THE PRODUCTION OF HYDROGEN SULPHIDE BY HEATING PARAFFINE AND OTHER HYDROCARBON MIXTURES WITH SULPHUR[1].

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The fact that H_2S may be made by heating together paraffine and sulphur has been long known[2]. Lidoff[3] made H_2S by adding a "petroleum naphtha" to sulphur at 350°-400°C. Brooks and Humphrey[4] reported a yield of 80-85 percent of the S as H_2S from heating a 2:1 mixture of oil and S, but made no statement as to purity of product, operating time, nor temperature employed. Hanley[5] has studied the reaction of fuel, cylinder and road oils, with 10 percent S, at temperatures of 150°-205°C. maintained for 3.5 to 24 hours. The yields of S as H_2S were for the most part 45 to 55 percent. A mixture of road oil and 10 percent S heated to 150°-205°C. is reported to have yielded 72.2 percent H_2S at the end of 3.5 hours.

The work described in this paper deals with the optimum conditions and the effect of certain catalysts on the production of pure H_2S by heating S and various hydrocarbons.

Experimental. The reaction mixture of hydrocarbon and sulphur contained in a 12 inch Pyrex test tube, equipped with stopper and delivery tube, was suspended in an electrically heated air bath and the gaseous product collected over water, saturated with H_2S, in graduated tabulated bottles. The purity of the H_2S was determined by treatment of a test portion of known volume in a gas pipette with a concentrated NaOH solution. The absorbed gas volume was accepted as that of H_2S. The yields were low and erratic. Much sulphur volatilized unchanged from the mixtures and collected in the delivery tubes.

To correct this 250 cc. Pyrex distilling flasks were substituted for the test tubes as containers, and lump pumice[6] was added to the reaction mixture. This gave a decided increase in yield of H_2S and fairly consistent results, although volatilization of some sulphur from the reaction mixture was apparent.

A catalyst was sought which would permit the reaction to proceed at a temperature sufficiently low to avoid volatilization of sulphur from the mixture. The effect of the presence of the following substances upon the temperature required for initial reaction, in mixtures of sulphur with paraffine, and asphalt, was studied: cadmium sulphide, finely divided iron, aluminum, zinc, copper, cobalt, nickel, lead, antimony, bismuth, silver, pumice, bone charcoal, silica, gilsonite, calcium oxide, arsenious oxide, lampblack, tar, the bleaching carbon "Norit" and anhydrous aluminum chloride. The gas from the generator was allowed to pass through a solution of cadmium chloride and at the appearance of precipitation of CdS the

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[1]Contribution from the Chemistry Department of Indiana University.

[2]Galletly. Chem. News. 24, 162 (1871).

[3]Lidoff. Chem. Zentralblatt. 53, 22 (1882).

[4]Brooks and Humphrey. J. Ind. and Eng. Chem. 9, 746 (1917).

[5]Hanley. Chem. and Met. Eng. 24, 693 (1921).

[6]The presence of pumice in the hard paraffine sulphur mixture was found advantageous, but in hydrocarbon oil sulphur mixtures it was without effect.

temperature within the generator was recorded. The substances found to cause appreciable lowering of the initial reaction temperature, with data, concerning paraffin, soft asphalt, and Gulf "B" Asphalt are given in the following table:

Experiment	Paraffine, M.P. 65°C. Grams	Powdered Sulphur Grams	Addition Agents	Temperature of Mixture at Initial H_2S Evolution. Degrees C.
1	10	3	none	265–270
2	10	3	1.0 g. Gilsonite	242
3	10	3	3.0 g. Gilsonite	240
4	10	3	1.0 g. Asphalt	256
5	10	3	5.0 g. Asphalt	240
6	10	3	0.5 g. bone charcoal	254
7	10	3	1.0 g. tar	254
8	10	3	3.0 g. lampblack	239
9	10	3	3.0 g. Gilsonite	240
10	10	3	2.0 g. Norite	259
11	5	3	5.0 g. Asphalt	240
12	10 soft asphalt	3	none	240
13	10 Gulf "B" asphalt	3	none	234

All of the above substances which caused a lowering of the temperature at which hydrogen sulphide was evolved, also anhydrous aluminum chloride, and cadmium sulphide were used as catalysts and their effect on the yield of gas determined.

