Hydrogen and any uncondensed gas passed through the ice cooled condenser to an exhaust line.

Reservoir and Pump System

A 500 ml. graduated flask, which served as the oil reservoir, was connected to an outlet at the bottom of the ice cooled condenser. The bottom of the separatory funnel was connected to a Merkle-Korff type bellows pump through a three way stopcock, where samples could be taken. A length of 1/8 inch stainless steel tubing connected the oil pump with the top of the reactor

through a glass fitting into which the hydrogen was also introduced.

Hydrogen Supply System

Hydrogen was supplied from a cylinder equipped with a regulator and needle valve. The hydrogen passed through a calibrated orifice and manometer to the fitting at the top of the reactor.

A very complete description of the apparatus is given by Haas (10).

METHODS

General Procedure for Testing Catalyst Activity

The test catalyst was ground with a mortar and pestle, and the amount to be used weighed and mixed with 40 grams of 1/16 inch diameter fish spines and a small amount of oil (previously weighed). Two pads of glass wool were weighed and placed on top of the stainless steel screen at the bottom of the reactor. The catalyst-fish spine mixture was then poured, a little at a time to prevent packing, on top of the glass wool. The remaining space in the reactor above the catalyst was then filled with a weighed amount of 1/8 inch fish spines (usually in the neighborhood of 30 grams). The joints on the reactor were greased and the reactor placed in the system. A weighed amount of oil was placed in the oil reservoir, the water to the condenser turned on, and the ice finger filled with ice. The Variac was turned on and when the reactor temperature was about 30°C. below the operating temperature, the oil pump was started and the time noted. The needle valve on the hydrogen supply was set to give a manometer reading corresponding to 2.46 cubic feet per hour.

The temperature and hydrogen rate were adjusted frequently during the run, and the ice finger kept full of ice. A piece of 1/8 inch steel tubing

was used as a siphon for keeping the water level constant in the ice finger, and it functioned very efficiently once initially started. Samples were taken every hour through the three-way stopcock in the line between the reservoir and the pump. Five minutes before the sample was taken the oil in the reservoir was mixed by blowing through a tube extending into the bottom of the oil reservoir. The sample weights were recorded.

At the end of a run, the Variac and oil pump were turned off, but the hydrogen was allowed to pass through the system for five minutes to remove any oil remaining in the reactor. The oil was removed from the reservoir and weighed. The reactor was allowed to cool for 15 minutes and then it was removed from the system and emptied. The total amount of material from the reactor was weighed, then the catalyst was separated by screening and it was stored in a sample bottle.

Pump Calibration

The pump stroke was set to give approximately the desired oil rate. The amount of oil put through in 1/2 hour was then weighed and the pump readjusted and another 1/2 hour run made and so on until the desired rate had been attained. At the start of the investigation the pump rate was 412 grams of oil per hour. At the end of run 14, the pump was reset to 418 grams per hour because the setting was changed slightly, by accident, during the run.

Analytical Methods

The sulfur content of the samples of oil were determined by the lamp sulfur method (1). All of the samples for the lamp sulfur determinations were dried with calcium chloride and filtered. ASTM distillation procedure (2) was used to obtain the distillation data tabulated in Table VI. The

specific gravity was determined using a Westphal balance.

Hydrogen Manometer Calibration:

A wet test meter was used to calibrate the orifice and manometer. The volume put through the meter in ten minutes, at a given mercury level in the manometer, was corrected for temperature, pressure, and water vapor pressure to give the volume in standard cubic feet of hydrogen per hour. This was done for a number of different manometer readings. The readings were then plotted against standard cubic feet and a convenient point was chosen on the curve close to 2.50 cubic feet per hour. The point gave a hydrogen rate of 2.46 cubic feet of hydrogen per hour, and that rate was used throughout this investigation.

MATERIALS

The oil used in the investigation was a straight run fuel oil from the Husky Oil Company refinery in Cody, Wyoming. The sulfur content was 2.09 percent and the average molecular weight about 200. Most of the sulfur was in the form of thiophenes or thiophanes (10). Prior to its use, the oil was stabilized by distillation with hydrogen bubbling into the still pot. The total recovery was 95.6 percent, and the sulfur content remained at 2.09 percent.

The hydrogen was obtained from the Whitmore Oxygen Company.

All of the catalyst samples were obtained from the Husky Oil Company. The following is a general history of the preparation of catalyst samples P#5, P#6, P#7, and P#8 as reported by the Husky Oil Company.

Spent catalyst was dissolved with 50 weight percent sulfuric acid at 210° F. Nickel carbonate was precipitated at 210°F., using approximately stoichio-

metric amounts of a saturated soda ash solution, and digested for a week. The carbonate was filtered out but was contaminated with iron and silica. A portion of the contaminated carbonate was disolved in weak sulfuric acid. All of the iron and silica was then removed by careful filtration.

The resultant solution contained 5.50 weight percent nickel, had a specific gravity of 1.2589 at 28.9°C, and had a pH of 4.5.

A solution of 222.7 grams of Na_2CO_3 per liter at 28.9°C was prepared from commercial washing soda. In each precipitation 225 cc of nickel solution and 130 cc of soda ash solution at 28.9°C were used. The actual amount of Na_2CO_3 used was 28.9 grams or 2.3% excess of stoichiometric requirements.

