

*The Chemical Constitution of a
Fraction of Peruvian Petroleum
Boiling Between 150°C. and 350°C.*

by

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THE CHEMICAL CONSTITUTION OF A FRACTION OF PERUVIAN
PETROLEUM BOILING BETWEEN 150° and 350° C.

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TABLE OF CONTENTS.

INTRODUCTION.

SOURCE OF PETROLEUM.

EXPERIMENTAL.

PURIFICATION.

Table I. Physical Properties.

MOLECULAR WEIGHT DETERMINATIONS.

Table II. Molecular Weights and Combustion
Analyses.

MOLECULAR REFRACTIONS.

Table III. Specific and Molecular Refractions.

MOLECULAR VOLUMES.

Table IV. Molecular Volumes.

DISCUSSION OF RESULTS.

SUMMARY.

BIBLIOGRAPHY.

THE CHEMICAL CONSTITUTION OF A FRACTION OF PERUVIAN
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INTRODUCTION.

The "Origin of Petroleum" is a subject that has been very widely discussed for a great many years with the result that the vegetable or animal theory has gained support at the expense of the theory of Mendeléeff, namely the hydrolysis of carbides. As an aid to the solution of this problem, many investigators have studied petroleums to determine their chemical composition. The work is complicated by the difficulty of isolating chemical individuals in the pure state and also by the lack of accurate knowledge of the chemical and physical properties of hydrocarbons, which can only be obtained by a study of synthetic compounds. However, as a result of much research, our knowledge of the composition of the majority of petroleums is fairly complete and the oil from nearly every field has been studied. A field which has been known for some considerable time, but which has not been developed until comparatively recent years, is that located in Peru. A point of interest is the total isolation of this field from any other producing on a commercial basis. This feature and the fact, that no

previous work has been done on this oil, led to the institution of this investigation.

SOURCE OF THE PETROLEUM.

The oil investigated was supplied by the Imperial Oil Refineries Ltd., Ioco, B.C. The accompanying map shows the location of the field.

In the Lobitos oilfield the beds consist of clay-shales with bands of calcareous sand-stone. The beds in the Negritos formation belong to the Clavilithes Series and contain the characteristic fossils. They consist of rather carbonaceous clay-shales and sand-stones.