It was found that when paraffine or ozokerite was used that carbon was the most effective, anhydrous aluminum chloride gave almost as good results, iron (80 mesh or less) was about 75 percent as effective, and in all other cases the effect was negligible. When flux oil or road oil was used none of the above had any appreciable effect. With black oil the gas yield was not affected by carbon but the purity was greater and with asphalt the yield was lowered slightly.

The following tables show some of the most characteristic runs with the various hydrocarbons. The yield is given in percent of sulphur as hydrogen sulphide. Varying proportions of the different substances were studied but the ratios shown gave the best results.

Ozokerite

Exp.		Yield H_2S, Percent
14.	20g. ozokerite, 6g. sulphur, 15g. pumice, 6g. gilsonite	44.1
15.	20g. ozokerite, 6g. sulphur, 15g. pumice, no catalyst	26.2
16.	20g. ozokerite, 6g. sulphur, 15g. pumice, 6g. lampblack	51.0

Paraffin

17.	20g. paraffin, 7.5g. sulphur, 15g. pumice, no catalyst	39.3
18.	20g. paraffin, 7.5g. sulphur, 15g. pumice, no catalyst	37.1
19.	20g. paraffin, 7.5g. sulphur, 30g. pumice, no catalyst	38.8

20.	20g. paraffin, 7.5g. sulphur, 30g. pumice, no catalyst	39.2
21.	20g. paraffin, 6.0g. sulphur, no pumice, 6g. gilsonite	29.5
22.	20g. paraffin, 6.0g. sulphur, no pumice, 6g. gilsonite	21.4
23.	20g. paraffin, 6.0g. sulphur, 15g. pumice, 6g. gilsonite	45.8
24.	20g. paraffin, 6.0g. sulphur, 20g. pumice, 6g. gilsonite	44.2
25.	20g. paraffin, 6.0g. sulphur, 15g. pumice, 6g. lampblack	47.0
26.	20g. paraffin, 7.5g. sulphur, 20g. pumice, 6g. lampblack	49.5
27.	20g. paraffin, 6.0g. sulphur, 20g. pumice, 6g. lampblack	48.0
28.	20g. paraffin, 6.0g. sulphur, 20g. pumice, 6g. lampblack	47.6
29.	40g. paraffin, 12g. sulphur, 20g. pumice, 6g. lampblack	59.5
30.	40g. paraffin, 20g. sulphur, 20g. pumice, 6g. lampblack	53.6
31.	40g. paraffin, 20g. sulphur, no pumice, no lampblack	22.5
32.	20g. paraffin, 7.5g. sulphur, no pumice, 30g. charcoal	49.1
33.	20g. paraffin, 7.5g. sulphur, no pumice, 15g. charcoal	45.1
34.	20g. paraffin, 7.5g. sulphur, 20g. pumice, 6g. $AlCl_3$ anhyd.	46.6
35.	20g. paraffin, 7.5g. sulphur, 20g. pumice, 6g. $AlCl_3$ anhyd.	48.3

In these runs with ozokerite and paraffin, as with the asphalt and oils, the temperature at which most of the gas came over was from 245° to 260°C. The temperature was then allowed to rise to 300°C. The yields are based on all the gas that came over up to that temperature. The purity of the gas up to 300°C. as shown by absorption in a dilute caustic soda solution was 100 percent.

On allowing the temperature to increase in the above mixture a greater volume of gas was obtained but with a decrease of purity. Samples of gas produced at 500°C. showed a purity of only 64 percent and the increase in yield up to that temperature was about 10 percent.

Asphalt

Exp.		Yield H_2S, Percent
36.	20g. asphalt, 6g. sulphur, 15g. pumice, no catalyst	33.3
37.	20g. asphalt, 6g. sulphur, 30g. pumice, no catalyst	29.2
38.	20g. asphalt, 6g. sulphur, 30g. pumice, 6g. lampblack	25.8
39.	20g. asphalt, 6g. sulphur, no pumice, no lampblack	31.6

The volume yield in the case of asphalt was so low that a study at higher temperatures was not made nor was the purity determined.