P#5: The nickel sulfate solution was heated to boiling with 9.576 grams of dry celite. The sodium carbonate solution was added slowly over a two hour period with stirring. The resultant solution and precipitate were filtered through a steam jacketed Buchner funnel. The precipitate was dried overnight in a 105°C oven.

P#6: The 9.576 grams of celite were not added until 140 cc of the nickel sulfate solution had been added to the sodium carbonate solution. The nickel sulfate solution was added in 100 minutes. Otherwise the procedure was the same as for P#5.

P#5 and P#6 were calcined at the same time in a muffle furnace at 800°F for 20 hours. Two separate catalyst chambers, each made from 6 inches of 1 inch standard steel pipe reduced to fit 1/8 inch copper tubing on each end, were used and the air rate through each was adjusted to approximately 2.0 ft^3 /hr. STP. With P#6 the initial air rate was approximately 0.2 ft^3/hr. After 90 minutes the air rate was about 1.0 ft^3/hr., and after two additional hours

was 2.0 ft^3/hr. Because of a low weight loss on calcination P#5 and P#6 were recalcined. During this second calcination, the temperature of the muffle furnace was allowed to go to 1450°F for a short time. After the period of overheating the muffle was maintained at 800°F for an additional 14 hours.

P#7: In the preparation of this catalyst sample 4.788 grams of celite were added to the nickel sulfate solution and the solution was heated to boiling. The sodium carbonate solution was added over a 30 minute period with stirring and was then boiled for 1½ hours. The total volume was increased to 355 cc by addition of water and was then filtered through a steam jacketed Buchner funnel. The precipitate was dried in a 205°F oven overnight.

P#8: The same procedure as for P#7 except nickel sulfate was added to the sodium carbonate and celite.

P#7 and P#8 were calcined simultaneously at 806°F for 87 hours. The air rate was 2.0 ft^3/hr. through each catalyst sample.

Gwynn #1 catalyst was prepared with celite FC from nickel sulfate precipitated with sodium carbonate. The precipitate was washed, dried, and pelleted. The calcine treatment given to Gwynn #1 samples is given in Table 2 and the analysis after calcining is given in Table 3.

Harshaw #1 catalyst was prepared from precipitated nickel hydroxide. Its calcine treatment and analysis after calcining are given in Tables 2 and 3 respectively.

SAMPLE CALCULATIONS

The calculations of the space velocity, catalyst weight balance, oil weight balances, and sulfur balances for run number 6 are presented as typical of all runs made.

A. Calculation of space velocity:

Data:

Pump rate	= 412 gm/hr
Catalyst weight	= 20 gms
Space Velocity = $\frac{412 \text{ gm/hr}}{20 \text{ gm}}$	= 20.6 hr^{-1}

B. Calculation of Catalyst Weight Balance:

Data:

Weight of catalyst in	= 20 gms
Catalyst plus inerts in	= 96.6 gms
Catalyst plus inerts out	= 98.6 gms
Percent catalyst loss = + $\frac{2.0 \times 100}{20.0}$	= +10.0%

C. Calculation of Oil Weight Balances:
(Overall and 1st and 2d hour)

Data:

Oil charged	= 420 gms
Oil recovered at end of run	= 340.2 gms
Weight loss by samples taken	= 69.0 gms
Total weight loss = 420 - 340.2 +	= 10.8 gms
Distributed losses = $\frac{10.8 \text{ gms}}{6 \text{ hrs}}$	= 1.8 gms/hr

C. Calculation of Oil Weight Balances (Cont'd)

Data:

Weight Loss by sample 1st hour	= 11.6 gms
Weight loss by sample 2d hour	= 12.3 gms
Distributed loss 1st hour	= 1.8 gms
Distributed loss 2d hour	= 1.8 gms
Weight Oil before correction 1st hour	= 420.0 gms

Weight oil after correction 1st hour = 420.0 - 1.8 - 11.6 = 392.5 gms

D. Calculation of Sulfur Balances:
(For 1st and 2d hours)

Data:

Initial sulfur	= 2.09%
1st hour sulfur	= 1.945%
2d hour sulfur	= 1.609
Weight oil before correction 1st hour	= 420. gms
Weight oil before correction 2d hour	= 406.6 gms

Sulfur removed during time interval 0-1 hour
$2.09 - 1.945\ (420)$ = 0.61 gms

Sulfur removed during time interval 1-2 hours
$1.945 - 1.609\ (406.6)$ = 1.36 gms

Weight of sulfur after correction 1st hour 1.945 (407.1) = 7.90 gms

Weight of sulfur after correction 2d hour 1.609 (392.5) = 6.31 gms

RESULTS

Since this investigation was mainly concerned with the method of catalyst preparation and/or treatment, operating conditions for the comparison runs were kept as nearly constant as possible. Haas (10) showed that desulfurization was independent of temperature between 625 and 675°F so 625°F was chosen as a standard comparison temperature. The hydrogen rate and space velocity (2.46 ft^3/hr and about 20.6 hr^{-1}) were both approximately the same as those used by Haas. The oil used was stabilized by distillation with hydrogen bubbling into the still pot. This permitted the distillation to a small percent bottoms without cracking, and also insured the removal of any light ends from the oil which might have been lost in the comparison unit. The sulfur content of the stabilized oil was the same as that of the oil charged to distillation.

