

PROCESS RESEARCH ON DESULFURIZATION OF PETROLEUM COKE

by

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The individual and combined effects of sodium hydroxide, sodium carbonate, hydrogen, and hydrogen sulfide on desulfurization of petroleum coke have been reported on the literature many times (1-5). Hutchings (1) shows that essentially complete desulfurization is obtained using a high ratio of NaOH to coke, a temperature of 750-865°F, and a 7-1/2 hour residence time. Lukasiwicz and Johnson (2) desulfurized delayed petroleum coke with sodium carbonates and determined an optimum temperature of 1,400°F. They obtained up to 67 percent desulfurization using 0.28 gm Na₂CO₃/gm coke. Seventy percent of the sulfur removed was recovered as a sodium sulfide wash solution. The balance came off as H₂S. Mason (3) demonstrated that hydrogen was relatively ineffective for desulfurization of fluid coke. Almost 6 hours were required for a 50 percent sulfur reduction at 1,300°F. Mason also showed that the sulfur content of fluid coke could be increased by reaction with a H₂S-H₂ mixture. Gorin (4) and others (5) have also shown the deleterious effect of H₂S on char desulfurization. And finally Johnson (6) discovered the combined effect of sodium hydroxide and hydrogen for desulfurization of calcined coke.

This paper presents data on desulfurization of fluid petroleum coke with hydrogen, with sodium hydroxide and hydrogen and, as an outgrowth of this work, sodium sulfide and hydrogen. A screening study wherein over 80 potential sulfur acceptors were reacted with ground fluid coke at 1,400°F, identified NaOH and KOH as effective reagents and, in general, confirmed the conclusion of previous workers. The use of hydrogen and relatively small amounts of NaOH with fluid coke was found to be a highly efficient desulfurization route. As with all sodium hydroxide or carbonate systems, most of the sulfur was recovered as soluble sodium sulfur compounds, primarily Ha₂S. Some sulfur was also recovered from the off gases, both as H₂S and COS. Experiments wherein the sodium sulfide product was substituted for the sodium hydroxide reactant gave substantial desulfurization resulting in significant simplification of the commercial process concept as described in U. S. Patents 3472622 (7) and 3472624 (8) assigned to Tidewater Oil Co. (now Getty Oil Company).

Fluid coke is a petroleum coke produced as small, low surface, essentially spherical, dense particles. Ninety-five percent

falls in the particle size range of 14 to 200 mesh. Table I shows typical properties. The sulfur content is, of course, dependent upon the sulfur content of the residuum feed to the fluid coker. Coke used in this work varied from 3.7 to 7.2 percent sulfur. Oxygen content and surface area are functions of particle size as shown in Table II. One step in fluid coking is the reheating of coke to reaction temperatures by burning with air. This is accomplished in the coker burner; product coke is also withdrawn from this vessel. Thus the last reaction in fluid coking is an oxidation and it is not surprising to find oxygen in the product. Nor is it surprising to find more oxygen on the smaller particles which have more geometric surface area per unit weight. The measured surface area (BET) also increases with decreasing particle size. Figure 1 is a photomicrograph of two typical coke samples and shows the essentially spherical form of each particle. The basic structure is shown in Figures 2 and 3. Coke is laid down in thin layers or "onion skins" with burning occurring between laydown of layers. These onion skins are quite evident, and in Figure 3, a seed particle is also evident. This structure was described previously by Dunlop, Griffin, and Moser (9).

Desulfurization with hydrogen alone was found to be diffusion limited as indicated by a direct relationship with surface area as shown in Figure 4. Fluid coke was screened to obtain the different particle size fractions and reacted at 1,400°F for 1 hour with hydrogen gas flowing through the bed. Maximum sulfur removal was approximately 40 percent; desulfurization of unscreened coke under the same conditions is approximately 15 percent.

In another series of experiments, fluid coke was reacted with an equal weight of NaOH at 1,200°F for 1 hour and without a sweep gas. The product mix was cooled, extensively washed with water, and analyzed for sulfur. Essentially complete desulfurization was obtained. Figure 5 is a photomicrograph which shows that the coke particle is literally torn apart by these severe conditions. Unfortunately, surface area on this treated coke was not measured, but from other work, it is estimated to be close to 100 m²/gram. Thus, NaOH obviously either eliminated or dramatically reduced the diffusion barrier evident for desulfurization with hydrogen alone. If a reduced NaOH concentration would "open up" the coke surface, more efficient desulfurization with hydrogen would be anticipated.

