

## IX. HYGAS PROCESSING.

(a) The outlet gases from the hydrogenation are freed from  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  in the Hygas unit. The gases rich in hydrocarbons are processed for gasoline, and the lean gas is sent to the cracking plant and the utility mains. The apparatus consists of an alkazid unit for removal of  $\text{H}_2\text{S}$  or  $\text{H}_2\text{S} + \text{CO}_2$ , an oil absorption unit for removing higher hydrocarbons, an organic sulfur converter, a  $\text{NaOH}$  absorber for final removal of  $\text{H}_2\text{S}$  and  $\text{CO}_2$ , and a gasoline plant for liquifaction and fractionation of the liquid products.

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(b) The outlet gases from the hydrogenation consist of:

- (1) Flashed gas from the coal and gasoline chamber effluent product;
- (2) Flashed gas from the recycled gas wash;
- (3) Flashed gas from the mud of the coal stalls;
- (4) Outlet gas from the coal and gasoline stripper distillation;
- (5) Outlet gas from the stabilizer;
- (6) Low temperature coke oven gas from the residue desulfurization.

(c) The flash from the liquid product is reprocessed; the sludge removal gas and the low temperature coke oven gas are sent to the utility mains or used directly for fuel.

(d) The liquid product and the absorption oil from the high pressure process are degassified by a multi-stage pressure breakdown, and then separated into rich and lean fractions. The individual steps are:

- (1) Flashing to 30 - 40 atmospheres: coal and gasoline and washed gas;
- (2) Flashing to about 0.1 atmospheres: coal and gasoline and washed lean gas;
- (3) Heating at atmospheric pressure in the stripper: A and B distillation gas;
- (4) Heating under pressure in the stabilizer: Stabilizer gas.

Amonia is removed from the lean gas by a water wash, H<sub>2</sub>S is removed with alkazid, and the gas is sent to the cracking plant or to fuel.

(e) The gasoline rich gas is freed from sulfur with alkazid caustic and further purified together with the pure coal rich gas. The mixture of the two gases treated with NaOH for removal of residual CO<sub>2</sub> and H<sub>2</sub>S, and then largely liquified as mixed rich gas in the gasoline plant. The residue gas from the gasoline is sent to the cracking unit.

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(f) Ammonia Absorption.

Rich and lean gas must be practically free of ammonia, or else ammonium bicarbonate is formed in the presence of CO<sub>2</sub> and water, which plugs the lines. The outlet power gas can contain only traces of ammonia. The ammonia absorption results partially from condensation in the gas lines and partially from complete washing with process water, where the water is circulated to a predetermined concentration of NH<sub>3</sub>. By adding fresh water and drawing off used water the NH<sub>3</sub> in the cycle is kept low. Condensate or process water previously freed from calcium must be used.

(g) Lean Gas.

In the lines so much condensation from the purified lean gas occurs in the absence of an absorber (up to five (5) m<sup>3</sup>/hour), that the original NH<sub>3</sub> content of about eight hundred (800) milligrams/m<sup>3</sup> is reduced to about thirty (30) milligrams/m<sup>3</sup>. The removal of H<sub>2</sub>S follows by means of a wash with D, K caustic (principally dimethyl and amino propionic acid) at fifteen (15) atmospheres pressure. The H<sub>2</sub>S content of the new gas is about ten (10) grams/liter and of the pure gas about one hundred (100) milligrams/m<sup>3</sup>. The purified gas is sent to the cracking unit. A part of the lean gas is bled off before the alkazid wash and sent to fuel.

(h) Coal Stall Rich Gas.