Catalysts of nickel oxide prepared by Haas (10) from precipitated nickel hydroxide and nickel carbonate showed no activity as desulfurization catalysts (or reagents). This fact was rather surprising since active catalysts have been prepared from both the hydroxide and carbonate. At the start of this investigation catalyst samples were prepared from spent nickel oxide by dissolving the spent catalyst in sulfuric acid, precipitating the carbonate, and subsequent calcining in air. These samples, P#5, P#6, P#7, and P#8, certainly showed activity in desulfurizing the feed oil. The reason for Haas' failure to produce active catalysts can only be guessed. Haas does not give the details of the procedures or amounts of reagents used in his precipitations, but it is thought that perhaps he used rather large excesses of sodium hydroxide and potassium carbonate in his precipitations. P#5, P#6, P#7, and P#8 were

precipitated with sodium carbonate only in slight excess (2.3%). Ueno (15) reports hydrogenation catalysts prepared by precipitating nickel carbonate from nickel sulfate and sodium carbonate solutions have the greatest activity when a slight excess of sodium carbonate is used. Catalyst samples P#7 and P#8 have the same history except for the fact that in the case of P#7 sodium carbonate was added to the nickel sulfate solution, and in the case of P#8 the nickel sulfate solution was added to the sodium carbonate solution. In the case of P#8 the sodium carbonate was always in excess throughout the precipitation while P#7 sodium carbonate was never in excess until near the end of the precipitation. Their difference in activity is hard to explain on this basis since the activities of P#5 and P#6 show that the sample which was prepared by adding sodium carbonate to nickel sulfate (P#5) has the highest activity. However not too much faith can be placed on the results of runs 1 and 2 (samples P#5 and P#6) because the catalysts losses are rather high and probably occured mostly at the beginning of the runs due to the catalyst washing out of its bed. The inert content of P#6 was almost twice as great as that of the other three samples and although the activity is shown on a nickel basis in Figure 1 there is no reason to believe that inert content does not contribute to activity. The work of Tits and Yur'ev (14) seems to indicate that inert content is a factor in activity. It is interesting to note that the calculated oxygen content of all three samples (see Table 1) increases with increasing activity. This fact seems to give the best general correlation of catalyst activity.

To determine the effect of high calcine temperature in an air stream on catalyst activity runs 5, 6, 7, 8, and 9 were made using Harshaw #1 catalyst and runs 10, 11, 12, 13, and 14 were made with Gwynn #1. Although there seems

to be a slight trend to a maximum activity at 1000°F with Harshaw #1 catalyst (Figure 1), the differences in activities at 800°, 900°, and 1000°F are very small and could easily be within the range of experimental error. Gwynn #1 shows no such trend with C-12 (run 12) being far out of line with respect to any such trend. About all that can be concluded is that activity falls off when nickel oxide is prepared by calcining the carbonate or hydroxide at temperatures above 1000°F.

The inconclusive results of calcine temperatures of 1000°F and below led to the activity evaluation of a Harshaw #1 and a Gwynn #1 sample which had been calcined, or maybe heated would be a better word, at 105°F in an air stream. The results with these two samples indicate that calcining can be done at low temperatures. Further study will be required at temperatures below 800°F to understand fully the effect of calcine temperature on catalyst activity but the results of this study seem to indicate that a low calcine temperature is the more attractive both from the standpoint of activity and economy.

The results of the two runs made with Gwynn #1 samples calcined at 1000°F in atmospheres other than air are inconclusive. From the results of these two runs one would conclude that the calcine atmosphere had no effect on the catalyst activity, however here again further study will be required to fully ascertain the effect of calcine atmosphere.

It has been postulated that the activity of nickel oxide catalysts is related to lattice distance of the nickel atoms in the nickel oxide crystal or to the energy level of the crystal. It was beyond the scope and purpose of this investigation to go into crystal structure determinations etc., but

a review of the literature on nickel oxide structure does furnish a little information. On the negative side, Clark et al (6) studied the crystal structure of nickel catalysts of widely different hydrogenation and de-hydrogenation activities prepared by various methods and concluded that the differences in activities were not due to a difference in the lattice type or dimensions. On the positive side, Rooksby (12) indicates that below about 200° C the nickel oxide lattice is distorted which may mean that crystals prepared at a temperature below 200°C should have a higher energy level and therefore a greater activity. Boswell and Iler (4) report that the ratio of active surface atoms to total nickel atoms present in a crystal decreased with increasing temperature of heating. They also report that nickel oxide is composed of very small crystals when prepared from the hydroxide at lower temperatures. Information on the structure of nickel dioxide (NiO_2) is very meager, but Clark et al (6) found it to be amorphous in their studies.

The above discussion certainly does not explain the high activity of catalysts calcined at lower temperatures and it was not so intended. It does show that additional work at lower temperatures is certainly in order.

Haas (10) concluded that nickel oxide desulfurizes by acting strictly as a chemical reagent. A cadmium chloride bubbler was used on the exhaust line in some of the runs made in this investigation and an evolution of hydrogen sulfide was always detected after a certain induction period. This leads one to believe that the nickel oxide acts as both a catalyst and reagent. It might even be postulated that the desulfurization is catalytic removing the sulfur as hydrogen sulfide followed by reaction of part of the hydrogen sulfide with the nickel oxide catalyst. Haas also stated that free nickel may be the active agent. As observed by Haas, some of the catalyst samples glowed

when emptied from the reactor in this investigation, otherwise no new information was gained on this question.

