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Distillation of New Albany Oil Shales

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The New Albany Shales The purpose of this work is to take up a study of oil shales, using those found in lower Indiana, the products derived from them by the various methods of distillation, and the properties of the products obtained by the distillation. The samples used in the following experiments were secured from borings made by the Railroaders Supply Company. These samples came from the shale beds of lower Indiana, from what is known as the New Albany shale. This shale has an outcropping in New Albany, Indiana, and also just north of that city. From there it drops downward at the rate of about twenty-five feet to the mile. The samples were secured twenty-six miles down the river and out from Corydon, Indiana. This shale bed is about eighty feet in thickness and belongs to the black shale type of the upper series of the Devonian age. It rests on the Corniferous and serves as a protection for this sand. It is overlapped by blue shales that run into the black shale without a definite break. It is soft under the bit and shows no perceptible oil content to the naked eye, but, under the microscope, it shows small globules of an oily content which is more in the form of resin. The samples used had been out of the ground for some time but showed no variation in appearance. The particles as they were used were very fine and easy to handle. The shale was not washed before retorting, as it was thought that the well mixed shale would give a rough estimate of the conditions that would be found in the field. Separate samples had been kept while the boring was done, but these were thoroly mixed, as it was not the purpose of this paper to study the shale by strata or layers. This shale is true to the type of all of the shales in the eastern part of the United States, and, as may be expected, this shale is composed largely of silicon dioxide, alumina, and calcium oxides. It may be classed in the clay shales. The following is a typical analysis of this shale:

Organic matter and water	13.32 %
Iron oxide and alumina oxide	13.015%
Calcium oxide	2.38 %
Phosphoric acid	.18 %
Magnesium oxide	6.07 %
Silicon dioxide	57.46 %
Water soluble compounds	3.32 %
Total	95.745%

This analysis is typical of all of the shales belonging to the black shale type that are found in the central part of the United States.

A microscopical study of the shales showed the presence of small globules of a resinous substance, well preserved parts of plants, and occasionally the skeleton of some minute animal. It also contained crystals of pyrites and other minerals. The shale contained 0.44 per cent of nitrogen and 2.89 per cent of sulfur. This large percentage of sulfur in the shale made the oil have a still larger percentage of sulfur.

EXPERIMENTAL WORK

Methods of Retorting The retorting of the shales was tried out in four different methods. 1. Atmospheric pressure. 2. The use of superheated steam. 3. Reduced pressure. 4. The insertion of copper in the vapor line. The methods are as follows:

Atmospheric Pressure 1. The apparatus used in this experiment was composed of a horizontal retort, 24 inches in length and two inches in diameter, holding a charge of 1200 grams of shale. This retort was connected to a 10 inch iron pipe, which was inserted for greater condensation. This in turn was connected with a 24 inch water cooled condensor. The oil was run into a 100 cubic centimeter graduated cylinder, while the gas was run through a tower containing a known solution of sulfuric acid. After the apparatus was set up, the heat, which was secured from a gas furnace, was turned on. The initial heat was approximately 400 degrees centigrade and the retort was kept at this heat for from one and one half to two hours. The flame was then turned higher and kept at this temperature for about an hour. Then the heat was run up to the final temperature, which in most cases was around 800 degrees Centigrade. A number of different methods of heating were tried but this one gave the best results. The fast heating lowered the yield of oil and also made the oil of a lower quality.

Superheated Steam 2. The apparatus used in this work was composed of the same retort and condensor as above and had as an addition a superheater and an extra condensor. The extra condensor was found necessary, as a part of the vapors were uncondensed in the first condensor. The superheater gave a temperature of about 600 degrees Centigrade, and the retort was heated rapidly to this temperature. The final temperature was about the same as in the case of the atmospheric pressure distillation.

Reduced Pressure 3. The apparatus for this type of retorting was the same as that of the atmospheric pressure, with the exception of the suction pump that was placed on the end of the vapor line. The temperatures reached were the same as in the above mentioned retorting but the time of retorting was lowered. The vacuum pressure which was applied was equivalent to 21 inches of mercury, or about 10.5 pounds of reduced pressure.

Insertion of Copper 4. This method was the same as number 1, only that metallic granular copper was inserted in the vapor line.

Yields from the Different Methods

In Table I are found the results of a number of the retortings that were made by the different methods and the conditions that were found in each run of the retort. The percentage of water has been omitted but this generally ran close to two gallons a ton. The gas was found to be about 1000 cubic feet a ton in the dry retorting and about 1400 cubic feet in the superheated steam retorting.