The coal rich gas consists of the gases from the coal stripper, the absorption oil, and the A-distillation rich gas. The coal stripping rich gas is reduced in NH<sub>3</sub> content from forty (40) grams/m<sup>3</sup> to thirty (30) milligrams/m<sup>3</sup> by washing with process water in two thorough steps. The absorption oil rich gas is similarly treated and the NH<sub>3</sub> reduced from two hundred (200) milligrams/m<sup>3</sup> to forty (40) milligrams/m<sup>3</sup>. After the NH<sub>3</sub> absorption these two (2) gases are combined with the NH<sub>3</sub> free A-distillation gas and the mixture purified. The coal stall rich gas passes through a three thousand (3,000) m<sup>3</sup> gasometer and is compressed in one stage to five (5) atmospheres. The condensation from the compressed cooled gas is added to the raw gasoline. The compressed gas is carefully washed twice with alkazid caustic (principally ethyl amino propionic acid) in order to remove

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CO<sub>2</sub> and H<sub>2</sub>S. The raw gas contains about forty (40) grams/m<sup>3</sup> H<sub>2</sub>S and about two hundred eighty (280) grams/m<sup>3</sup> CO<sub>2</sub>, which are reduced to about two hundred (200) milligrams/m<sup>3</sup> and one (1) gram/m<sup>3</sup> respectively. The gas is finally given a wash with middle oil or diesel oil to remove heavy hydrocarbons so that they will not cake in the sulfur conversion over iron oxide catalyst at three hundred (300) to four hundred (400) degrees centigrade. Oil absorption and organic sulfur conversion which also operates at five (5) atmospheres have been shown to be unnecessary. After the organic sulfur purification the gas is reduced to 0.3 atmospheres and after purification of the gasoline rich gas is sent to the NaOH absorber.

(i) Gasoline Stall Rich Gas.