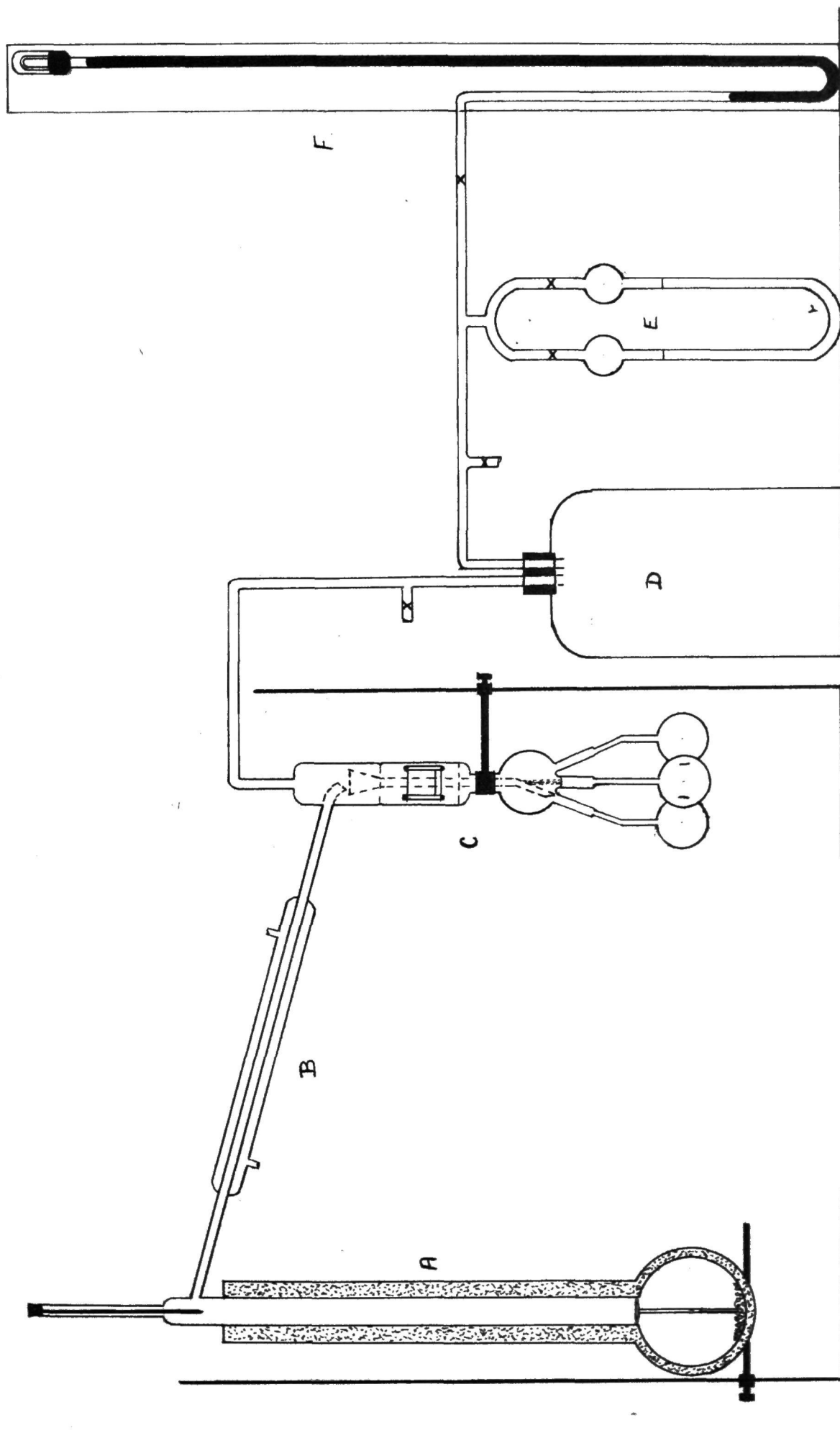
A complete detailed description of the Geological formation is given by T. O. Bosworth in "Geology and Palaeontology of North-West Peru".

EXPERIMENTAL.

The properties of the petroleum and of the fraction investigated were as follows: -

	<u>D₂₀²⁰</u>	<u>B. P. Range</u>	<u>Pressure</u>	<u>Sulphur</u>
Crude Petroleum	.8340	65 - 370° -75% off	760 mm.	0.10%
Fraction	.8315	130 - 340° C.	760 mm.	0.03%

It has been found that oils having a boiling point above 200° decompose materially when distilled at atmospheric pressure, consequently reduced pressure was used in order to prevent thermal decomposition. The diagram represents the apparatus which was made of pyrex glass. The still A had a column 50 x 3 cms. which was lagged with asbestos as was the flask. Flasks varying from 2000 c.c. to 100 cc. were used in the various stages according to the amount of distillates available. Glass beads were used in the column as a refluxing surface but the still got plugged and caused considerable trouble. In place of the beads, small glass tubes 2.5 x 0.5 cm. (internal diameter) were packed in perpendicularly and found to be very efficient. The distillate receiver C¹ was found invaluable in the distillations at reduced pressure. The bottle D acted



as a pressure equalizer and was connected in turn to a sulphuric acid manometer E and a mercury manometer F, the former being used to give an accurate control of pressure. The pressure was reduced by means of an ordinary water pump.

Four gallons of the oil were distilled. Owing to the difficulty of keeping such an apparatus absolutely airtight, constant pressure was maintained by drawing off air and letting it in at the same rate. To obtain a fraction having a constant range of 2° or 3° an average of six distillations were necessary.

The fractions obtained showed slight unsaturation corresponding to an iodine number of 2 - 3. The first four distillates had a terpene-like odor which was scarcely discernable in the others. All fractions were colorless, except the last four which were slightly yellow.

PURIFICATION.

Treatment with liquid sulphur dioxide had no effect on the distillates. In this particular the oils differ from those examined by Krieble and Seyer². Sulphuric acid (1.84 gr.) was then tried as a means of purification.