There has been some question on the method of calculating the amount of sulfur removed during a time interval (see part D, sample calculations). Admittedly it is an approximate method since no account is taken of the fact that during a time interval sulfur is removed from the oil and results in a small weight loss. This makes the values slightly low, however since the amount of sulfur in the oil is small, since the amount of sulfur removed is even smaller, and since most of the sulfur is removed during the first two time intervals the calculated values are only about 1% low. Relative activity is really the important consideration not absolute activity so relative activity comparisons will be affected very little because all values are low by about the same amount.

It has also been suggested that the samples taken for analysis also effect the amount of sulfur removed making it lower than it should be since the first sample taken has only been through the catalyst bed once (and so on for the subsequent samples) and has sulfur compounds present which would be removed otherwise. This is probably so to a certain extent however again, the relative activity relationships of various catalyst samples would not be changed much.

SUMMARY OF RESULTS

The results obtained in this investigation of desulfurization of a fuel oil with nickel oxide catalysts may be summarized as follows:

(1) Active nickel oxide catalysts may be prepared by dissolving spent catalyst in sulfuric acid, precipitating the carbonate, and calcining the precipitate in an air stream in the neighborhood of 800°F.

(2) Fresh Harshaw #1 and Gwynn #1 catalysts show a decrease in activity upon calcining at temperatures in excess of 1000°F.

(3) From the standpoint of economy of operation and catalyst activity, a low calcine temperature is indicated.

(4) Nickel oxide acts both as a catalyst and a chemical reagent in desulfurizing fuel oil.