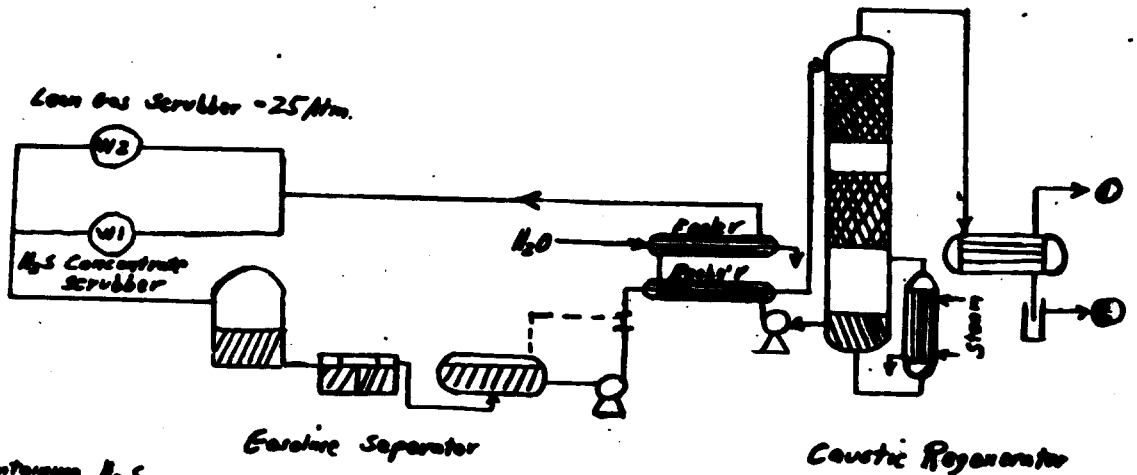
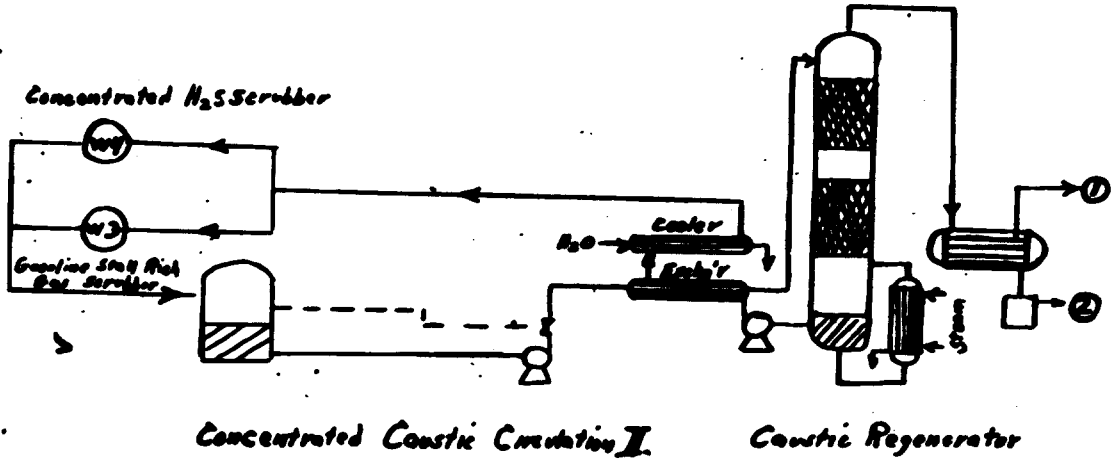
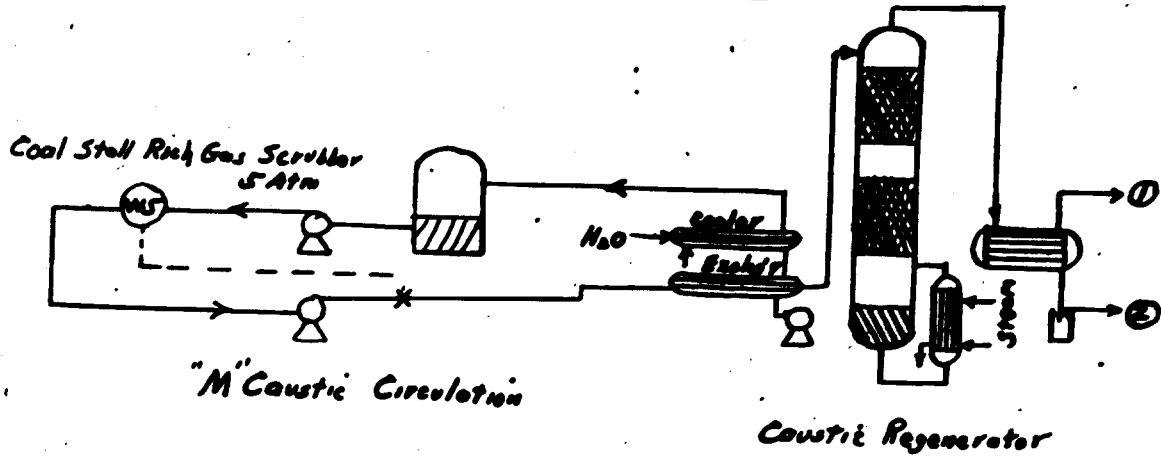
The gasoline rich gas consists of the flash from the liquid product of the primary hydrogenation, the gasoline chamber, and the B-distillation gas. The stabiliser gas is pure and is sent directly to the inlet of the power gas unit. The flash gas from the primary hydrogenation contains about thirty (30) grams/m<sup>3</sup> of NH<sub>3</sub> and must be processed in a packed absorber with process water to reduce this content to about thirty (30) milligrams/m<sup>3</sup>. The gas from the gasoline chamber is ammonia free. The two gases from the B-distillation gas are washed with water after the NH<sub>3</sub> removal. The gasoline rich gas passes through a two thousand (2,000) m<sup>3</sup> gasometer and finally after compression to 0.4 atmospheres by a turbe-blower goes to an alkasid wash. The condensate from the compression is added to the raw gasoline in a bell-bottomed absorber; the H<sub>2</sub>S is removed with alkasid Dik-caustic. The H<sub>2</sub>S is reduced from about forty (40) grams/m<sup>3</sup> to about three hundred (300) milligrams/m<sup>3</sup>. The gasoline rich gas and coal rich gas are then purified together in an NaOH absorber, removing the last traces of H<sub>2</sub>S and CO<sub>2</sub>, after which it is sent to the power gas plant. The H<sub>2</sub>S content of the mixed rich gas is 0.0 milligrams/m<sup>3</sup>.