Experiments with NaOH, H₂ and coke were made over the operating range of 800 to 1,600°F and 0.0 to 0.40 #NaOH/#coke. Aqueous NaOH (usually 50 percent solution) was sprayed onto coke particles in a liquids-solids blender. Thirty grams of the mix was placed in a quartz tube, hydrogen flow was started and the mix brought to reaction temperature. After a run, the samples were cooled, washed to remove sodium compounds - mostly sulfides - and the coke analyzed for sulfur. Figure 6 shows that

1,200°F to 1,400°F is the optimum temperature range; Figure 7 that 90 percent desulfurization can be obtained with 0.13 #NaOH/#coke at 1,220°F, with a 1 hour reaction time. The cokes from these runs were indistinguishable from raw coke under the same microscope used for the earlier photomicrographs. Data for these runs is shown in Table III. Residual sodium analyses were not made on these desulfurized cokes; however, later work showed that sodium on coke treated in this manner normally assayed 0.1 to 0.7 wt. percent.

Experiments with a 6.0 percent sulfur coke showed similar results although the percentage desulfurization was somewhat reduced. Figure 8 and Table IV shows data from two series of experiments; one run as indicated for the earlier experiments, the other using a larger reactor, a fluid bed, and a different system for addition of the hydroxide. Five hundred sixty grams of coke were loaded into the reactor, fluidized with nitrogen, and heated to 1,200°F. At this point, gas flow was switched to hydrogen and a 50 percent aqueous solution of NaOH admitted to the bed slowly through an atomizing nozzle. Addition of the desired quantity required 22 to 33 minutes after which the reaction was continued for one hour. Essentially the same results were obtained for the two systems.

At this point in this development it appeared that desulfurization was primarily due to the strong getter effect of sodium for sulfur and that hydrogen simply facilitated the transfer of sulfur from the coke to the sodium. It appeared that the getter was necessary to minimize the partial pressure of H₂S; without it, desulfurization would be severely restricted. Primarily to test this theory, several runs were made in which sodium sulfide was substituted for sodium hydroxide. These runs were mostly carried out in the larger reactor utilizing 560 grams of coke and varying amounts of sodium sulfide. The sodium sulfide came from two sources. Wash solutions from desulfurization runs with NaOH were spray dried to obtain an essentially anhydrous product having a sodium to sulfur mole ratio of 2.14 to 1. For other runs, vacuum dehydrated sodium sulfide trihydrate was used. The dehydration was accomplished in nickel crucibles at a pressure of 200 microns with a maximum temperature of 360°F reached in 6 to 8 hours. The trihydrate is theoretically 40.9 percent water; 37.7 percent was recovered, indicating that 3.2 percent water was not removed. When dried slowly the trihydrate remained as flakes which were easily ground to -40 mesh. If dehydration proceeded too rapidly the flakes would melt and form a fused mass unsuitable for further use. All dried Na₂S was stored in a dry, inert atmosphere.

Needless to say the desulfurization results were not what were expected. Sulfur reduction did drop, but less than anticipated. Table V shows comparisons between the NaOH and Na₂S systems for both cokes. For the higher sulfur coke desulfurization dropped from 76 to 45 percent. For the lower

sulfur coke, desulfurization dropped from 91 percent to 64 percent; however, additional residence time increased desulfurization with Na_2S as shown in Figure 9.

The significant point in this discovery is its effect on an overall process concept. All sulfur removal is as volatile sulfur compounds, i.e., H_2S and COS . These can be recovered easily from the gas stream. Sodium sulfide can be separated from the coke by washing, spray dried and recycled directly without conversion back to the hydroxide form. This is shown in Figure 10.

The wash step is still undesirable. For one thing it is costly, for another inefficient as it does not remove all the sodium added. Typical results show 0.1 to 0.7 wt. percent residual sodium. One more approach was attempted to substitute size classification for washing. Coke was screened to obtain two separate fractions: 60 to 80 mesh and 150 to 200 mesh. The 150 to 200 mesh sample was impregnated with NaOH and reacted to convert it to the sulfide form. The recovered particles were not washed. One hundred forty grams were mixed with 290 grams unreacted 60 to 80 mesh coke. This mix was reacted with hydrogen at $1,200^\circ\text{F}$ for two hours. After reaction, the 60 to 80 mesh coke was separated and analyzed. It was then washed and reanalyzed. Results are shown on Table VI. As can be seen some sodium was transferred to the larger particles, thus necessitating the wash. Thus this experiment failed to find a way to eliminate the washing step. However, the desulfurization results were considerable better than obtained with Na_2S and equally as good as with NaOH . Sixty nine percent desulfurization was obtained. This 69 percent compares to 66 percent obtained in one hour with NaOH and an estimated 50-55 percent that would have been obtained with the same quantity of Na_2S .