ACKNOWLEDGMENT

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APPENDIX

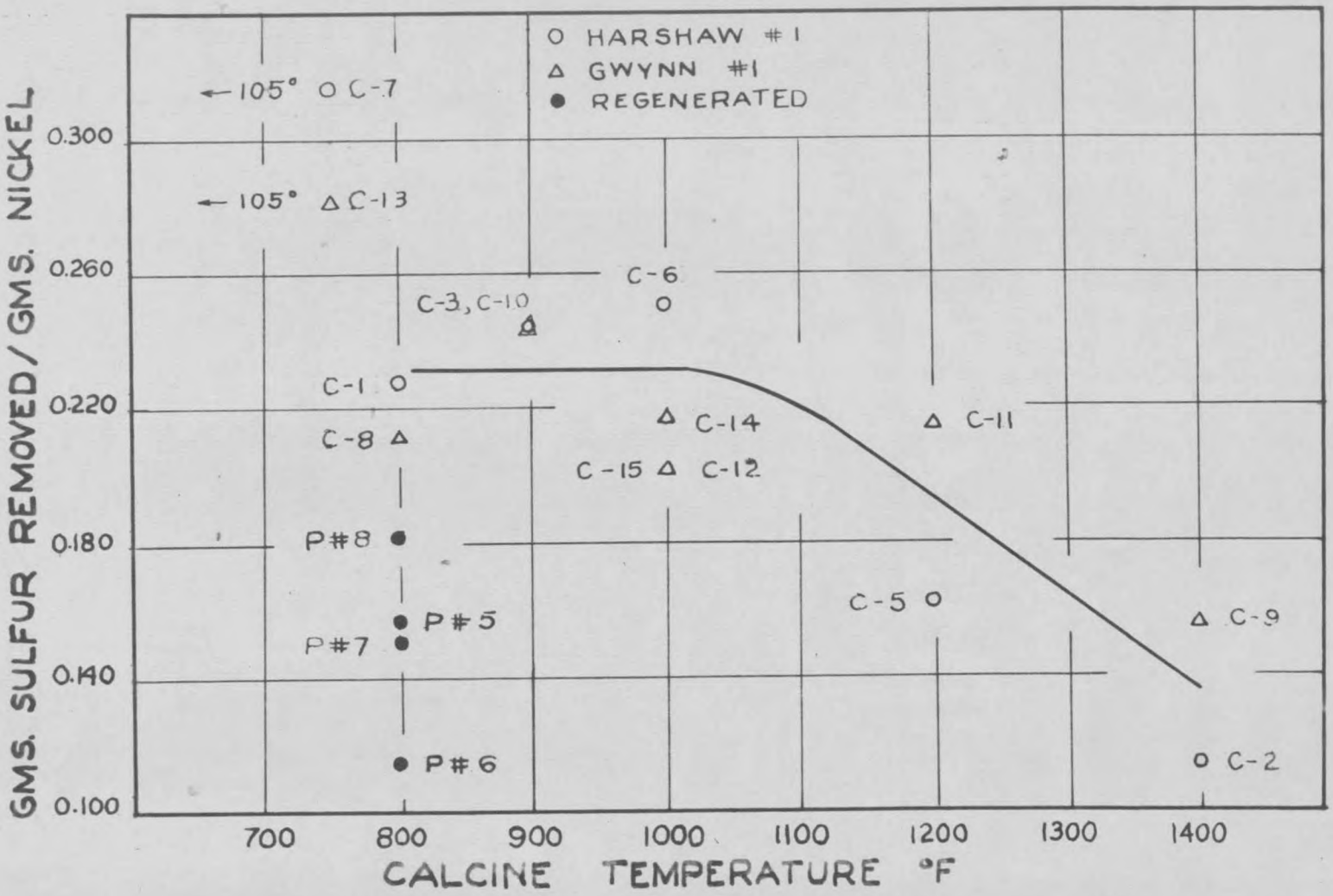

Figure 1 Catalyst Activity as a Function of Calcine Temperature

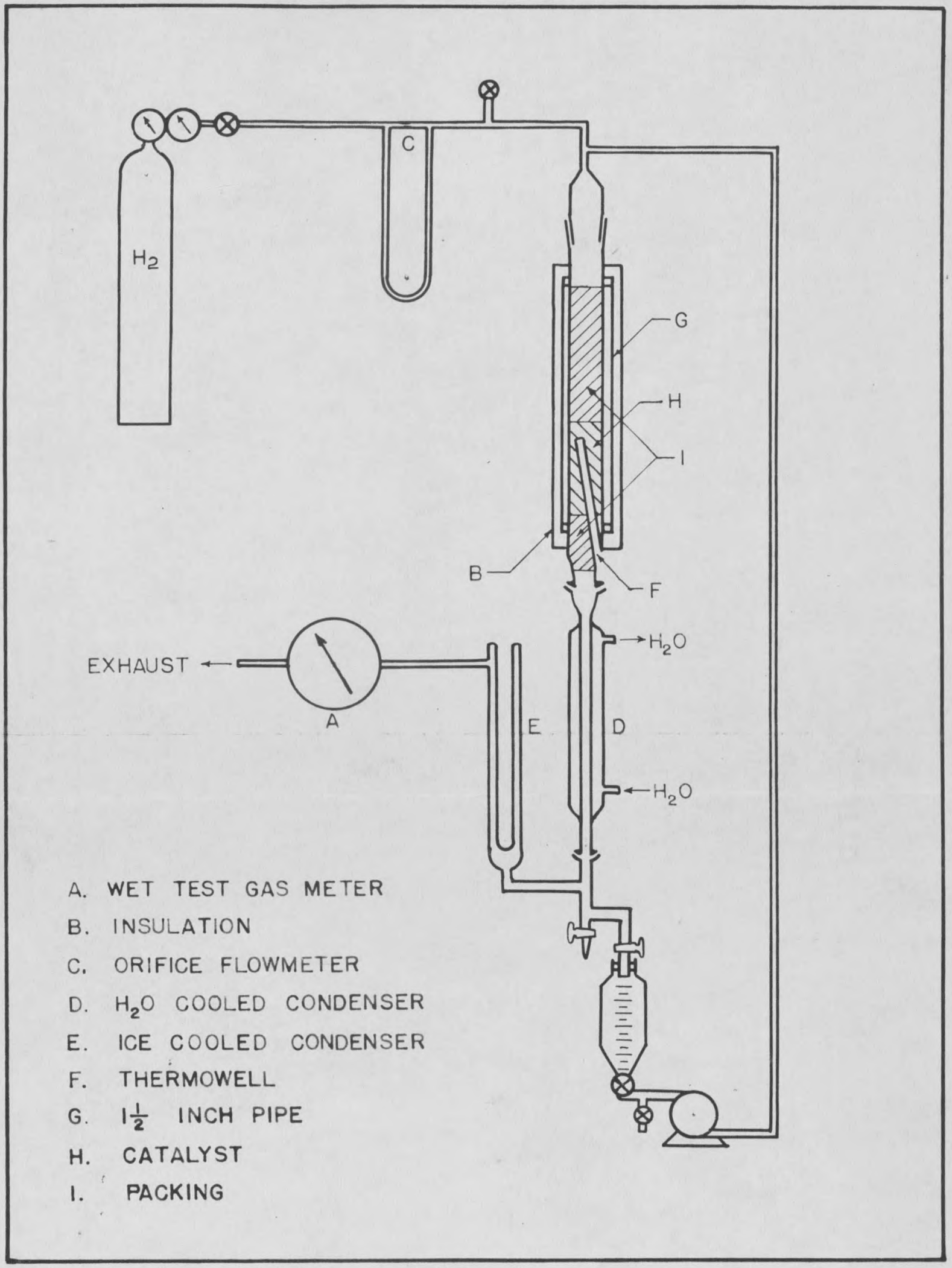

Figure 2 Comparison Unit

TABLE I
DATA ON REGENERATED CATALYST SAMPLES

	P#5	P#6	P#7	P#8
pH of filtrate	9 approx.	8.76	8.68	8.69
Nickel Content, grams	15.505	x	x	x
Wt. of Celite	9.576	x	4.788	x
Wt. of oven dried material	43.731	53.993	44.686	42.963
Calc. Wt. $NiCO_3$	31.358	x	x	x
Wt. dry inerts calc.	12.373	22.635	13.328	11.605
Wt. Calcined Material 1st. Calcination	37.963	46.780	38.167	36.874
Calc. Wt. Nickel Oxide	25.590	24.145	24.839	25.269
Apparent Formula Nickel Oxide	$NiO_{2.39}$	$NiO_{2.05}$	$NiO_{2.21}$	$NiO_{2.31}$
Wt. Calcined Material 2d. Calcination	37.498	46.280		
Calc. Wt. Nickel Oxide	25.125	23.645		
Apparent Formula, Oxide	$NiO_{2.28}$	$NiO_{1.93}$		

