THE HYDROCARBONS IN LOUISIANA PETROLEUM.

By Charles E. Coates and Alfred Best.

Received September 1, 1903.

The excitement which followed the discovery of the Beaumont oil field in Texas and the speculation which attended its development, have, to some extent, drawn the attention of the public from the development of the petroleum fields of Louisiana. Of these, the fields at Welsh and at Jennings have already passed into a solidly commercial condition, while at Anse la Butte, and at numerous other points in Southern Louisiana. oil has been found in considerable quantity. It is the intention of the writer to publish later an account of the chemical nature of the various oil pools in Louisiana. In view of the fact, however, that very little information is available in regard to this matter, it has been considered advisable to present here the results of some work done in this laboratory during the past six months. Early in the spring, samples of oil were secured from Beaumont, Texas, and from the oil fields near Welsh, Jennings, and Breaux Bridge in Louisiana. These oils were distilled from Engler flasks with the usual precautions. Their fuel values were determined with a Parr calorimeter, which gave concordant results on duplicate determinations and proved in every way satisfactory.

In the distillations, it was found that the time taken influenced the results to such an extent that no measurements were concordant above 300°. This is, doubtless, due to the decomposition of the higher fractions, these breaking down slowly into fractions both of lower boiling-point and of higher boiling-point than the original fraction.

The following table shows the results of these examinations:

In the table the distillations were made in duplicate and agreed fairly well. The relative evolution of hydrogen sulphide, at low temperatures, is worth consideration, both from the standpoint of pumping the crude oil and of refining it. The figures obtained for the Beaumont oil differ somewhat from those previously published. It would seem that it had gotten heavier than it was when the Lucas well was first opened, and it also shows a general rise in the boiling-points of the fractions. There are now no gushing wells at Beaumont, and many which once pro-

	Texas. Beaumont.	La. Welsh.	La. Jennings.	La. Breaux Bridge.
Specific gravity 25° C.	0.9228	0.9276	0.9093	0.9392
Distillation begins	150° C.	230° C.	200° C.	240° C.
Distillation, Engler flasks, 760 mm.	per cent.	per cent.	per cent.	per cent.
To 150° C.	none	none	none	none
150°–200°	2	none	none	none
200°–250°	8	2	13	1
250°–300°	26	17	28	15
300°–350°	26	23	24	22
350°–to asphalt	30	49	30	53
Asphalt residue	8	9	5	9
H_2S evolved on heating	in large quantities 115°–150°	in very small amount at 230°	in small quantity 200°	in very small amount at 240°
Color of lower fractions	yellow	nearly colorless, light yellow on standing	colorless, yellowish on standing	slightly yellow
Fuel value in B. T. U.	19923	19000	19814	19300
Illuminating oil fractions to 300°	36	19	41	16
Estimated depth of well	1200	700 (?)	1000	600
Per cent. sulphur in crude oil	1.96	0.32	0.39	0.20

duced oil on pumping, have been abandoned. The field at Jennings is of greater area, and less initial pressure. The proved field there is growing and the wells, while not phenomenal, are considered profitable. There is, as yet, no reason to fear that the field is losing in producing power. This is also true of the Welsh field. The geology of these oil deposits is still somewhat obscure. It has been suggested that they are pools, gathered under pressure in the top of a dome with sharply descending sides. Such a deposit would possibly be larger when the angle of the dome was more obtuse. There are, throughout Southern Louisiana, certain elevations of an otherwise flat country. They are generally of limited area and rise only a very few feet above the surrounding plain. These elevations are considered superficial indications of gas pressure beneath and, consequently, of oil. There is also a certain amount of seepage, and some springs show oil in their water. None of these indications are reliable as establishing the existence of an oil pool, which fact, however, would seem to make it probable that many such pools may still remain undiscovered.

In the following investigation the sample sent from Breaux Bridge was taken, first, because it was sent in considerable quantity. The methods employed were those suggested by Mabery in his recent investigations of the Texas oils, and by Richardson and Wallace in their paper on the Beaumont field. A similar treatment of Jennings and Welsh fields will follow as soon as time permits.

The oil in question was sent by the Moresi Co., of Jeanerette, La. It was taken from a 600-foot stratum at Anse la Butte, near Breaux Bridge, La. This is considered a shallow well. There are others at Anse la Butte which are 1000 feet deep and produce 15 to 30 barrels daily. The crude oil was low in sulphur, an analysis, by the Carius method, showing only 0.2 per cent. It was black, viscous and had a not unpleasant odor, somewhat resembling turpentine. The specific gravity, at 25°, was 0.9392. Distilled in an Engler flask, at atmospheric pressure, it gave no gasoline and 16 per cent. illuminating oil—the fractions up to 300° C. Heated to 350° C., 22 per cent. more oil was obtained. Heated above this to asphalt, the distillate was a dark, heavy, fluorescent oil with a somewhat unpleasant odor. After the limit of the thermometer employed, 400°, was reached, it was removed and distillation continued until little more oil came over. The residue, amounting to about 9 per cent., was heated in an open dish until it was about one-fourth evaporated. The resulting mass was asphaltic in its nature, being hard, black and shiny, with a conchoidal fracture. It had a specific gravity of 1.123. On burning in a closed platinum crucible, as in coal analysis, the following results were obtained:

Volatile matter	71.0
Fixed carbon	28.6
Ash	0.4

Compared roughly with paving asphalt, the physical qualities of this residue appeared only fair.

