[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE, NO. 34.]

ON THE HYDROCARBONS IN HEAVY TEXAS PETROLEUM.[1]

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THE heavy petroleums that hitherto have been looked on as only fit for fuel are capable, if properly refined, of yielding valuable products. This is especially true of the deposits recently exploited in Wyoming, Texas, and in other sections. The Corsicana oil in Texas has been shown by Mr. Clifford Richardson to yield an oil that may be refined into gasoline, burning oil, and other products ordinarily obtained from light petroleums. Large areas of oil territory have recently been developed in Texas that yield oils of higher specific gravity, and that are of value for what they contain of the higher products. The rapid development of Texas oil territory bids fair to advance the state into an equivalent place with California as oil-producing territory.

As to the hydrocarbons which compose the heavy Texas oil, nothing whatever has hitherto been known. It is practically impossible to separate any of its constituents by the ordinary method of distillation. This examination of the Texas oil was undertaken with the purpose of ascertaining the principal series of hydrocarbons which compose the crude oil.

The specimen was obtained from a large territory owned by the Forward Reduction Company, of this city. The crude oil was very thick and dark in color. Its specific gravity at 20° was 0.9500. A determination of sulphur by the Carius method gave 0.94 per cent. These heavy oils almost invariably contain water suspended, and it is almost impossible to remove the water by drying, and the oil can not be distilled while it contains water on account of violent bumping. Under atmospheric pressure, scarcely any of the oil distilled below 240°. After drying by standing a long time in a warm place with fused calcium chloride, when distilled in vacuo under 13 mm. pressure, the distillates collected in the following proportions and gave the specific gravity annexed:

[1] The work in this paper was the subject of a thesis by Mr. Buck for the degree of Bachelor of Science.

150°	150°–230°	230°–300°	Above 300°
10 per cent.	32 per cent.	21 per cent.	37 per cent.
0.8753	0.9222	0.9602	Very thick.

Next 500 grams were distilled under 25 mm. up to 310°, leaving a residue in the flask of 175 grams. The distillations were repeated several times until larger quantities collected at the following temperatures:

125°–130°	140°–145°	160°–165°	175°–180°	195°–200°	215°–220°
0.8744	0.8848	0.8986	0.9095	0.9231	0.9373

225°–230°	240°–245°	270°–275°
0.9432	0.9478	0.9559.

For the removal of benzene hydrocarbons and other impurities, the constituents with lower boiling-points were treated several times with fuming sulphuric acid, then washed with sodium hydroxide and water. The remaining oil was nearly colorless. In order to prevent decomposition of the less stable constituents with higher boiling-points by the fuming acid, the heavy oil was dissolved in light gasoline. After the solution became colorless, the gasoline was distilled off, leaving the heavy oil. By this method, it is possible to purify any of the distillates with high boiling-points without decomposition.

The fraction 125°–130° (25 mm.), after treatment with the fuming acid, gave as its specific gravity 0.8711, very little less than the specific gravity of the unpurified distillate, indicating that very little else was contained in this fraction but the principal hydrocarbon. A determination of the molecular weight of the oil at the freezing-point of benzene gave 196; required for $C_{14}H_{26}$, 194. The index of refraction was also determined and the molecular refraction calculated from it was 62.39; required for $C_{14}H_{26}$, 62.34. A combustion of the oil gave 86.56 per cent. of carbon, and 13.46 per cent. of hydrogen; required for $C_{14}H_{26}$, carbon 86.59, hydrogen 13.41.

The fraction 140°–145° (25 mm.) was purified in the same manner, and the same determinations were made. The results of the determinations of carbon and hydrogen, molecular weight determinations and molecular refraction led to the formula of the hydrocarbon $C_{15}H_{28}$.

By the same method of purification, the fraction 160°–165° (25 mm.) was obtained nearly colorless, and it then gave as its specific gravity 0.8894, only slightly less than the specific gravity of the unpurified oil. Determinations of carbon and hydrogen, of its molecular weight and molecular refraction, gave results leading to the formula $C_{16}H_{30}$.