2. J. Amer. Chem. Soc. 46, 1921

It was found to have very slight action. The acid layer, on settling after agitation of the mixture, varied from light yellow in the first fraction to a brown in the last. The decrease in volume was negligible in the first seven distillates, and amounted to very little in those of highest boiling point. It was found impossible to obtain a colorless acid layer even after prolonged sulphuric acid treatment, and the distillates still exhibited slight unsaturation with alkaline permanganate.

Resort was then made to fuming sulphuric acid (15 % SO_3). This caused a dark brown layer. Treatment was continued with this reagent till, on subsequent treatment with sulphuric acid, the acid layer became colorless.

The oil was washed with water to remove most of the acid, and the remainder neutralized with dilute sodium hydroxide. After treatment with the latter, washing with water was continued till phenolphthalein gave no red coloration.

Each fraction was dried over calcium chloride and then subjected to two distillations over sodium. These distillations resulted in no changes in boiling point worthy of note, and the residue in the still remained unchanged.

The purified oils were all colorless and odorless, excepting the first two, which had an odor resembling that of turpentine. A qualitative test for unsaturation was made on each by shaking with a dilute aqueous solution of

potassium permanganate and sodium carbonate. No evidence of unsaturation was shown.

Table I gives the physical properties of the purified distillates. In the case of density, the values before and after treatment are given. The decrease in density was not sufficient to indicate the removal of a hydrocarbon, and this was substantiated by the small decrease in volume during acid treatment. At this point it might be mentioned that evidence of two other hydrocarbons was available. These collected around 135° and 152° at 750 mm. pressure, but the amounts were not sufficient for further identification. The odor of turpentine was very pronounced; in the case of the 135° fraction it was quite irritating.

TABLE I.

B.P.	Pressure	Density D_{20}^{20}		Refractive	Rotation
degrees C.	m.m.	Before	After	Index 20°	1 dm. tube
1. 169 - 172	750	.7996	.7884	1.4348	0.0
2. 188 - 190	750	.8075	.7978	1.4393	0.0
3. 132 - 135	60	.8288	.8198	1.4504	0.0
4. 145 - 148	60	.8342	.8219	1.4519	0.0
5. 154 - 156	60	.8395	.8262	1.4542	0.0
6. 169 - 172	60	.8442	.8317	1.4570	0.008L
7. 149 - 152	20	.8526	.8421	1.4649	0.017L
8. 161 - 164	20	.8589	.8466	1.4622	0.008L
9. 155 - 158	9	.8598	.8420	1.4619	0.021D
10. 167 - 169	9	.8612	.8442	1.4632	0.104D
11. 178 - 181	9	.8755	.8540	1.4686	0.221D

The refractive indices were measured on a Pulfrich Refractometer at 20°, the sodium D line being used. The decrease at number eight is of interest.

The rotations were measured on a Jose and Jan Fric Saccharimeter of the same type as used by the U. S. Bureau of Standards. The measurements were taken in a 400 m.m. tube and recorded in Ventzke degrees. By using the relation, circular degree = .34657 V°, and reducing to one decimeter tube, the specific rotations were obtained.

The quantitative values are very small, but the optical activity from a qualitative point of view is of interest. This property has been questioned by Mabery³, as he examined many distillates and found no rotation. However Kriebble and Seyer⁴, in an investigation on the Tar Sands of Northern Alberta, found optical activity. No doubt distillation at too high a temperature is responsible for racemization.

MOLECULAR WEIGHT DETERMINATIONS.

These determinations were made by the freezing-point depression method, using benzene as a solvent. In order to decrease the error due to temperature and supercooling effects, advantage was taken of a device due to O. Maass.⁵ This consisted of applying a brass rod, previously cooled

3. J. Amer. Chem. Soc. 41, 1919.

4. J. Amer. Chem. Soc. 46, 1919.

5. Proc. R. S. C. 1919

in a carbon-dioxide ether bath, to a platinum point sealed into the inner tube. The error due to supercooling was thus decreased and from .03 - .04° supercooling was used. Also the error due to the convergent temperature effects was reduced, since freezing occurred with the cooling bath kept only from 1 - 1.5° cooler than the inner tube. By this means the true freezing point was more nearly obtained, and the errors in molecular weight determinations were not over 1 - 2 %.

