II. THE HYDROCARBONS IN LOUISIANA PETROLEUM.

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This article is a continuation of one published in this Journal, November, 1903. The same methods were employed and the results, taken together, give a fairly complete chemical survey of the various petroleums so far discovered in Louisiana. During the year 1904, three new samples were received. One was from Bayou Bouillon, near St. Martinsville, one was from near Bayou Laroupe on the extreme northeastern limit of the oil territory; one was from near Many, on the extreme western limit. Only the first was received in sufficient quantity for an extended investigation. Of the second, about 200 cc. were sent, this being taken from a prospecting well since abandoned. The third was an oil-bearing sand. The following is the result of the preliminary examination:

	Bayou Bouillon.	Bayou Laroupe.
Specific gravity 25°	0.9669	0.9604
Distillation begins (Engler flask)	275° C.	265° C.
Fraction to 300°, per cent	11	6
Fraction 300°–350°	62	7
H_2S evolved on heating	very little	none
Color of lower fraction	yellow	yellow
Estimated depth of well	900 ft.	400 ft.
Per cent. sulphur in crude oil	0.57	low
Residue	asphaltic	asphaltic
Fuel value, B. T. U.	18500	

The oil sand was extracted with gasoline and the gasoline evaporated, leaving about 40 cc. of black oil as a residue. This, distilled, gave about 10 cc. from 300-350° and about .10 cc. from 350-380°, the residue being asphaltic. Extracted with carbon bisulphide, the sand yielded 5.46 per cent. oil. By drying the sand at 100° for four hours, 0.4 per cent. water was found. In order to compare this oil with one of known properties the following data were obtained:

	Oil sand.	Bayou Bouillon.
Refractive index 25°—fraction 300°–350°.	1.4833	
Refractive index 25°—fraction 350°–380°.	1.5200	
Combining the two fractions:		
Refractive index 300°–380°	1.5013	1.5080
Specific gravity	0.9047	0.9059

The two oils behaved the same towards sulphuric acid and were

similar in physical appearance. These facts taken in conjunction with the above physical constants, would indicate that they are of the same chemical nature. As they represent the extreme eastern and western limits of the Louisiana field, this conclusion is not without interest.

The asphaltic residue obtained had about the same general properties as those described in the previous article. In order, however, to get some data on the technical value of the so-called lubricating fraction, the fraction obtained from the Welsh oil boiling from 300–360° was tested with an Engler viscosimeter, and gave, at 29°, 3.63 as compared with water. Tested with a standard Pennsylvania Railroad pipette at 38°, it gave 2.1 as compared with water. These are about the figures which would be given by the ordinary "mineral" lubricating oils.

The remainder of this article has to do with the nature of the hydrocarbons found in the fraction up to 300°, the so-called illuminating fraction, from Jennings, Welsh, and Bayou Bouillon, that from Breaux Bridge having been discussed already. These fractions were obtained by distilling the crude oil at 760 mm. and collecting the distillate to 300°. Upon redistillation under reduced pressure they all behaved in the same way. It was again found exceedingly difficult to obtain a subfraction of a constant boiling-point, those purified most carefully showing some decomposition even when redistilled at 20 mm. pressure after fuming sulphuric acid ceased to remove anything further. The fractions finally taken for combustion were purified with fuming sulphuric acid, washed with water, then with sodium hydroxide, then with water, dried over calcium chloride and redistilled under diminished pressure. There was much loss by the acid treatment. The subfractions of high boiling-point were dissolved in gasoline before the acid treatment, the gasoline being subsequently removed by distillation. The molecular weights in all cases were determined by the freezing-point method with benzene as a solvent, and the refractive indices with an Abbé refractometer. The distillations were made at different pressures, which was necessitated by the condition of the local water works, these being in process of repair, and owing to the irregularity of the pressure, the figures given for the boiling-points are only approximate.

The Jennings Illuminating-oil Fraction.—Upon treatment as described above, a number of fractions were obtained, of which

three were taken for combustion. The first boiled at 110–115° at 80 mm. Distilled at 760 mm., it boiled at 180–185°. It was water-white and had a marked odor of turpentine, but showed no optical activity in the polariscope. Specific gravity at 22° was 0.8373. Molecular weight found, 150. Calculated for $C_{11}H_{20}$, 152. Combustion gave: Carbon, 86.70; hydrogen, 13.10. Calculated for $C_{11}H_{20}$; Carbon, 86.84; hydrogen, 13.16. Refractive index at 25°, 1.4535. Molecular refraction: Calculated, 48.53; found, 48.76.

The second fraction boiled at 150–155° at 80 mm. It had none of the turpentine odor. Specific gravity at 22° was 0.8649. Molecular weight found was 180. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.72; hydrogen, 13.41. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4692. Molecular refraction: Calculated, 57.74; found, 57.93.

The third fraction boiled at 200–205° at 80 mm. Specific gravity at 22° was 0.8801. Molecular weight found, 225. Calculated for $C_{16}H_{28}$, 220. Combustion gave: Carbon, 87.59; hydrogen, 12.91. Calculated for $C_{16}H_{28}$: Carbon, 87.27; hydrogen, 12.73. Refractive index at 25°, 1.4805. Molecular refraction: Calculated, 69.44; found, 71.05.

The Welsh Illuminating-oil Fraction.—The first fraction boiled at 145–150° at 80 mm. Specific gravity at 22° was 0.8551. Molecular weight found, 171. Calculated for $C_{12}H_{22}$, 166. Combustion gave: Carbon, 86.57; hydrogen, 13.43. Calculated for $C_{12}H_{22}$: Carbon, 86.74; hydrogen, 13.26. Refractive index at 25°, 1.4662. Molecular refraction: Calculated, 53.13; found, 53.52.