Flux Oil

Exp.		Yield H_2S, Percent
40.	10g. flux oil, 12.5g. sulphur, 10g. pumice, no catalyst	31.4
41.	10g. flux oil, 12.5g. sulphur, 10g. pumice, no catalyst	31.1
42.	20g. flux oil, 20.0g. sulphur, 20g. pumice, 6g. lampblack	44.6
43.	23g. flux oil, 15.0g. sulphur, 20g. pumice, 6g. lampblack	43.1
44.	20g. flux oil, 25.0g. sulphur, 20g. pumice, 6g. lampblack	43.9
45.	22g. flux oil, 20.0g. sulphur, 20g. pumice, 6g. lampblack	45.0
46.	30g. flux oil, 20.0g. sulphur, 20g. pumice, 6g. lampblack	46.1

The purity at 300°C. was 100 percent, at 350° the purity was 95.7 percent, and at 500° the purity was 25 percent.

Black Oil

This oil was a medium weight lubricating oil, black in color, and probably containing considerable free carbon.

Exp.		Yield H_2S Percent
47.	20g. black oil, 25g. sulphur, 20g. pumice, 6g. lampblack..........	49.0
48.	20g. black oil, 20g. sulphur, 20g. pumice, 6g. lampblack..........	53.3
49.	30g. black oil, 20g. sulphur, 20g. pumice, 6g. lampblack..........	61.9
50.	30g. black oil, 20g. sulphur, 20g. pumice, 6g. lampblack..........	61.0
51.	40g. black oil, 20g. sulphur, 20g. pumice, 6g. lampblack..........	65.9
52.	40g. black oil, 20g. sulphur, 20g. pumice, 6g. lampblack..........	68.3
53.	40g. black oil, 20g. sulphur, no pumice, no lampblack...........	68.0
54.	40g. black oil, 20g. sulphur, no pumice, no lampblack............	66.3
55.	40g. black oil, 10g. sulphur, no pumice, no lampblack...........	67.0

The purity at 300°C. when lamp black was used was 100 percent. When no lampblack was used it was 96 percent. This indicates that lampblack might retard the cracking of the oil. Above 300°C. the purity rapidly dropped in each case and reached approximately 25 percent at 500°C.

Road Oil

Exp.		Yield H_2S Percent
56.	20g. road oil, 10g. sulphur, 10g. pumice, 6g. lampblack..........	65.6
57.	45g. road oil, 15g. sulphur, 20g. pumice, 2g. Cadmium Sulphide...	67.4
58.	20g. road oil, 10g. sulphur, no pumice, no catalyst..............	67.3
59.	45g. road oil, 15g. sulphur, no pumice, no catalyst..............	70.0
60.	40g. road oil, 10g. sulphur, no pumice, no catalyst..............	69.7

Summary and Conclusions

Finely divided carbon is a decidedly positive catalyst for the preparation of hydrogen sulphide by the action of sulphur on hydrocarbons. When lampblack is added to paraffin and ozokerite sulphur mixtures, the yields are practically doubled. In the case of road oil and flux oil the addition of finely divided carbon has no effect. With asphalt the carbon seems to slightly lower the yield, while with black oil the yield is unaffected but the purity of the gas is higher.

Evidently the reason that the addition of carbon does not cause an increase in yields with the oils and asphalt is that they contain sufficient free carbon to catalyze the reaction.

Anhydrous aluminum chloride is also a positive catalyst and about equal to carbon. The catalytic effect is not additive to that of carbon because it did not produce an increase of yields in the oils. Finely divided iron, 80 mesh and less, is about 75 percent as effective as lampblack but, like $AlCl_3$ it is not additive to that of free carbon for it did not cause an increase of yields with the oils.

A much lower percentage of H_2S is found in the gas produced at temperatures above 300°C.