A clear picture of the reaction mechanism for coke desulfurization with sodium compounds and hydrogen has not really evolved although certain items are known. The getter effect of NaOH is helpful but unessential except where virtually complete desulfurization is required. It appears that the primary role of sodium is to eliminate or reduce the diffusion limitation which prevents effective desulfurization with hydrogen alone. Surface areas in desulfurized cokes were 30 to 60 m^2/gm compared to 10-12 m^2/gm on the raw coke. The partial pressure effect of H_2S , obvious in other work on coke and coal chars, is not limiting when sodium is present. Concentrations up to 5 percent H_2S plus COS had to occur in the initial stages of reaction. Some sodium either reacts with the coke particle or migrates into it to such a position that it cannot be removed by washing. However, no direct relationship was found between percent desulfurization and residual sodium. While not detailed in this report, there is evidence that the amount of sodium left on the coke is a function of the partial pressure of water vapor during the reaction.

In summary, the data obtained in this study is, consistent with that reported by other investigators of NaOH and H_2O - H_2 systems. Up to 97 percent desulfurization was obtained when processing with the NaOH- H_2 route. However, this data also shows up to 74 percent sulfur removal in a Na_2S - H_2 system. Eighty to 90 percent desulfurization is believed attainable by this route with further process optimization. The high partial pressure of H_2S that occurs in this Na_2S - H_2 system does not appear to significantly retard sulfur removal.

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TABLE I

Typical Properties of Fluid Coke

Ultimate Analysis, wt.%

Carbon	87.83
Hydrogen	2.08
Nitrogen	1.34
Sulfur	(3.8-7.2)
Oxygen	1.33*
Ash	0.2

Physical Properties

Density, gm/cc	1.524
Surface Area, m ² /gm	10-12*

Screen Analysis

+14 Mesh	3.7
+60	26.4
+80	61.6
+100	75.7
+150	91.3
+200	98.5
-200	1.5

*Varies with particle size

TABLE II
Properties of Fluid Coke Size Fractions

<u>Tyler Mesh</u>	<u>Surface Area</u> <u>m²/gram</u>	<u>Oxygen, wt.%</u>
-35+60	8	1.19
-60+80	10	1.25
-80+100	16	1.33
-100+150	21	1.31
-150+200	38	1.48
-200		1.39

TABLE III
Desulfurization of Fluid Coke with NaOH and H₂

<u>Run No.</u>	<u>Temp.</u> <u>°F</u>	<u>NaOH/Coke</u> <u>wt./wt.</u>	<u>H₂</u> <u>V/V/hr.</u>	<u>Time, Min.</u>		<u>Sulfur</u> <u>wt.%</u>	<u>% Desul-</u> <u>furization</u>
				<u>Preheat</u>	<u>Reaction</u>		
Feed Coke	-			-	-	3.78	-
<u>Effect of Temperature</u>							
53D	1,200	0.10	530	8	60	0.51	86.5
63D	1,400	0.10	530	8	60	0.60	84.2
70A	1,600	0.10	530	8	60	2.14	43.7
<u>Effect of NaOH/Coke at 1,220°F</u>							
31B	1,220	0.25	530	90	60	0.10	97.4
44A	1,220	0.25	530	90	60	0.22	94.2
33B	1,245	0.15	530	90	60	0.32	91.5
34B	1,210	0.05	530	90	60	1.51	60.3
41A	1,220	0.05	530	90	60	1.37	63.9
40B	1,225	0.05	530	90	60	1.10	71.1
34A	1,210	0.00	530	90	60	3.01	20.8
<u>Effect of NaOH/Coke at 1,030°F</u>							
35A	1,030	0.40	530	90	60	0.16	95.8
35B	1,020	0.25	530	90	60	0.36	90.5
36A	1,040	0.15	530	90	60	0.67	82.4
36B	1,030	0.05	530	90	60	2.25	40.8
42A	1,030	0.05	530	90	60	2.38	37.4
42B	1,035	0.00	530	90	60	3.51	7.6

TABLE III (cont.)

Desulfurization of Fluid Coke with NaOH and H₂

<u>Run No.</u>	<u>Temp.</u> <u>°F</u>	<u>NaOH/Coke</u> <u>wt./wt.</u>	<u>H₂</u> <u>V/V/hr.</u>	<u>Time, Min.</u>		<u>Sulfur</u> <u>wt.%</u>	<u>% Desul-</u> <u>furization</u>
				<u>Preheat</u>	<u>Reaction</u>		
<u>Effect of NaOH/Coke at 820°F</u>							
37A	820	0.40	530	90	60	0.73	80.8
37B	830	0.25	530	90	60	0.94	75.3
38A	815	0.15	530	90	60	1.20	68.4
38B	830	0.05	530	90	60	2.84	25.3
43B	815	0.05	530	90	60	3.18	16.3
43A	820	0.00	530	90	60	3.78	0.1
<u>Effect of Time</u>							
53A	1,200	0.10	530	8	15	0.96	74.7
53B	1,200	0.10	530	8	30	0.87	77.1
53C	1,200	0.10	530	8	60	0.51	86.6
53D	1,200	0.10	530	8	120	0.47	87.6