TABLE II
FRESH CATALYST TREATMENT

Run No.	Sample No.	Type Catalyst	Calcine Conditions	Wt. Change on Calcine		Nickel Content of Sample gms.
				Orig. wt.	Final wt.	
5	C-1	Harshaw #1	20 hrs. in air stream 800°F	23.946	20.007	10.715
6	C-3	" "	20 hrs. in air stream 900°F	23.998	19.977	10.762
7	C-6	" "	20 hrs. in air stream 1000°F	23.942	19.689	10.752
8	C-5	" "	20 hrs. in air stream 1200°F	23.955	18.798	10.750
9	C-2	" "	20 hrs. in air stream 1400°F	24.004	18.768	10.772
10	C-8	Gwynn #1	20 hrs. in air stream 800°F	25.280	20.656	7.840
11	C-10	" "	20 hrs. in air stream 900°F	25.303	21.105	8.069
12	C-12	" "	20 hrs. in air stream 1000°F	25.285	20.215	8.047
13	C-11	" "	20 hrs. in air stream 1200°F	25.252	19.711	8.063
14	C-9	" "	20 hrs. in air stream 1400°F	25.277	19.830	8.114
16	C-13	" "	20 hrs. in air stream 105°F	25.298	22.594	8.135
17	C-14	" "	20 hrs. no outside gas 1000°F	25.284	20.251	8.130
18	C-15	" "	20 hrs 2ft^3 N_2/hr at 1000°F	25.256	20.041	8.076
19	C-7	Harshaw #1	20 hrs in air stream 105°F	unknown	23.211	10.765
15	#34	Prepared by Bowen Research Corporation at North Branch, N.J. Nickel content 70.84%. No other details available.				13.404

TABLE III
CATALYST ANALYSIS

Harshaw #1	$Ni(OH)_2$ Parent Compound
Nickel	53.24%
Carbon	4.47
Silica	17.34
Oxygen by difference	24.95
Total	100.00%

Gwynn #1	$NiCO_3$ Parent Compound
Nickel	38.44%
Carbon as Graphite	2.22
Carbon as Carbonate	0.15
Silica	37.00
Oxygen by difference	22.19
Total	100.00%

TABLE IV
OPERATING CONDITIONS

Run No.	Catalyst Type	Oil Wt. gms	% loss	Wt. gms	% loss	Hydrogen Rate ft^3/hr	Space velocity hr^{-1}	Gms S removed per gm catalyst	Gms removed per gm nickel
1	P#5	20.0	11.1	420	7.78	2.46	20.6	0.0650	0.158
2	P#6	20.0	29.0	420	4.47	2.46	20.6	0.0380	0.114
3	P#7	20.0	1.0	420	4.21	2.46	20.6	0.0620	0.150
4	P#8	20.0	2.5	420	2.84	2.46	20.6	0.0770	0.182
5	C-1	20.0	+1.0	420	2.43	2.46	20.6	0.122	0.228
6	C-3	20.0	+10.0	420	2.57	2.46	20.6	0.132	0.245
7	C-6	19.6	+10.2	420	2.43	2.46	21.0	0.136	0.252
8	C-5	18.8	+4.3	420	2.21	2.46	21.9	0.0931	0.163
9	C-2	18.8	+2.0	420	3.69	2.46	21.9	0.0655	0.114
10	C-8	20.5	+8.3	420	1.81	2.46	20.1	0.0805	0.212
11.	C-10	20.6	+7.8	420	2.96	2.46	20.0	0.0942	0.246
12	C-12	20.0	+6.0	420	3.26	2.46	20.6	0.0810	0.202
13	C-11	19.5	+4.1	420	2.02	2.46	21.2	0.0888	0.216
14	C-9	19.9	+5.0	420	7.34	2.46	20.7	0.0638	0.157
15	#34	20.0	9.5	420	0.72	2.46	20.9	0.112	0.168
16	C-13	22.6	3.5	420	4.89	2.46	18.5	0.101	0.281
17	C-14	20.3	+8.4	420	2.02	2.46	20.6	0.0872	0.218
18	C-15	20.0	+9.0	420	2.34	2.46	20.9	0.0820	0.203
19	C-7	23.0	+5.2	420	2.10	2.46	18.2	0.148	0.316

TABLE V
SULFUR BALANCES

Run No.	Average Reactor Temp °F	Time in Hours	% S	Wt in gms before correction oil	Corrections Wt of sample	Corrections Losses	Wt in gms after correction oil	Wt in gms after correction Sulfur	Sulfur removed during time interval
1	625	0	2.09	420	-	-	420	8.78	-
		1	1.985	420	16.7	5.5	397.8	7.89	0.44
		2	1.947	397.8	13.6	5.4	378.8	7.37	0.15
		3	1.892	378.8	11.0	5.4	362.4	6.85	0.21
		4	1.848	362.4	10.7	5.5	346.2	6.40	0.16
		5	1.808	346.2	12.2	5.4	328.6	5.94	0.14
		6	1.744	328.6	323.1	5.5	000.0	5.64	0.21
									1.31
2	625	0	2.09	420	-	-	420	8.78	-
		1	2.02	420	14.3	3.2	402.5	8.14	0.29
		2	1.99	402.5	11.5	3.1	387.9	7.71	0.12
		3	1.99	387.9	11.1	3.1	373.7	7.43	0.00
		4	1.958	373.7	26.4	3.1	344.2	6.74	0.12
		5	1.910	344.2	17.9	3.1	323.2	6.17	0.17
		6	1.891	323.2	320.0	3.2	000.0	6.05	0.06
									0.76
3	625	0	2.09	420	-	-	420	8.78	-
		1	1.961	420	10.7	3.0	406.3	7.97	0.54
		2	1.891	406.3	13.4	2.9	390.0	7.38	0.28
		3	1.820	390.0	17.1	2.9	370.0	6.73	0.28
		4	1.820	370.0	14.5	3.0	352.5	6.41	0.00
		5	1.785	352.5	18.1	2.9	331.5	5.91	0.12
		6	1.780	331.5	328.5	3.0	000.0	5.85	0.02
									1.24
4	625	0	2.09	420	-	-	420	8.78	-
		1	2.06	420	10.9	2.0	407.1	8.39	0.13
		2	1.92	407.1	11.9	2.0	393.2	7.55	0.57
		3	1.848	393.2	14.1	1.9	377.2	6.96	0.28
		4	1.795	377.2	16.0	2.0	359.2	6.45	0.20
		5	1.771	359.2	12.2	2.0	345.0	6.10	0.09
		6	1.692	345.0	343.0	2.0	000.0	5.80	0.27
									1.54