The second fraction boiled at 165–170° at 100 mm. Specific gravity at 25° was 0.8679. Molecular weight found, 186. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.58; hydrogen, 13.42. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4666. Molecular refraction: Calculated, 57.74; found, 57.45.

The third fraction boiled at 175–180° at 33 mm. Specific gravity at 28°, 0.8736. Molecular weight found, 236. Calculated for $C_{17}H_{32}$, 236. Combustion gave: Carbon, 86.30; hydrogen, 13.44. Calculated for $C_{17}H_{32}$: Carbon, 86.44; hydrogen, 13.56. Refractive index at 25°, 1.4760. Molecular refraction: Calculated, 76.14; found, 76.27.

The Bayou Bouillon Illuminating-oil Fraction.—The first fraction

boiled at 140–145° at 33 mm. Specific gravity at 25°, 0.8557. Molecular weight found, 179. Calculated for $C_{13}H_{24}$, 180. Combustion gave: Carbon, 86.44; hydrogen, 13.17. Calculated for $C_{13}H_{24}$: Carbon, 86.67; hydrogen, 13.33. Refractive index at 25°, 1.4691. Molecular refraction: Calculated, 57.74; found, 58.54.

The second fraction boiled at 170–175° at 33 mm. Specific gravity at 29°, 0.8871. Molecular weight found, 221. Calculated for $C_{16}H_{28}$, 220. Combustion gave: Carbon, 87.00; hydrogen, 12.67. Calculated for $C_{16}H_{28}$: Carbon, 87.27; hydrogen, 12.73. Refractive index at 25°, 1.4828. Molecular refraction: Calculated, 69.44; found, 70.77.

The third fraction boiled at 190–195° at 33 mm. Specific gravity at 27°, 0.8966. Molecular weight found, 235. Calculated for $C_{17}H_{30}$, 234. Combustion gave: Carbon, 87.23; hydrogen, 12.66. Calculated for $C_{17}H_{30}$: Carbon, 87.18; hydrogen, 12.82. Refractive index at 25°, 1.4883. Molecular refraction: Calculated, 74.04; found, 75.16.

The fourth fraction boiled at 200–205° at 33 mm. Specific gravity at 27°, 0.9006. Molecular weight found, 249. Calculated for $C_{18}H_{32}$, 248. Combustion gave: Carbon, 87.30; hydrogen, 12.57. Calculated for $C_{18}H_{32}$: Carbon, 87.1; hydrogen, 12.9. Refractive index at 25°, 1.4916. Molecular refraction: Calculated, 78.64; found, 79.73.

The fifth fraction boiled at 225–230° at 33 mm. Specific gravity at 28°, 0.9104. Molecular weight found, 262. Calculated for $C_{19}H_{34}$, 262. Combustion gave: Carbon, 86.81; hydrogen, 12.55. Calculated for $C_{19}H_{34}$: Carbon, 87.02; hydrogen, 12.98. Refractive index at 25°, 1.4972. Molecular refraction: Calculated, 83.94; found, 84.26.

From an inspection of the foregoing results, it is evident that in the Jennings oil, the series C_nH_{2n-2} and C_nH_{2n-4} are represented, in that from Welsh, the series C_nH_{2n-2} alone was found, while in that from Bayou Bouillon, there were the series C_nH_{2n-2} and C_nH_{2n-4}. Just what the nature of these hydrocarbons is, it is difficult to say, but the existence of the compound $C_{11}H_{20}$ would seem to make it improbable that they are derivatives of dihexahydrodiphenyl as suggested by Mabery and also by Richardson. This question is now under investigation in this laboratory. We have in no case found either optical activity or evidence of an unsaturated compound. We have

obtained the compounds $C_{11}H_{20}$, $C_{10}H_{18}$ and C_8H_{14}, all showing the same properties as the series C_nH_{n-2} referred to above. The results of this work will be published shortly.

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A FULLER STUDY OF THE NEUTRAL SULPHITE METHOD FOR DETERMINING SOME ALDEHYDES AND KETONES IN ESSENTIAL OILS.

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PAPERS on this subject have been read at two different times by the author, as follows: October 15, 1903, published in the *Journal of the Franklin Institute*, December 1903, and February 19, 1904.[1] The work was based upon work of Tiemann,[2] Dodge[3] and Heusler,[4] in which neutral sulphites were used to react with the aldehydic constituents of certain essential oils, and the amount of aldehyde present was determined by differences of volume as measured in cassia flasks, etc. Alkali was formed by the reaction, and was indicated by phenolphthalein and, by neutralizing the alkali as formed, the end of the reaction could be ascertained.

The author measured the amount of standard acid required to neutralize the alkali and by calculating the amount, was able to determine the percentage with a fair degree of accuracy. He was in error, however, in judging the extent of the application of the reaction, as in his earlier experiments only citral, cinnamic aldehyde, benzaldehyde, vanillin and formaldehyde were tried, all of which react, although they, as now shown, react differently. These successes were a little misleading.

Burgess,[5] in a paper read December 28, 1903, several months after the reading of the earliest one by the author, but almost coincident with its publication, points out the reactions with citral, cinnamic aldehyde, carvone and pulegone, and states that the same would probably be true of citronellal and olefinic aldehyde.

[1] *J. Soc. Chem. Ind.*, March 31, 1904.
[2] *Ber.*, **31**, 3334.
[3] *Am. Chem. J.*, **12**, 55 (1890).
[4] *Ber.*, **24**, 1805.
[5] *Analyst*, p. 78, 1904.