TABLE IV
Desulfurization of Fluid Coke with NaOH and H₂

Run No.	<u>Quartz Tube</u>			<u>Pilot Plant</u>		
	<u>143</u>	<u>142</u>	<u>141</u>	<u>CD 12</u>	<u>CD 13</u>	<u>CD 16</u>
Reaction Temp., °F	1,200	1,190	1,200	1,200	1,200	1,200
Time, Minutes						
NaOH Addition	-	-	-	28	22	33
Reaction Time	<u>60</u>	<u>60</u>	<u>60</u>	<u>60</u>	<u>60</u>	<u>60</u>
Total Time	60	60	60	88	82	93
H ₂ Flow Rate V/V/Hr.	1,510	1,510	1,510	1,640	1,640	915
NaOH/Coke wt./wt.	0.05	0.10	0.15	0.065	0.078	0.147
Sulfur Analyses, wt.%						
Raw Coke	6.0	6.0	6.0	6.0	6.0	6.0
Desulfurized Coke						
Before Wash	*	*	*	4.0	5.0	*
After Wash	2.02	1.55	1.28	1.99	1.87	1.42
% Desulfurization	66	74	79	67	69	76
Residual Sodium,						
After Wash, wt.%	0.63	0.86	*	0.49	0.46	0.71

*Not determined

TABLE V
Desulfurization of Fluid Coke
Comparison of NaOH-H₂ and Na₂S-H₂ Systems

Run No.	Coke A		Coke B	
	CD-78	CD-16	CD-81	33B*
Reactant	Na ₂ S	NaOH	Na ₂ S	NaOH
Reactant/Coke, wt./wt.	0.135	0.147	0.15	0.15
Reaction Temp. °F	1,220	1,200	1,250	1,245
H ₂ Flow, V/V/Hr.	780	915	1,780	530
Sulfur Analyses, wt.%				
Raw Coke	6.0	6.0	3.8	3.8
Desulf Coke, Washed				
After 30 min.	4.25		1.75	
60	3.30	1.42	1.35	0.32
90	2.50		1.15	
120	-		1.00	
% Desulf @60 min.	45	76	64	91
% Desulf @90 min.	58	79**	70	94**
Residual Sodium, @ 60 min., After Wash	0.68	0.71	0.80	*
Na/S Mole Ratio in Wash	2.49	2.29***	2.39	*

* Not Determined
** Estimated
***Average 12 runs.

TABLE VI

Desulfurization of Fluid Coke
Use of Sodium Sulfide Carrier

Raw Coke, -60+80 Mesh, 6.0% S, grams	290
Reacted Coke with Na ₂ S, -150+200 Mesh, grams	140
Na ₂ S/Raw Coke, wt./wt.	0.056
Reaction Temperature, °F	1,200
Reaction Time, hrs.	2
Sulfur Analyses, -60+80 Mesh, wt.%	
Raw Coke	6.0
Before Wash	2.70
After Wash	1.86
% Desulfurization	69
Sodium Analyses, -150+200 Mesh, Recycle Coke, wt.%	
Start of Run	6.81
End of Run	1.40

PLATE 1

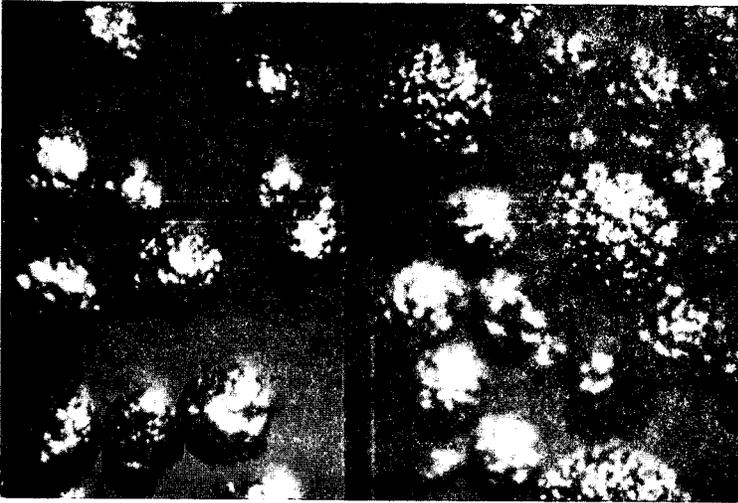


Figure 1. Fluid coke particles, untreated.