(j) Alkasid Plant. (Fig. 26)

The so-called alkasid caustic has the property of almost completely absorbing H<sub>2</sub>S or H<sub>2</sub>S + CO<sub>2</sub> at twenty (20) degrees to forty (40) degrees centigrade, and of releasing it at about

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FIG. 26  
Flow Sheet of Alkozid Unit



① = Gas containing  $H_2S$   
② = Condensate " "

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one hundred degrees centigrade. The apparatus consists of an absorber, a regenerating column, coolers, heat exchangers and pumps. The lean gas, the gas from outlet water recovery, and the gasoline-rich gas are washed in two (2) bell-bottom absorbers with D.K.-caustic (principally dimethyl amino acetic acid) the co-rich gas with M-caustic (principally methyl amino propionic acid) in two (2) packed columns. The saturated caustic goes to intermediate storage in the Dik-caustic system and from there is pumped through a heat exchanger counter current to the hot regenerated caustic from the regenerator column. In the lean gas washing system there is a gasoline separator between the heat exchanger and the tank to remove condensate up to seventy (70) degrees centigrade. The column is filled with rings and the kettle is fed with direct and indirect steam. The steam outlet connection leads to the side of the circulating kettle, which contains the tube bundle for indirect heating. The division between direct and indirect steam is determined by the specific gravity of the caustics, which must be controlled to prevent corrosion. After degasification to an economic degree, where the gas is cooled in a water cooler attached to the column, the hot caustic is pumped from the kettle through a heat exchanger counter current to the cold saturated caustic, through a water cooler, back to the absorber. For the twenty-five (25) atmosphere absorber there is a booster pump between the cooler and the absorber. In the coal rich gas system there is an intermediate storage tank for saturated caustic like the one for regenerated caustic after the cooler. From this tank the caustic is pumped to the five (5) atmosphere absorber.

(k) Production of High Purity Hydrogen Sulfide.

The gas from the stripper column of the lean gas absorber system contains about fifty (50) percent  $H_2S$  and fifty (50) percent  $CO_2$ , which results from the large  $CO_2$  excess in the lean gas and which will be absorbed in caustic. The gas will be washed once with Dik-caustic in a bell-bottomed absorber to concentrate the  $H_2S$ . The saturated caustic from this wash will be regenerated together with the  $CO_2$  free saturated caustic from the gasoline rich gas absorption. The stripper gas from this caustic cycle contains about ninety (90) percent  $H_2S$ . The stripper gas from the coal rich gas M-caustic contains about ten (10) percent  $H_2S$ .

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and ninety (90) percent  $\text{CO}_2$ . The ratio of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  approximately corresponds to that of the lean gas and therefore will be concentrated in a washer, and the caustic will be regenerated with the caustic from the lean gas system. In this concentrating washer the exit gas from enriching washer (20%  $\text{H}_2\text{S}$ ), the outlet gas from the waste water recovery (5-8%  $\text{H}_2\text{S}$ ), and the outlet gas from the middle oil desulfurization unit (10%  $\text{H}_2\text{S}$ ) are washed for the production of high purity  $\text{H}_2\text{S}$ .

(1) Report of Operation of the Alkazid Unit.

The alkazid unit was put into operation in June 1943. No basic difficulties have been experienced. Wet aluminum corrosion occurred only on heating tubes of a column, and appears as pitting. Iron corrosion occurred to a greater extent on the water side of numerous coolers. Strong benzine condensation in the lean gas washer caused considerable trouble by pump abrasion and by carry over in the caustic to the intermediate storage and the columns. A benzine separator remedied this in normal operation. By degassing the caustic in the columns, a small but continual caustic loss occurred. A lower caustic inlet temperature and a layer of tower packing above the inlet corrected this condition. Increased oxygen content reduced the effectiveness of the M-caustic, and regeneration with potash made no improvement. The efficiency of the caustic cooler and  $\text{H}_2\text{S}$  condensers was often impaired by water side fouling.