An attempt was made to refine the illuminating oil fraction by sulphuric acid, in the usual way, washing with sodium hydroxide. It was found practically impossible to secure a water-white product. The most nearly colorless products obtained turned yellow in a few days, on standing in an open Erlenmeyer flask. About 15 per cent. of sulphuric acid was used, and there was a loss of about 12 per cent. of oil, though these figures could probably be reduced in practice. The refined oil was tested in an ordinary flat-wick lamp. It burned freely with a somewhat smoky yellow flame and a pleasant resin-like, aromatic odor, differing altogether from that of ordinary kerosene. Upon replacing the lamp chimney with one considerably taller, the yellow flame became white and no longer smoked. As the oil was almost free from sulphur, the fraction, up to 300°, was burned without refining at all and seemed to do as well as the refined oil. Still, considering the limited quantity of illuminating oil present, its poor quality and the small amount of asphalt, it would seem that, in the present state of chemical technology, the Breaux Bridge oil is fitted mainly for fuel purposes. For these it is well adapted, containing but little sulphur and being slightly higher in fuel value than the California petroleums, which are now used for fuel in large quantities. Its lubricating qualities have not, as yet, been tested, though it is said to have been used locally with good results.

In order to obtain fractions suitable for combustion, 500 cc. portions were distilled from a liter distilling flask, with the following results:

	Per cent.
Below 220° C.—atmospheric pressure	none
220°-240° C.—atmospheric pressure	0.3
240°-260° C.—atmospheric pressure	2.
260°-280° C.—atmospheric pressure	8.
280°-300° C.—atmospheric pressure	6.
300°-320° C.—atmospheric pressure	5.
160°-200° C.—at 60 mm. pressure	5.
200°-245° C.—at 60 mm. pressure	11.
245°-285° C.—at 60 mm. pressure	20.
285°-320° C.—at 60 mm. pressure	6.

This was repeated several times until a considerable quantity collected at certain points. The corresponding fractions were then mixed and the series subjected to fractional distillation at 60 mm. It was found exceedingly difficult to obtain a fraction with a constant boiling-point. Portions which came over at, say 165°-167°, would, on redistillation, break up into a series of products, ranging from 150°-180°, the portion remaining in the flask always being darkened and showing some decomposition After considerable trouble, three fractions were obtained, boiling at 110°-115°, 160°-165°, and 210°-215°, respectively. These were shaken with fuming sulphuric acid, washed with water, sodium hydroxide, and water again, then dried over calcium chloride, and redistilled. In order to prevent decomposition of the higher hydrocarbons, the 210°-215° fraction was dissolved in gasoline before adding the sulphuric acid, and the gasoline subsequently distilled off, as recommended by Mabery and Buck.[1] Each fraction lost considerably on the acid treatment, but the amount was not measured, since so much sulphuric acid was used as to preclude its use, practically, in refining.

The 110°-115° (60 mm.) fraction boiled at 205°-210° at 760 mm., with slight decomposition; it was water-white, and had an odor so strongly resembling turpentine that it was difficult to distinguish them, one from the other. This odor was not affected by the acid treatment. A portion of the oil was polarized, but showed no optical activity. This odor is so marked that a similar distillate, obtained in the Jennings refinery, is now being offered for sale as a turpentine substitute, and the makers claim it answers its purpose well. The specific gravity of the 110°-115° fraction was 0.8479 at 27°. Its molecular weight was determined by the

---

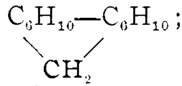
[1] This Journal, **22**, 555.

freezing-point method, benzene being used as a solvent; 161 was found; calculated for $C_{12}H_{22}$, 166. A combustion of the oil gave, for carbon, 86.4 per cent., and for hydrogen, 13.38; calculated for $C_{12}H_{22}$, carbon, 86.74 per cent.; hydrogen, 13.26.

The 160°-165° fraction (60 mm.) was treated in the same way as the preceding one. It had none of the turpentine-like odor. Its specific gravity at 29° was 0.8785. Its molecuar weight, by the freezing-point method, with benzene, was 189; calculated for $C_{14}H_{26}$, 194. On combustion it gave, for carbon, 86.79 per cent., and for hydrogen, 13.1. Calculated for $C_{14}H_{26}$, carbon, 86.59 per cent.; hydrogen, 13.41.

The 210°-215° fraction (60 mm.) was treated as was the preceding. Its specific gravity at 29° was 0.9009. Its molecular weight, by the freezing-point method, was 233; calculated for $C_{17}H_{30}$. 234. Upon combustion it gave, for carbon, 87.15 per cent., and for hydrogen, 12.72 per cent. Calculated for $C_{17}H_{30}$, carbon, 87.18 per cent.; hydrogen, 12.82 per cent.

From the above figures it is evident that the series C_nH_{2n-2} and C_nH_{2n-4} are the main constituents of this oil. This corresponds with the conclusions reached by Mabery and Buck[1] on some Texas oil, and also by Mabery[2] on the Beaumont oil. Mabery considers the series C_nH_{2n-2} as belonging to the dicyclic polymethylene series, in which view Richardson and Wallace concur. By analogy, the series C_nH_{2n-4} might be looked upon as being desired from dihexahydrofluoren, $\underset{\diagdown\; CH_2 \;\diagup}{C_6H_{10}—C_6H_{10}}$; but there is, as yet, little positive evidence as to the structure of either series. They are almost certainly not unsaturated aliphatic compounds, however, for they do not behave as though unsaturated. If they are cyclic compounds, they might respond to Nikiforoff's methods of consecutive decomposition under increased pressure, which has succeeded in producing benzene derivatives of excellent quality from Russian petroleum. That Louisiana petroleum does undergo progressive decomposition, under continued distillation, has been established in the course of this investigation.



---

[1] *Loc. cit.*

[2] This Journal, 1901, p. 264.

LOUISIANA STATE UNIVERSITY,
BATON ROUGE.