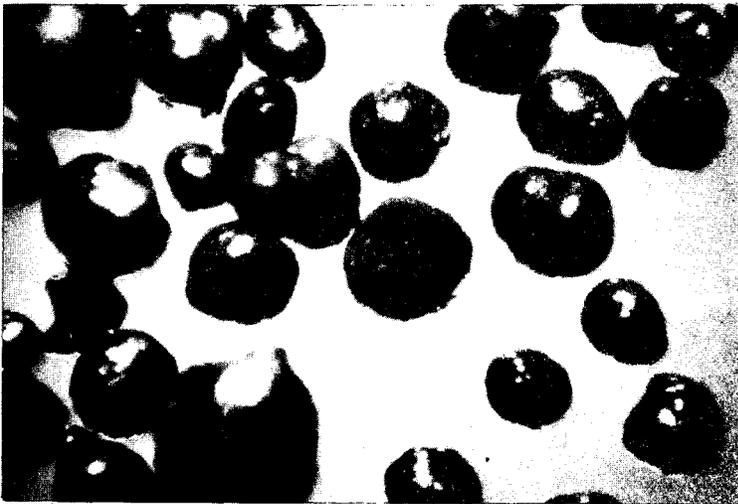


Figure 2. Fluid coke particle showing "onion skin" structure.

PLATE 2

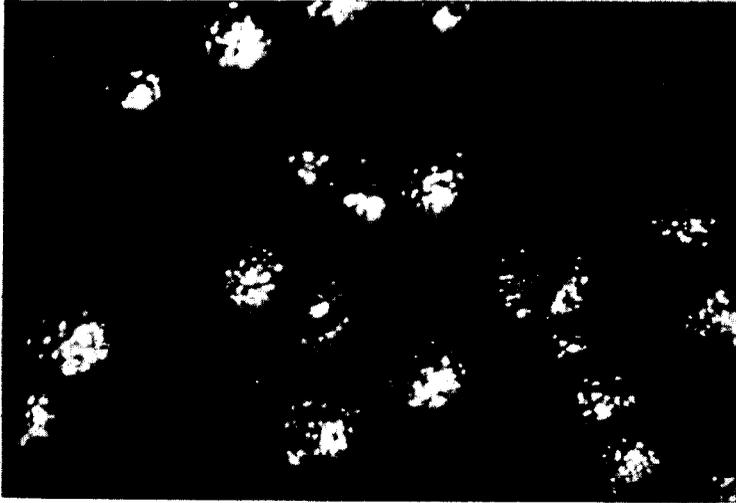


Figure 3. Fluid coke particle showing "onion skins" and seed particle.