TABLE I

Method of Distillation	Oil, gal. per ton	Ammonium sulfate per ton	Time of retorting
1	10.5	11.32 lbs.	5 hours
1	9.	....	5 hours
1	9.5	....	5 hours
1	11.0	14.38 lbs.	5 hours
1	8.3	10.26 lbs.	5 hours
1	12.1	12.63 lbs.	5 hours
1	10.4	12.09 lbs.	5 hours
1	7.15	......	3 hours
1	7.9	10.13 lbs.	3 hours
1	8.5	9.74 lbs.	3 hours
1	9.2	10.63 lbs.	3 hours
2	11.68	17.63 lbs.	3 hours
2	11.72	22.846 lbs.	3½ hours
2	9.4	23.73 lbs.	3½ hours
2	12.1	26.32 lbs.	3½ hours
2	10.2	27.83 lbs.	3½ hours
2	9.5	21.32 lbs.	3½ hours
2	10.5	....	3½ hours
3	10.3	15.83 lbs.	4 hours
3	11.2	14.87 lbs.	4 hours
3	10.6	14.36 lbs.	4 hours
3	9.7	12.16 lbs.	4 hours
3	10.1	....	4 hours
3	9.0	....	4 hours
3	9.6	13.184 lbs.	4 hours
4	9.0	11.284 lbs.	4½ hours

1. Atmospheric pressure, 2. Superheated steam, 3. Reduced pressure, 4. Average, over hot copper.

It will be seen that the retorting with superheated steam gives the largest yield of both the oil and the ammonium sulfate, that the reduced pressure is next, and that the atmospheric pressure is the lowest in the yield of all the desired products. Another factor that seems to play an important part in the results of the retorting of the shales is the rate and length of heating. In the case of the dry distillation of the shale the slower rate of heating, with consequently the longer period of time in the retort, seems to raise the yield of the oil considerably. In the case of the ammonium sulfate, it is also easy to see from the table that the length of heating is an important factor, for the longer the heating is carried out, the longer it stays at the high temperature, and the high temperature seems to assist in the formation of the ammonia that is carried over. From a study of the table on retorting it would seem that as far as the yield is concerned the superheated steam is the best, the reduced pressure next, with the atmospheric pressure as the least desirable. A study of the oil, however, will tend to change this inference.

EXPERIMENTAL WORK ON THE OILS

In studying the oils it is only natural that they should be studied first as the crudes and then as the fractions. The nitrogen content was determined by the Kjeldahl method and was found to be very satisfactory. The sulfur was determined in the Parr calorimeter and special care was taken in all of the different stages to keep them as near as possible to the standard method. The iodine numbers were determined by Pittman, Jacobs, and Dean[1], method. The time which the oil was allowed to stand was thirty minutes.

The following table gives the analysis of the different crudes as obtained by the various methods:

TABLE II

Oil	Nitrogen	Sulfur	Iodine Number	S. G.	B. t. u.
Normal pressure	1.82%	1.73%	121.2	.876	18367
Reduced pressure	1.04%	1.52%	90.6	.831	19827
Superheated steam	1.98%	1.99%	163.0	.927	17392
Over hot copper	1.26%	0.67%	118.0	.869	18194
Fast heating at N. P.	1.91%	1.85%	146.3	....	....

General Characteristics of the Oils True to the characteristics of all shale oils those under study were of a reddish black color yet they varied in their intensity. Naturally the oil run with superheated steam was the darkest and also the highest in viscosity, the atmospheric pressure oil came

[1]U. S. Bureau of Mines, Technical Paper, No. 163, p. 13.

next. while the reduced pressure was the lightest in color and also in viscosity. The superheated steam oil gave a reddish fluorescence. very much like that of well petroleum. The odor of the oils was practically the same in all cases, but the oil run with steam gave the most pronounced odor. This odor was that of the nitrogen and sulfur complex compounds. In studying the quality of the oils as crudes, it is very easy to see from Table II that the amount of nitrogen and sulfur in the oils is so great as to be exceptionally objectionable to the refiner. One of the oils was run over hot copper and the results of the experiment can readily be seen in the taking up of the sulfur and also the lowering of the nitrogen content. The atmospheric pressure oil has been taken as a standard. and. considering it from this standpoint, we can see that the oil that was run off with superheated steam gives a much larger percentage of both nitrogen and sulfur, that the oil that was run off with reduced pressure gives a much lower percentage of nitrogen and also a slight lowering of the sulfur content. The iodine number of the oils seems to decrease as the specific gravity decreases, with the superheated steam oil as the highest and the reduced pressure oil as the lower. After the study of the crudes as such was made, they were fractionated and the fractions were studied from the same angle. Table III gives the results of the fractionation and also the tests that were made on the different oils.