TABLE V (cont'd.)
SULFUR BALANCES

Run No.	Average Reactor Temp °F	Time in Hours	% S	Wt gms before corr. oil	Corrections wt of sample	Corrections Losses	Wt in gms after correction oil	Wt in gms after correction Sulfur	Sulfur removed during time interval
5	625	0	2.09	420	-	-	420	8.78	-
		1	1.795	420	14.6	1.7	403.7	7.22	1.20
		2	1.670	403.7	13.0	1.7	389.0	6.50	0.51
		3	1.573	389.0	10.2	1.7	377.1	5.94	0.38
		4	1.547	377.1	11.9	1.7	363.5	5.55	0.10
		5	1.518	363.5	14.1	1.7	347.0	5.26	0.11
		6	1.478	347.7	346.0	1.7	000.0	5.10	0.14
									2.44
6	625	0	2.09	420	-	-	420	8.78	-
		1	1.945	420	11.6	1.8	406.6	7.90	0.61
		2	1.609	406.6	12.3	1.8	392.5	6.31	1.36
		3	1.538	392.5	17.3	1.8	373.4	5.74	0.28
		4	1.481	373.4	14.5	1.8	357.1	5.29	0.21
		5	1.452	357.1	13.3	1.8	342.0	4.97	0.10
		6	1.428	342.0	340.2	1.8	000.0	4.86	0.08
									2.64
7	625	0	2.09	420	-	-	420	8.78	-
		1	1.769	420	11.7	1.7	406.6	7.20	1.35
		2	1.642	406.6	11.8	1.7	393.1	6.45	0.52
		3	1.538	393.1	16.3	1.7	375.1	5.77	0.41
		4	1.496	375.1	9.5	1.7	363.9	5.44	0.16
		5	1.438	363.9	14.9	1.7	347.3	5.00	0.21
		6	1.419	347.3	345.6	1.7	000.0	4.90	0.06
									2.71
8	625	0	2.09	420	-	-	420	8.78	-
		1	1.915	420	11.4	1.6	407	7.80	0.74
		2	1.812	407	14.7	1.5	390.8	7.08	0.42
		3	1.730	390.8	11.6	1.5	377.7	6.53	0.32
		4	1.705	377.7	13.6	1.6	362.5	6.18	0.09
		5	1.685	362.5	10.8	1.5	350.2	5.90	0.07
		6	1.653	350.2	348.6	1.6	000.0	5.77	0.11
									1.75

TABLE V (cont'd.)
SULFUR BALANCES

Run No.	Average Reactor Temp °F	Time in Hours	% S	Wt gms before corr. oil	Corrections Wt of Sample	Corrections Losses	Wt in gms after correction oil	Wt in gms after correction Sulfur	Sulfur Removed During time Interval
9	625	0	2.09	420	-	-	420	8.78	-
		1	1.981	420	15.3	2.6	402.1	7.97	0.46
		2	1.922	402.1	10.0	2.6	389.5	7.49	0.24
		3	1.883	389.5	12.3	2.6	374.6	7.06	0.15
		4	1.871	374.6	14.3	2.5	357.8	6.69	0.04
		5	1.792	357.8	12.6	2.6	342.6	6.15	0.28
		6	1.775	342.6	340.0	2.6	000.0	6.04	0.06
									1.23
10	625	0	2.09	420	-	-	420	8.78	-
		1	1.84	420	10.6	1.3	408.1	7.51	1.05
		2	1.765	408.1	11.6	1.2	395.3	6.97	0.31
		3	1.745	395.3	11.5	1.3	382.5	6.68	0.08
		4	1.720	382.5	13.4	1.3	367.8	6.32	0.10
		5	1.70	367.8	15.0	1.2	351.6	5.98	0.07
		6	1.688	351.6	350.3	1.3	000.0	5.91	0.04
									1.65
11	625	0	2.09	420	-	-	420	8.78	-
		1	1.891	420	12.6	2.1	405.3	7.66	0.84
		2	1.790	405.3	11.8	2.0	391.5	7.00	0.41
		3	1.738	391.5	14.4	2.1	375.0	6.52	0.20
		4	1.712	375.0	12.1	2.1	360.8	6.18	0.10
		5	1.670	360.8	16.3	2.0	342.5	5.72	0.15
		6	1.598	342.5	340.4	2.1	000.0	5.44	0.24
									1.94
12	625	0	2.09	420	-	-	420	8.78	-
		1	1.931	420	14.2	2.3	403.5	7.79	0.67
		2	1.870	403.5	10.2	2.3	391.0	7.31	0.25
		3	1.780	391.0	8.6	2.3	380.1	6.76	0.35
		4	1.748	380.1	14.3	2.2	363.6	6.35	0.12
		5	1.692	363.6	13.9	2.3	347.4	5.87	0.20
		6	1.683	347.4	345.1	2.3	000.0	5.81	0.03
									1.62