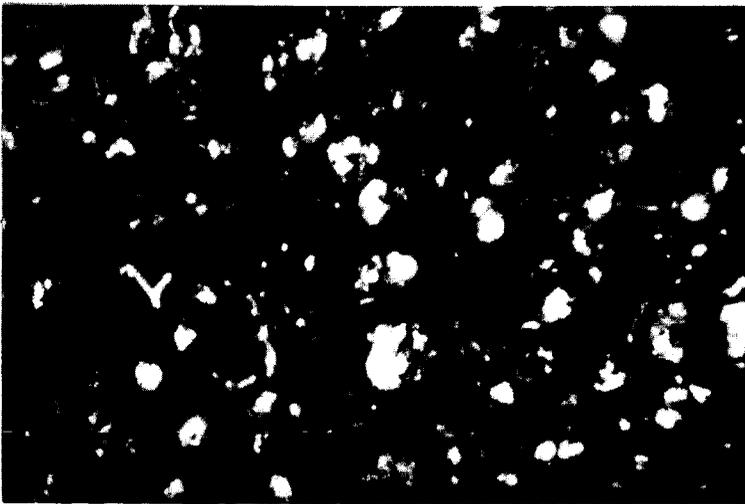
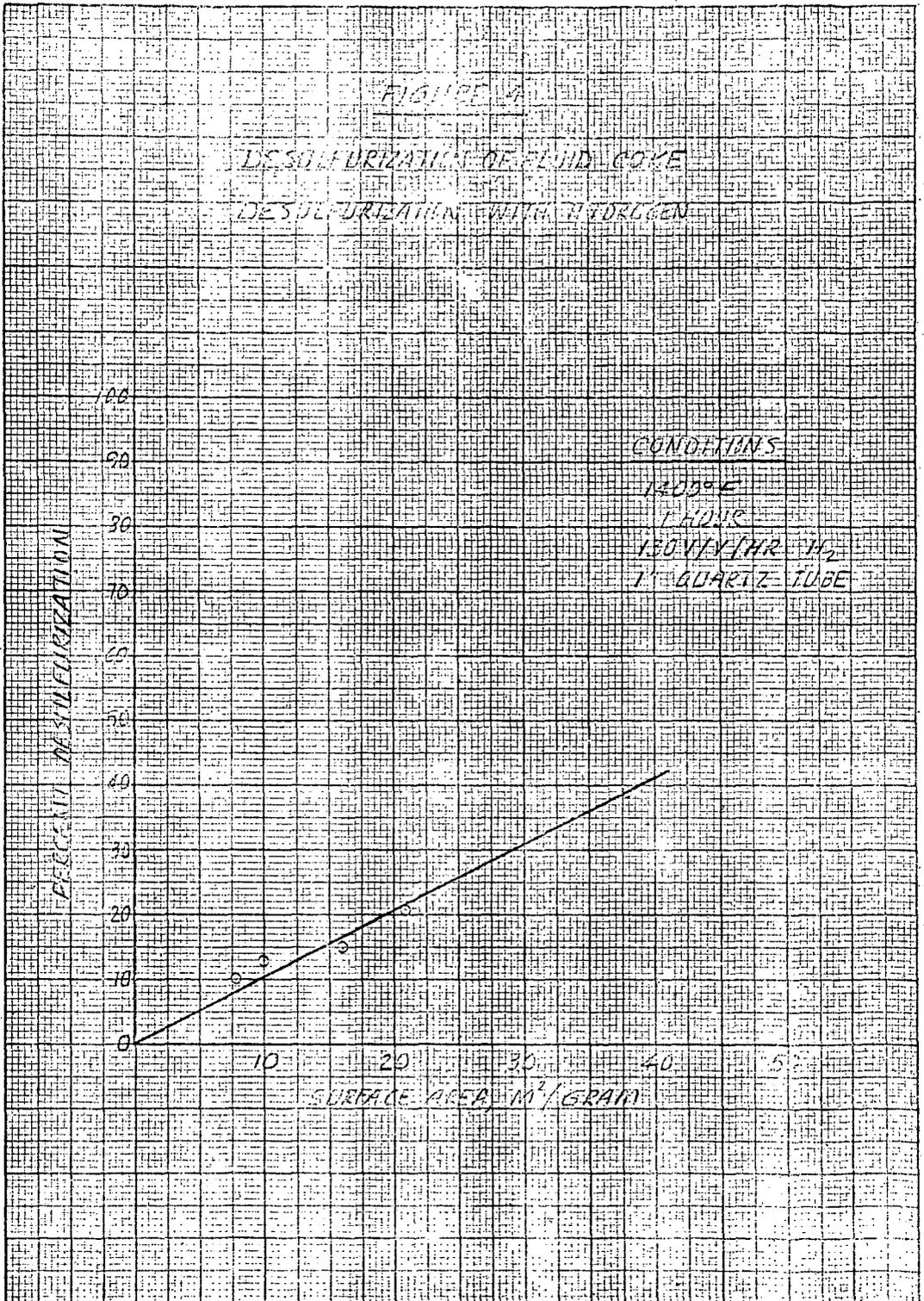


Figure 5. Fluid coke after reaction at 1,200°F, 1 hour, and with 1.0 gm NaOH/gm coke.