TABLE III

OIL FROM NORMAL PRESSURE DISTILLATION

Fraction	Temp.	Nitrogen	Sulfur	Iodine No.	Loss to sulfuric acid
Crude	......	1.82 %	1.73%	121.2	......
10	262° F	0.382%	....	137.0	31%
20	308° F	0.730%	......	132.0	33%
30	364° F	1.120%	....	117.0	37%
40	408° F	1.410%	....	112.0	41%
50	453° F	1.610%	....	120.0	54%
60	541° F	1.580%	....	114.0	57%
70	501° F	1.490%	....	83.0	62%
80	582° F	1.580%	....	91.0	68%
90	....	1.610%	......	119.0	77%

I. B. P. 164° F. Coke. 11.2%.

OIL FROM OVER HOT COPPER DISTILLATION

Fraction	Temp.	Nitrogen	Sulfur	Iodine No.	Loss to sulfuric acid
Crude	....	1.26%	.67 %	118	
10	273° F	......	.63 %	133	
20	312° F	......	.709%	125	
30	371° F	......	.671%	112	
40	412° F	......	.612%	109	
50	576° F	......	.607%	121	
60	493° F	......	.553%	103	
70	524° F	......	.487%	87	
80	576° F	......	.449%	91	
90	....	......	.396%	119	

I. B. P.. 161° F. Coke, 12%.

OIL FROM SUPERHEATED STEAM DISTILLATION

Fraction	Temp.	Nitrogen	Sulfur	Iodine No.	Loss to sulfuric acid
Crude	....	1.98 %	1.99 %	163.4	....
10	267° F	.412%	1,962%	174.0	33%
20	318° F	.753%	2.049%	154.0	41%
30	397° F	1.231%	2.023%	146.0	46%
40	486° F	1.42 %	2.008%	135.0	55%
50	538° F	1.706%	1.937%	141.0	66%
60	491° F	1.734%	1.863%	127.0	68%
70	542° F	1.668%	1.735%	116.0	73%
80	579° F	1.721%	1.679%	136.0	79%
90	......	1.77 %	....	143.0	87%

I. B. P., 167° F. Coke, 18%.

OIL FROM REDUCED PRESSURE DISTILLATION

Fraction	Temp.	Nitrogen	Sulfur	Iodine No.	Loss to sulfuric acid
Crude	....	1.04 %	1.52 %	90.6	....
10	234° F	.211%	1.55 %	97.0	15 %
20	309° F	.453%	1.619%	89.0	20.5%
30	352° F	.651%	1.493%	74.0	28.0%
40	395° F	.772%	1.506%	63.0	34.0%
50	481° F	.935%	1.417%	69.0	39.0%
60	533° F	.904%	1.380%	62.0	47.0%
70	496° F	.869%	1.336%	53.0	59.0%
80	562° F	.928%	1.351%	61.0	66.0%
90	....	.977%	1.183%	82.0	74.0%

I. B. P., 156° F. Coke, 10.3%.

The fractionations were carried out in a 500 cubic centimeter Engler's distilling flask, using the standard method.[1] The heat was secured from a Bunson flame, protected from the flask by means of an asbestos mat. The distillation was carried on with atmospheric pressure up to the temperature of 527° F. Then the vacuum distillation was begun and the lubricating fractions were secured in this manner. The nitrogen, sulfur, and iodine numbers were determined in the same manner as that of the crudes. The loss to sulfuric acid was determined in the graduated testing bottles. It was carried on by taking five cubic centimeters of the oil and fifteen cubic centimeters of concentrated sulfuric acid. This was shaken well, cooled, and allowed to stand for half an hour. It was again shaken, cooled, and enough sulfuric acid was added to bring it up to the graduated part of the neck of the bottle. The remaining oil was read and designated as the part that was insoluble in acid. The amount that was lost was calculated and this was termed the amount due to the loss to sulfuric acid. By looking over the table on distillation it can be seen that the loss to sulfuric acid in the earlier fractions is opposite to the iodine numbers, that the nitrogen increases as the fractionation is carried on, and that the sulfur decreases in the heavier fractions.

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[1]Bureau of Mines. Technical Paper No. 166.

CONCLUSIONS

From the study of the New Albany shale oils, the following conclusions may be drawn for this type of shale:

First, that the superheated steam method of retorting is the best, as far as the yield of oil and ammonium sulfate is concerned

Second, that the reduced pressure method is the best as far as the quality of the oil is concerned and that this is due to the internal reactions of the retort.

Third, that the superheated steam method gives the larger percentage of nitrogen and sulfur, because a part of the original bitumen is carried over by the steam.

Fourth, that the sulfur and nitrogen are in the shale and also the oil, in combination with each other, and that the percentage of the two elements in the oil is dependent upon the conditions of retorting, for these conditions may be for the sulfur to recombine with the hydrocarbons or that the nitrogen may also recombine with the loss of the sulfur.

Fifth, that the iodine numbers and consequently the true unsaturation is proportionate to the specific gravity of the crude.

Sixth, that the loss to sulfuric acid does not mean that it is a test for the unsaturates present, but is a sum of the unsaturates and the compounds that are soluble in the acid.

Seventh, that the retorting for oil is best done by allowing slow heating and plenty of time in the retort.