(m) Power Gas Plant.

The power gas plant serves to condense the liquifiable gases and fractionates them into  $\text{C}_3$ ,  $\text{C}_4$  and gasoline fractions. The gas mixture containing about fifteen (15) percent  $\text{CH}_4$ , fifteen (15) percent  $\text{C}_2$ ,  $\text{H}_6$ , twenty-four (24) percent  $\text{C}_3\text{H}_8$ , twenty-eight (28) percent  $\text{C}_4\text{H}_{10}$ , nine (9) percent  $\text{C}_5$  and heavier and ten (10) percent residue gas ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{N}_2$ ) is compressed to twenty-five (25) atmospheres in a two stage machine, and the entrained lube oil is then removed with an oil wash. The oil wash consists of a small packed absorber over which liquid product is trickled. The lube oil is knocked down to the kettle. The gas from the oil wash is cooled to about sixty (60) degrees with water. Gas and condensate together are sprayed into column 1. In column 1 the

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IX. HYGAS PROCESSING. (m)(Cont'd.)

residue gas,  $\text{CH}_4$ ,  $\text{C}_2$ ,  $\text{H}_6$ ,  $\text{C}_3\text{H}_8$  goes overhead and the  $\text{C}_4$  and heavier fraction is taken from the kettle. The kettle product is fed to column 3 through a heat exchanger, where  $\text{C}_4\text{H}_{10}$  is removed overhead and the remainder from the kettle. This column operates at seven (7) atmospheres, and the pressure is controlled by the water flow to the  $\text{C}_4\text{H}_{10}$  condenser. Part of the condensate is used to reflux column 3 and part is removed as product through a cooler and a displacement meter to intermediate storage. The kettle product is passed through a cooler, a displacement meter, and is added to raw gasoline. The heads from column 1 are partially condensed and are used to reflux the column. The residue gas goes through a  $\text{NH}_3$ -water wash, a silica gel drier, and an  $\text{NH}_3$  refrigerated cooler at  $10^\circ\text{C}$ . The condensate and residue gas are sent to a separator, purified, and sprayed into column 2. In this column the residue gas ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ) goes overhead and the propane is taken from the kettle. Reflux is obtained with  $\text{NH}_3$  refrigeration at  $-35^\circ$  and is fed to the top of the column. The propane is removed as product through a cooler and displacement meter to an intermediate tank. The residue gas is expanded to ten (10) atmospheres in the first stage, to five (5) atmospheres in the second stage, and is sent to the cracking plant as power gas residue. Between the first and second stages the gas is sent over a gas heater and finally used for drying the saturated silica gel.

(n) Operation of the Compressor Building.

Because of operating errors and particularly because of flaws in construction a great number of difficulties occurred. By the end of 1942 the coal rich gas compressors were generally satisfactory during their operating time. Both machines were destroyed near the end of 1943 due to the failure of the piston rods, which was traced to faulty construction. Two-stage power gas compressors were substituted as alternates for the Borsig compressors. These had various disadvantages, particularly too weak frames. One machine was strengthened. The refrigerating machine was poorly erected in some respects. Valve plate breakage caused by faulty material was frequent in all machines. One machine sustained damage by failure of lubrication. The rotary blower for Bi-rich gas was often under repair because of the rotor.

(o) Report of Operation of the Power Gas plant.

The power gas plant went into operation in January and April of 1943 without difficulty and has operated without trouble.



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IX. HYGAS PROCESSING. (o)(Cont'd.)