NOTES
DESULFURATION OF FLUID COKE
EFFECT OF TEMPERATURE
NaOH-H₂ SYSTEM

PERCENT DESULFURATION

100
90
80
70
60
50
40
30
20
10
0

1600 1500 1400 1300
TEMPERATURE, °F

RUN LENGTH 1 HOUR
H₂ FLOW RATE 530 V/V HR
NaOH/COKE 0.10
PREHEAT TIME 8 MINUTES

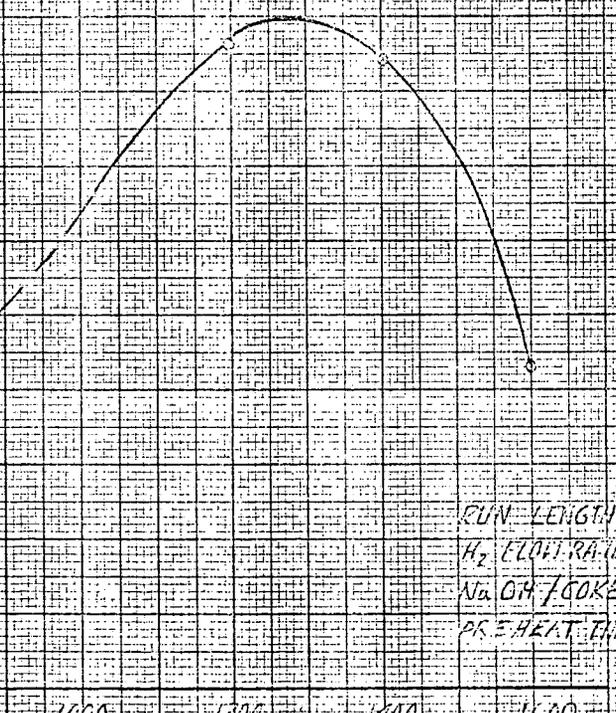
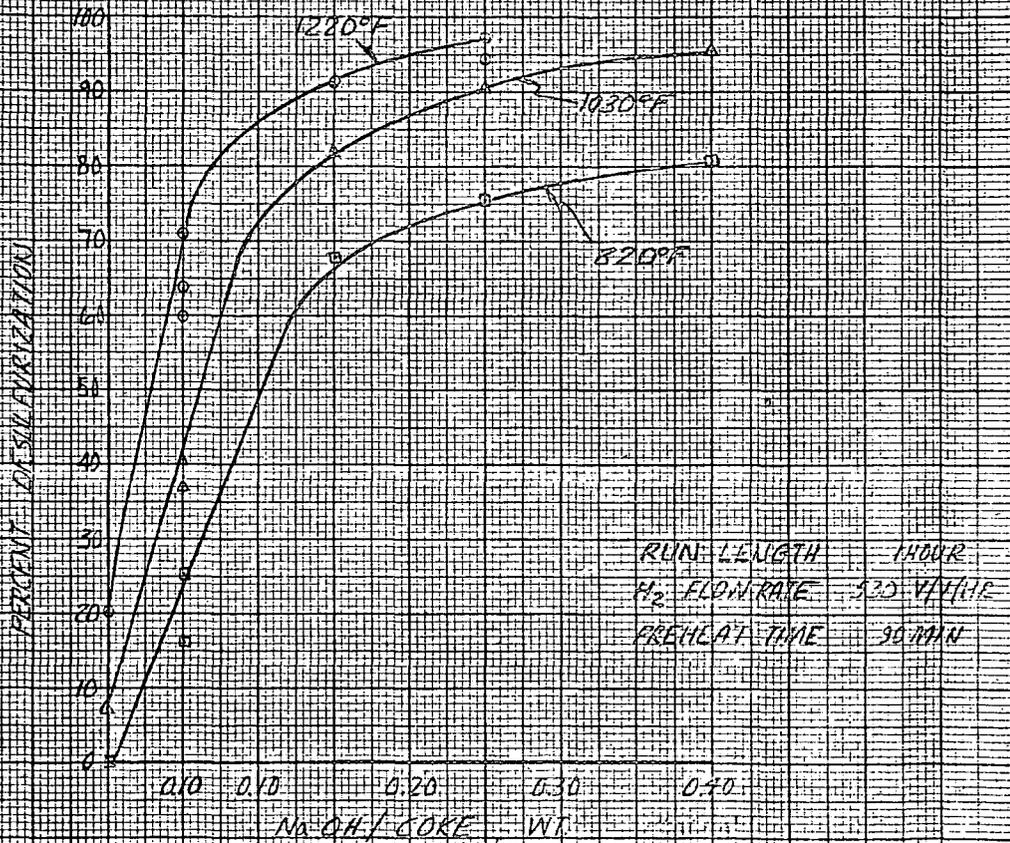


FIGURE 7
DESULFURIZATION OF FLUID COKE
EFFECT OF NaOH CONCENTRATION AND TEMPERATURE
NaOH-H₂ SYSTEM



KEUFFEL & ESSER CO.