TABLE V (cont'd.)
SULFUR BALANCES

Run No.	Average Reactor Temp °F	Time in hours	% S	Wt gms before corr. oil	Corrections wt. of sample	Corrections losses	Wt in gms after correction oil	Wt in gms after correction Sulfur	Sulfur removed during time interval
13	625	0	2.09	420	-	-	420	8.78	-
		1	1.912	420	19.5	1.4	399.1	7.63	0.75
		2	1.81	399.1	16.2	1.4	381.5	6.90	0.41
		3	1.73	381.5	12.2	1.4	367.9	6.36	0.31
		4	1.715	367.9	13.6	1.5	352.8	6.05	0.05
		5	1.680	352.8	11.5	1.4	339.9	5.71	0.12
		6	1.654	339.9	338.5	1.4	000.0	5.60	0.09
									1.73
14	625	0	2.09	420	-	-	420	8.78	-
		1	1.949	420	13.8	5.1	401.6	7.84	0.59
		2	1.930	401.6	14.8	5.2	381.6	7.35	0.08
		3	1.858	381.6	16.0	5.1	360.5	6.70	0.27
		4	1.810	360.5	14.4	5.1	341.0	6.16	0.17
		5	1.795	341.0	11.5	5.2	324.3	5.82	0.05
		6	1.760	324.3	319.2	5.1	000.0	5.61	0.11
									1.27
15	625	0	2.09	420	-	-	420	8.78	-
		1	1.865	420	16.8	0.5	402.7	7.52	0.95
		2	1.760	402.7	13.6	0.5	388.6	6.84	0.42
		3	1.652	388.6	14.1	0.5	374.0	6.19	0.42
		4	1.613	374.0	11.5	0.5	362.0	5.85	0.15
		5	1.570	362.0	15.1	0.5	346.4	5.44	0.16
		6	1.528	346.4	345.9	0.5	000.0	5.28	0.15
16	625	0	2.09	420	-	-	420	8.78	-
		1	1.765	420	20.3	3.4	396.3	7.00	1.37
		2	1.665	396.3	11.3	3.4	381.6	6.35	0.40
		3	1.618	381.6	12.0	3.4	366.2	5.93	0.18
		4	1.572	366.2	16.1	3.4	346.7	5.45	0.17
		5	1.537	346.7	10.6	3.4	332.7	5.11	0.12
		6	1.525	332.7	329.2	3.5	000.0	5.01	0.04
									2.28

TABLE V (cont'd.)
Sulfur Balances

Run No.	Average Reactor Temp °F	Time in Hours	% S	Wt gms before corr. oil	Corrections wt of sample	Corrections losses	Wt in gms after correction oil	Wt in gms after correction sulfur	Sulfur removed during time interval
17	625	0	2.09	420	-	-	420	8.78	-
		1	1.903	420	13.4	1.4	405.2	7.71	0.79
		2	1.834	405.2	9.9	1.4	393.9	7.22	0.28
		3	1.778	393.9	12.8	1.4	379.7	6.75	0.22
		4	1.703	379.7	10.9	1.4	367.4	6.25	0.28
		5	1.660	367.4	10.0	1.4	356.0	5.91	0.16
		6	1.648	356.0	354.5	1.5	000.0	5.85	0.04
									1.77
18	625	0	2.09	420	-	-	420	8.78	-
		1	1.943	420	11.0	1.6	407.4	7.90	0.62
		2	1.812	407.4	11.2	1.7	394.5	7.15	0.53
		3	1.77	394.5	11.1	1.6	381.8	6.76	0.17
		4	1.76	381.8	20.5	1.6	359.7	6.34	0.04
		5	1.752	359.7	12.2	1.6	345.9	6.06	0.03
		6	1.681	345.9	344.2	1.7	000.0	5.80	0.25
									1.64
19	625	0	2.09	420	-	-	420	8.78	-
		1	1.638	420	16.2	1.5	402.3	6.59	1.90
		2	1.455	402.3	12.2	1.4	388.7	5.66	0.74
		3	1.370	388.7	11.5	1.5	375.7	5.14	0.33
		4	1.322	375.7	11.3	1.4	363.0	4.80	0.18
		5	1.280	363.0	13.0	1.5	348.5	4.46	0.16
		6	1.252	348.5	347.0	1.5	000.0	4.35	0.09
									3.40

TABLE VI
INSPECTION DATA FOR FUEL OIL

A. S. T. M. Dist. °F

First Drop	460
5%	500
10%	518
20%	534
30%	546
40%	556
50%	566
60%	576
70%	586
80%	600
90%	620
End Point	660
Recovery	98%
Bar. Pressure in mm of Hg.	638
Specific Gravity	0.868
Weight Per Cent Sulfur	2.09%