The results of molecular weights and combustion analyses indicate the presence of the hydrocarbons given in Table II.

TABLE II.

	M. W.	<u>Found</u>	C.	H.	M. W.	<u>Calculated</u>	C.	H
C ₁₀ H ₂₀	140.5		85.87	14.13	140		85.71	14.29
C ₁₁ H ₂₂	153		85.45	14.31	154		85.71	14.29
C ₁₂ H ₂₄	169		85.87	14.20	168		85.71	14.29
C ₁₃ H ₂₆	182		85.55	14.04	182		85.71	14.29
C ₁₃ H ₂₄	179		86.38	13.88	180		86.66	13.34
C ₁₄ H ₂₆	196		86.72	13.50	194		86.60	13.40
C ₁₅ H ₂₈	210		86.77	13.50	208		86.54	13.46
C ₁₆ H ₃₂	225		85.68	14.09	224		85.71	14.29
C ₁₇ H ₃₄	239		85.54	14.45	238		85.71	14.29
C ₁₈ H ₃₆	250		85.45	14.22	252		85.71	14.29
C ₁₉ H ₃₆	267		86.62	13.48	264		86.36	13.64

MOLECULAR REFRACTIONS.

The specific rotations given in Table III were obtained by substituting the densities and refractive indices in Lorentz and Lorenz formula $r = \frac{1}{d} \frac{n^2 - 1}{n^2 + 2}$.

The product of the specific rotations and theoretical molecular weights gave the molecular refraction given in the third column. The values in the next column are the summation of the atomic refractions, using 2.418 for a singly bound carbon and 1.100 for hydrogen.

The previous statement, that no unsaturation was evident from treatment with alkaline permanganate, is substantiated by the consistent differences between calculated and found values given in the last column.

TABLE III.

	<u>Spec. Refraction</u>	<u>Found</u>	<u>Calculated</u>	<u>Difference</u>
C ₁₀ H ₂₀	.3308.	46.36	46.18	4.50
C ₁₁ H ₂₂	.3299	50.86	50.80	4.31
C ₁₂ H ₂₄	.3280	55.17	55.42	4.63
C ₁₃ H ₂₆	.3282	59.80	60.04	-0.72
C ₁₃ H ₂₄	.3279	59.08	57.84	4.52
C ₁₄ H ₂₆	.3275	63.60	62.46	4.74
C ₁₅ H ₂₈	.3282	68.34	67.08	4.50
C ₁₆ H ₃₂	.3248	72.84	73.88	4.93
C ₁₇ H ₃₄	.3264	77.77	78.50	4.57
C ₁₈ H ₃₆	.3264	82.34	83.12	3.79
C ₁₉ H ₃₆	.3259	86.13	85.54	

MOLECULAR VOLUMES.

These values were calculated by dividing the theoretical molecular weights by their corresponding densities at 20° compared to water at 20°.

Kopp⁶ was the first to point out the relations between molecular volumes of liquids. He found that his results were most regular when taken at the boiling point, since the boiling points of most liquids are approximately two-thirds of their respective critical temperatures, and

6. Lieb. Ann. 41, 1842, 79; 96, 1855, 153, 303;
96, 1855, 171.

therefore corresponding temperatures. As the densities of these hydrocarbons at their boiling points are not available, the results obtained by using the densities at 20° are in error, since they are not corresponding functions.

Our meagre knowledge of the structure of these hydrocarbons and their physical properties, results in no accurate data on atomic volumes. Cohen⁷ gives the mean difference for CH₂ as 15.9, the value for double bond nil, for singly bound C the value 11, and for H 5.5. Using this data for calculating the molecular volume of the first hydrocarbon results in the value 220; the found value is 177.7. This contraction can only be accounted for by ring structure. Willtstätter⁸ has compared the values of molecular volumes for paraffins and cycloparaffins, as well as those of the olefines and cycloparaffins. In each case the ring structure is accompanied by contraction; this value is by no means a constant, but varies from 14.8 to 27.4 in the former, and from 6.4 to 26.4 in the latter.

From these considerations, it is apparent that the molecular volume does not aid materially in the identification of these types of hydrocarbons. However the differences for CH₂ and the molecular volumes given in Table IV seem to substantiate the results already reached.