FIGURE 3

DESULFURIZATION OF FLUID COKE

EFFECT OF SCALE UP
NAOH-H₂ SYSTEM

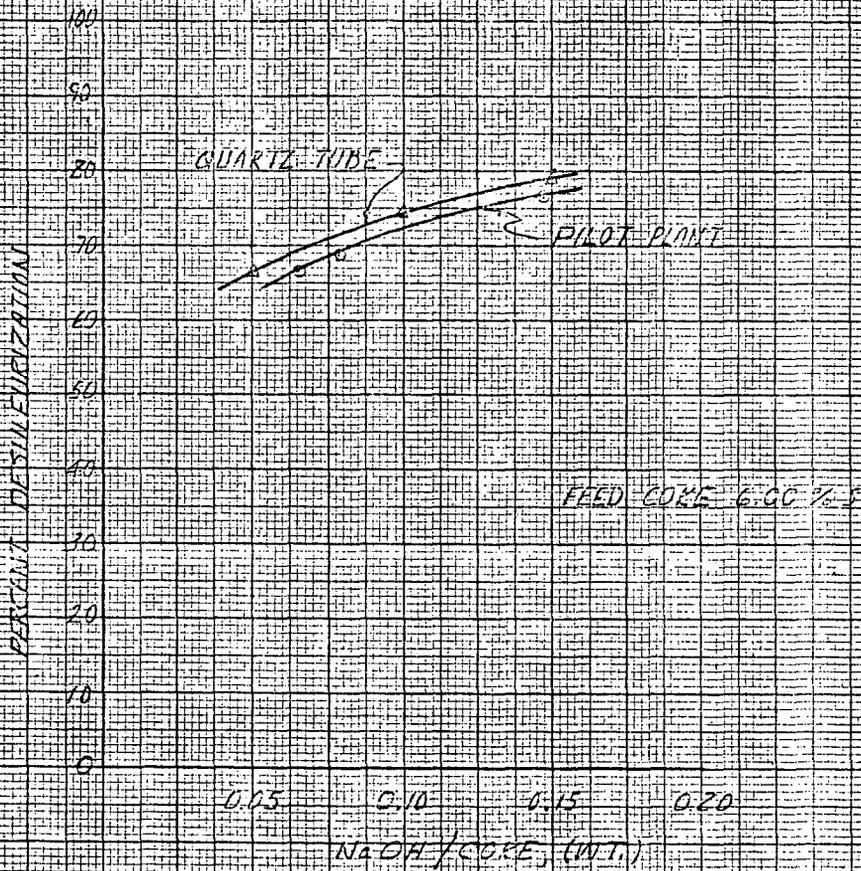


FIGURE 9
DESULFURIZATION OF FLUID CORE
COMPARISON OF $\text{Na}_2\text{S}-\text{H}_2$ AND $\text{NaOH}-\text{H}_2$ SYSTEMS

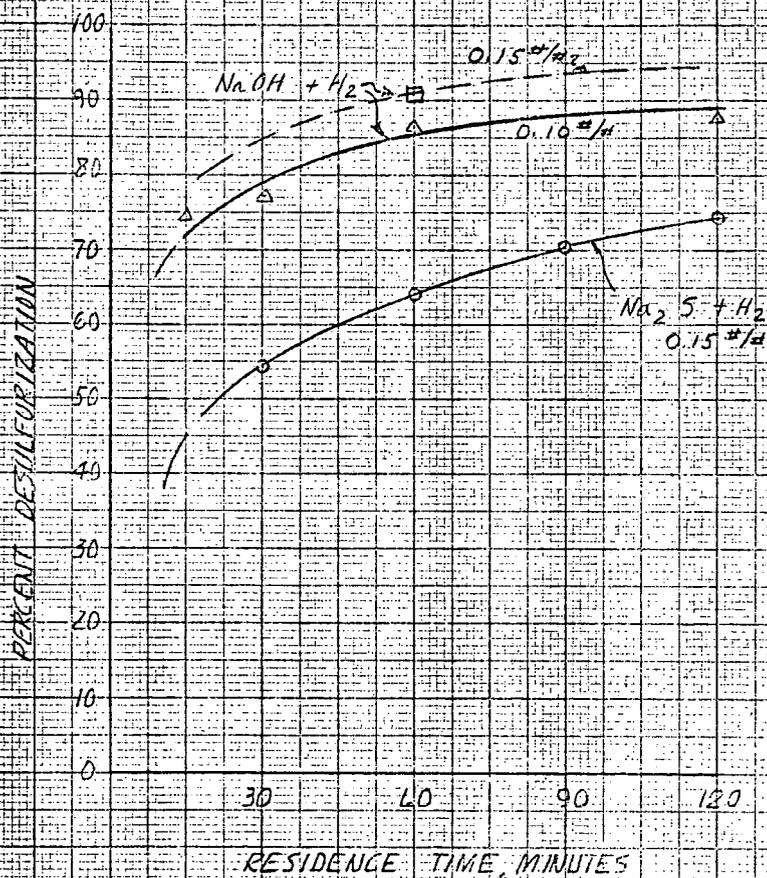


PLATE 3

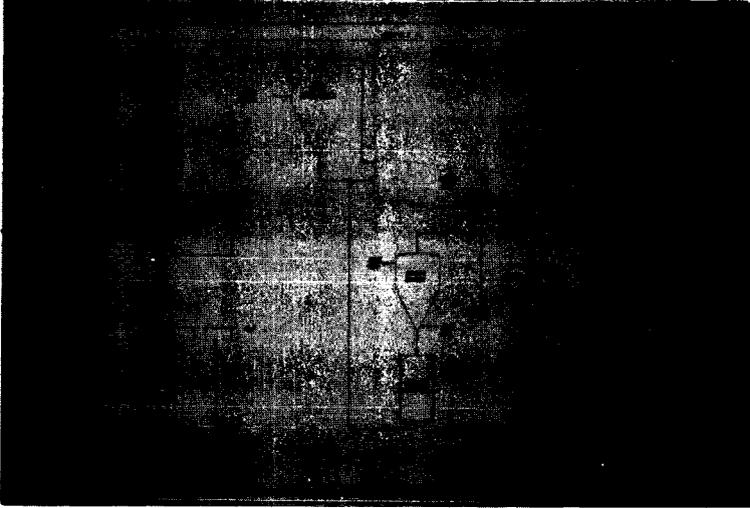


Figure 10. Flow diagram for fluid coke desulfurization with Na_2S and H_2 .