The performance guarantees were in no manner met, particularly the A-plant. Principal faults were poor separation in the columns and a poor performance of the ammonia dephlegmator and ammonia precooler. This was partially remedied by increasing the length of column B-1 and exchanging the dephlegmator of column B-2 for two (2) unit coolers, and providing separators and pumps. The Uhde Company of Dortmund had guaranteed, and to make good it was necessary to build a new plant.

OPERATING RESULTS

<u>Yield</u>		
Nat-gasoline		98.0 %
Butane		93.0 %
Propane		81.0 %
	? (illegible) ?	
In nat-gasoline	C <sub>4</sub>	5.0 %
	C <sub>5</sub> and higher	95.0 %
In butane	C <sub>3</sub>	5.0 % (wt.)
	iso C <sub>4</sub>	61.0 % "
	n C <sub>4</sub>	33.5 % "
	C <sub>5</sub> and higher	0.5 % "
In propane	C <sub>2</sub>	15.0 % "
	C <sub>3</sub>	12.5 % "
	C <sub>4</sub>	7.5 % "
Power gas	C <sub>2</sub>	4.2 % "
	C <sub>3</sub>	30.0 % "
	C <sub>4</sub>	65.4 % "
	C <sub>5</sub> and higher	0.4 % "
Vapor pressure		
▲ 40°		10.2 atm
▲ 15°		1.3 atm
Hourly quantities		
Inlet mixed rich gas		4,450. m <sup>3</sup> /hr
Nat. gasoline		0.9 tons/hr
Power butane		2.2 tons/hr
Power propane		1.1 tons/hr
Residue gas		1,500. m <sup>3</sup> /hr
Mixed rich gas to cracking plant		550. m <sup>3</sup> /hr

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X. SULFUR PROBLEM.

(a) In order to remove asphalts in a satisfactory manner, a definite partial pressure of  $H_2S$  is necessary in the recycle gas stream to the coal stalls. Due to the low sulfur content of the raw coal (0.5 to 0.8 percent) and the diluent oil (0.3 percent), and also due to the heavy sulfur requirement of the iron oxide catalyst, the coal paste at Wesseling has elementary sulfur injected into it amounting to 1.25 to 1.5 percent of solids in the coal paste.

(b) After the conversion in the stall, the sulfur becomes bound chemically with: the iron of the catalyst, the tail gas, the discharge water of the effluent, the distillation and ammonia wash, and the tail gas. It is also to be found in the caustic wash of the rich gas and gasoline. The sulfur in the coking residue and the caustic is lost, while that in the discharge water and tail gas is recovered to a large extent. The discharge water is freed from  $H_2S$  by gasification with  $CO_2$ .

(c) In the alkazid unit, the tail gas feed for the gas cracking unit and the rich gas for the fuel gas unit are concentrated and stripped of  $H_2S$ . The concentrated  $H_2S$  (approximately ninety (90) percent) is used for sulfurizing the feed to the gasoline stalls, hence the sulfur soluble in the feed eventually turns up in the crude gasoline, in the gasoline stall rich gas, and in the discharge water. The non-absorbed sulfur is taken back into the alkazid unit. The sulfur losses can be summed up as follows:

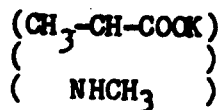
- (1) Coking residue;
- (2) In the purified gas in the alkazid unit due to incomplete washing;
- (3) The discharge water from the gasification;
- (4) The caustic wash from the raw gasoline.

(d) In the alkazid unit, either  $H_2S$  or  $H_2S + CO_2$  are absorbed alkazid caustic at room temperature. Upon reheating, the  $H_2S$  is stripped out and the caustic used over again. Two kinds of caustic are used, concentrated caustic and N-caustic. The former consists of N-dimethyl amino potassium acetate  $(CH_3)_2N-CH_2-COOK$  and this is highly selective in absorbing  $H_2S$  in contrast to  $CO_2$ .

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X. SULFUR PROBLEM. (d)(Cont'd.)