7. Organic Chemistry, Part II, Structure 1920

8. Willtstätter, Ber., 40, 1907.

TABLE IV.

C ₁₀ H ₂₀	177.7	15.5
C ₁₁ H ₂₂	193.2	12.0
C ₁₂ H ₂₄	205.2	16.5
C ₁₃ H ₂₆	221.7	-3.6
C ₁₃ H ₂₄	218.1	15.4
C ₁₄ H ₂₆	233.5	13.8
C ₁₅ H ₂₈	247.3	17.6
C ₁₆ H ₃₂	264.9	18.1
C ₁₇ H ₃₄	283.0	15.9
C ₁₈ H ₃₆	298.9	10.6
C ₁₉ H ₃₆	309.5	

DISCUSSION OF RESULTS.

Hydrocarbons, corresponding to those identified in this research, have been found by other investigators. The densities and refractive indices appear to be a distinctive feature of these oils, in that they are higher than those obtained by Mabery⁹ in Ohio and Canadian petroleums and lower than those found by Kriebel and Seyer¹⁰ in the Tar Sands of Northern Alberta. The latter point out the difference between the found molecular volumes, and those

9. Am. Chem. J., 19, 1897; 33, 1905.
10. J. Amer. Soc., 46, 1921

calculated from atomic volumes for C and H in straight chains, the contractions indicating ring structure. In the present research differences were also found, but the contractions were not quite so large, indicating less dense ring structure and more side chains. The densities and refractive indices also substantiate this.

The optical activity displayed by some of the hydrocarbons isolated in this investigation is also of interest. The plant theory of the origin of petroleum has gained considerable support of late years. This property, as well as the terpene-like odor of some of the oils, seems to favor this theory. It is hardly conceivable that we should have optical activity in compounds formed by the hydrolysis of carbides. The temperature, that would exist in this process, would also preclude optical activity, since temperatures over 360° cause racemization of most of our optically active compounds.

SUMMARY.

Eleven hydrocarbons have been isolated, and two of lower boiling points than those tabulated have been indicated. Analysis indicates the presence of $C_{10}H_{20}$, $C_{11}H_{22}$, $C_{12}H_{24}$, $C_{13}H_{26}$, $C_{16}H_{32}$, $C_{17}H_{34}$, $C_{18}H_{36}$ of the C_nH_{2n} series and $C_{13}H_{24}$, $C_{14}H_{26}$, $C_{15}H_{28}$ and $C_{19}H_{38}$ of the C_nH_{2n-2} series. Evidence has also been given for the presence of C_8H_{16} and C_9H_{18} of the C_nH_{2n} series.

BIBLIOGRAPHY.

7. Cohen, J. B., Organic Chemistry, Part II.,
Structure 1920.
6. Kopp, Lieb, Ann. 41, 1842, 79; 96, 1855, 153,303;
96, 1855, 171.
2. Krieble, V. K. and Seyer, W. F., "A Chemical
Investigation of
the Asphalt in the
Tar Sands of Northern
Alberta."
Journal of the American Chemical Society, 46, 1921,
1337.
4. " " " " " "
10. " " " " " "
5. Maass, O.- "Note on a Modified Form of Freezing
Point Apparatus". Section III., 1919,
97 - 99. Transactions
Royal Society of Canada.
3. Mabery, C. F.- "The Genesis of Petroleum as Revealed
by its Nitrogen Constituents".
Journal of American Chemical Society,
41, 1919, 1690.
9. Mabery, C. F. - "The Constituents of Pennsylvania,
Ohio and Canadian Petroleums between
150° and 220°. American Chemical
Journal, 19, 1897, 419.
"On the Composition of Petroleums.I.
The Hydrocarbons in Ohio Trenton
Limestone Petroleum". American
Chemical Journal, 33, 1905, 251.
1. Seyer, W. F., - "A Receiving Apparatus for Practical
Distillation at Low Pressures" Journal
of the American Chemical Society, 46,
1924, 1209.
8. Willstätter, R., and Bruce, J.- "Tur Kenntnis der
Cyclobutanreihe".
Berichte der Deutschen
Chemischen Gesellschaft,
40, 1907, 3981.