After treatment with the fuming acid, the fraction 175°–180° (25 mm.) gave as its specific gravity 0.8966, essentially the same as that of the unpurified oil. The formula established by the same determinations as the others was $C_{17}H_{32}$.

The specific gravity of the fraction 195°–200° (25 mm.), after purification with fuming sulphuric acid, was 0.9070. Determinations of carbon and hydrogen, and molecular weight, led to the formula $C_{19}H_{36}$, although the low percentage of hydrogen indicated that the distillate contained some of the hydrocarbon with less hydrogen. The distillate 215°–220° (25 mm.) gave as its specific gravity, after purification, 0.9163. Its formula, established by analysis and determination of molecular weights, is $C_{21}H_{38}$.

The fraction 240°–245° (25 mm.) gave as its specific gravity 0.9306. No other determinations were made of this oil than its molecular weight, which corresponded to the formula $C_{23}H_{42}$. The fraction 270°–275° (25 mm.) was extremely viscous, and could be purified only by dissolving in gasoline. It gave a clear, slightly yellow oil, with a specific gravity 0.9410, practically the same as the unpurified distillate. Determinations of carbon and hydrogen, of molecular weight and molecular refraction, corresponded to the formula $C_{25}H_{46}$.

It appears, therefore, that this heavy Texas oil contains hydrocarbons from $C_{14}H_{26}$ to $C_{19}H_{36}$ of the series C_nH_{2n-2}, and higher hydrocarbons $C_{21}H_{38}$ to $C_{25}H_{46}$ of the series C_nH_{2n-4}. From the slight changes in specific gravity after thorough agitation with fuming sulphuric acid, it appears that these condensed methylenes constitute the chief body of the crude oil which distils within these limits. The first series is satisfied by assuming that the molecule is composed of two methylene rings connected in the same manner as diphenyl, with a sufficient number of methyl side-chains to account for the formula or with connecting carbon atoms between the rings. The study of the constituents of Texas, California, and Canadian petroleums, with high boiling-points, is now in progress.

A summary of the results obtained in the examination of this petroleum is given in the following table:

	B. P. (25 mm.)	Sp. gr.	Index of refraction.	Molecular refraction Calculated.	Found.
$C_{14}H_{26}$	125°–130°	0.8711	1.4713	62.34	62.39
$C_{15}H_{28}$	140°–145°	0.8788	1.4746	66.94	66.70
$C_{16}H_{30}$	160°–165°	0.8894	1.4672	71.55	69.40
$C_{17}H_{34}$	175°–180°	0.8966	1.4721	76.14	73.85
$C_{19}H_{36}$	195°–200°	0.9020	1.4928	85.35	84.70
$C_{21}H_{38}$	215°–220°	0.9163	1.4979	92.46	92.91
$C_{25}H_{46}$	270°–275°	0.9410	1.5152	110.87	111.00

[CONTRIBUTION FROM THE LABORATORY OF HYGIENE, UNIVERSITY OF PENNSYLVANIA.]

AN EXPERIMENTAL STUDY OF THE GAS-PRODUCING POWER OF BACILLUS COLI COMMUNIS UNDER DIFFERENT CONDITIONS OF ENVIRONMENT.

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THE power which some bacteria possess of liberating certain gaseous elements and compounds from suitable culture media has been the subject of a number of investigations. These investigations have brought to light many interesting facts, and have established methods of diagnostic value based upon gas production. Dr. Theobald Smith, in the account of his now classic experiments upon fermentation, has given a number of species which produce gases, the necessary conditions, quantity of gas produced, etc. Various analyses are on record, also, of the gas liberated, these analyses being more or less detailed depending upon the point of view of the investigator and the time when the work was done. Among the earlier workers we find, generally, that they were content with the determination of the amount of carbon dioxide. The residual gas, being found to be explosive, was accepted as hydrogen.

Later studies have been made with more care, and in consequence the presence of other gases has been recognized. Pammel and Bennett[1] have studied the action of several gas-producing organisms with especial attention to their behavior toward

[1] This Journal, 18, 157 (1896).