M-caustic is principally N-methyl amino potassium propionate.



and this is equally effective for  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . The removal and concentration of  $\text{H}_2\text{S}$  occurs as follows (Fig. 26). The lean gas is washed in scrubber W2 with concentrated caustic, removing the  $\text{H}_2\text{S}$  as opposed to  $\text{CO}_2$ . The absorption in the caustic is determined by titration against  $\text{H}_2\text{SO}_4$  and the quantity of gas determined. One volume of gas to one volume of caustic is known as "One Point Absorption."

(e) The saturated caustic from scrubbers W2a and W2b is regenerated in columns M1 and M2 by open and coil steam. The relative proportion of the two steam quantities is fixed by the specific gravity of the caustic, which must be kept exact, due to corrosion on one hand and volume contraction on the other.

(f) With regeneration, the  $\text{H}_2\text{S}$  concentration is approximately fifty (50) percent and can be scrubbed within scrubber W4 once again with concentrated caustic. The caustic from scrubber W4 and also from the gasoline stall rich gas washer, W3a and b, are regenerated together, releasing only the  $\text{H}_2\text{S}$ . This concentrate is approximately ninety (90) percent strength and can be used directly for sulfurizing the middle oil.

(g) The gas discharged from scrubber W4 contains approximately twenty (20) percent  $\text{H}_2\text{S}$ . The gas discharged from scrubber W1 goes through the after burning unit in which  $\text{H}_2\text{S}$  is converted into  $\text{SO}_2$ . The final  $\text{H}_2\text{S}$  content in the  $\text{SO}_2$  is very small.

(h) The rich gas from the coal stalls is washed in scrubber W5 with M-caustic which absorbs equally well  $\text{H}_2\text{S}$  and  $\text{CO}_2$ . The saturated caustic is regenerated in the stripping columns M1 and M2. Due to the high  $\text{CO}_2$  content in this gas the  $\text{H}_2\text{S}$  amounts to only fifteen (15) percent and must be concentrated in scrubber W1.

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K. SULFUR PROBLEM. (Cont'd.)

IMPORTANT FACTS ABOUT THE ALKAZID UNIT

H <sub>2</sub> S content	g/cu.met	mg/cu.met	Vol/% H <sub>2</sub> S	Quantity cu.met/hr
Lean gas raw	8.7			15,000
Lean gas pure		80		
Coal stall rich gas raw	35.			4,000
Coal stall rich gas pure		221		
Gasoline stall rich gas raw	39.			2,400
Gasoline stall rich gas pure		330		
Blower gas	78.			700
Tail gas W1a/b	4.			2,000
Tail gas D1/2			48	800
Tail gas D2/3			91	120
Tail gas M1/2			18	1,000

	Custic type	Scrub- ber	Feed In- jected cu.met/hr	Recirc. quantity cu./met/hr	Gas cc/cc	Steam direct tons/hr	Steam indirect tons/hr	Sp.Grav. @ 20°C.
Froth caustic	Concent.	W1	32		16			
	"	W2	22		23			
	"	W3	16		15			
	"	W4	16.		18			
	M	W5	64		—			
Regen. caustic	Concent.	D1/2		54	4 - 6	4	3	1,155
	"	D2/3		32	4 - 6	3,5	2,5	1,155
	M	M1/2		64	7 - 10	4	3	1,175

SULFUR BALANCE

Entrance

Elem. Sulfur	350 tons
S in TK <sub>4</sub>	276
S in oils	22
	<u>648</u>

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X. SULFUR PROBLEM. (Cont'd.)

Exit

Coking residue	406 tons
Tail gas from after burner	72
S lost in phenol removal	52
Expansion loss	24
S residue in heating gas	18
S residue in mud gas	17
S residue in tail gas from methane cracker	16
S in NH <sub>3</sub> wash	16
S in exhaust water not recoverable	22
	<u>648 tons</u>
S in 6434 feed	183 tons