

On the Composition of Japanese Petroleum, I.

By

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(Received June 12, 1923)

K. Kobayashi¹, S. Shimidzu², C. F. Mabery and S. Takano³ and T. Katayama⁴ have already investigated the composition of Japanese petroleum. The results of their investigations show that Japanese petroleum is composed for the greater part of hydrocarbons of the polymethylene series or naphthene. In addition to this, the geological survey of the oil fields in Japan⁵, presented some evidence to support the above statement brought forward by the chemists. Although no doubts exist that polymethylene hydrocarbons constitute the main part of our petroleum, the studies made by these investigators provided no further knowledge of the exact constitution of the hydrocarbons, and moreover, were concerned specially with the fractions boiling at a higher temperature than 98°.

The authors, therefore, have undertaken the present study to isolate polymethylene hydrocarbons in pure condition and to ascertain their constitutions by chemical means.

The specimen used in this investigation was Nishiyama oil, Echigo, obtained by the kindness of Dr. T. Fujii. It was a dark green oil, having the sp. gr. 0.8230, and was composed of the following three portions :

Temp.	below 150°	150—300°	above 300°
Distillate %	23.2	47.3	29.5

¹ Kogyo Kwagaku Zasshi, **5**, 321; **13**, 1277.

² Ibid., **7**, 915.

³ Am. Chem. J., **25**, 297 (1901).

⁴ Kogyo Kwagaku Zasshi. **16**, 1341; **17**, 273.

⁵ C. Engler u. H. v. Höfer: Das Erdöl. **II**. 467 (1909); J. Takahashi: Scie. Reports Tohoku Imp. Univ. (III). **I**, 143 (1922).

The first portion was distilled under ordinary pressure three times in six successive portions :

TABLE I.

	Fraction.	Yield. %	d_{4}^{20}
1	32—50°	3.4	0.6525
2	50—70°	5.6	0.6841
3	70—90°	8.8	0.7196
4	90—120°	42.5	0.7529
5	120—150°	26.7	0.7773
6	above 150°	13.0	0.8151

2,350 gm. of the third fraction boiling at 70—90°, were shaken first with fuming sulphuric acid containing 7% SO₃, and afterwards with a mixture of sulphuric and nitric acids, being left in contact with the mixed acids for some hours, and then washed with water. It was then treated with 1% caustic potash solution, washed with water and dried over calcium chloride; finally distilled on metallic sodium in a dephlegmator.

The oil freed from aromatic and unsaturated hydrocarbons by the treatments above mentioned, was fractionated three times at 10° intervals, and then twice at 5° intervals. The fractions boiling at 75—85° after five distillations, amounted to 757 gm. having sp.gr. 0.7340.

This portion was carefully distilled following S. Young's descriptions¹. The oil to be distilled, was kept in a flask which connected with a six column dephlegmator, and was slowly distilled so that the drops of distillate fell at the rate of about one per second. After the 15th. distillation, the operation was continued at the rate of one drop of distillate every two seconds, and the liquid was collected in a flask cooled by ice water. The correction of boiling point for the barometric pressure during the operation was made, (0.04° per 1 m. m.) and the bulb of the thermometer was covered with a little cotton-wool to prevent super-heating.

¹ Distillation principles and processes, 100 (1921).

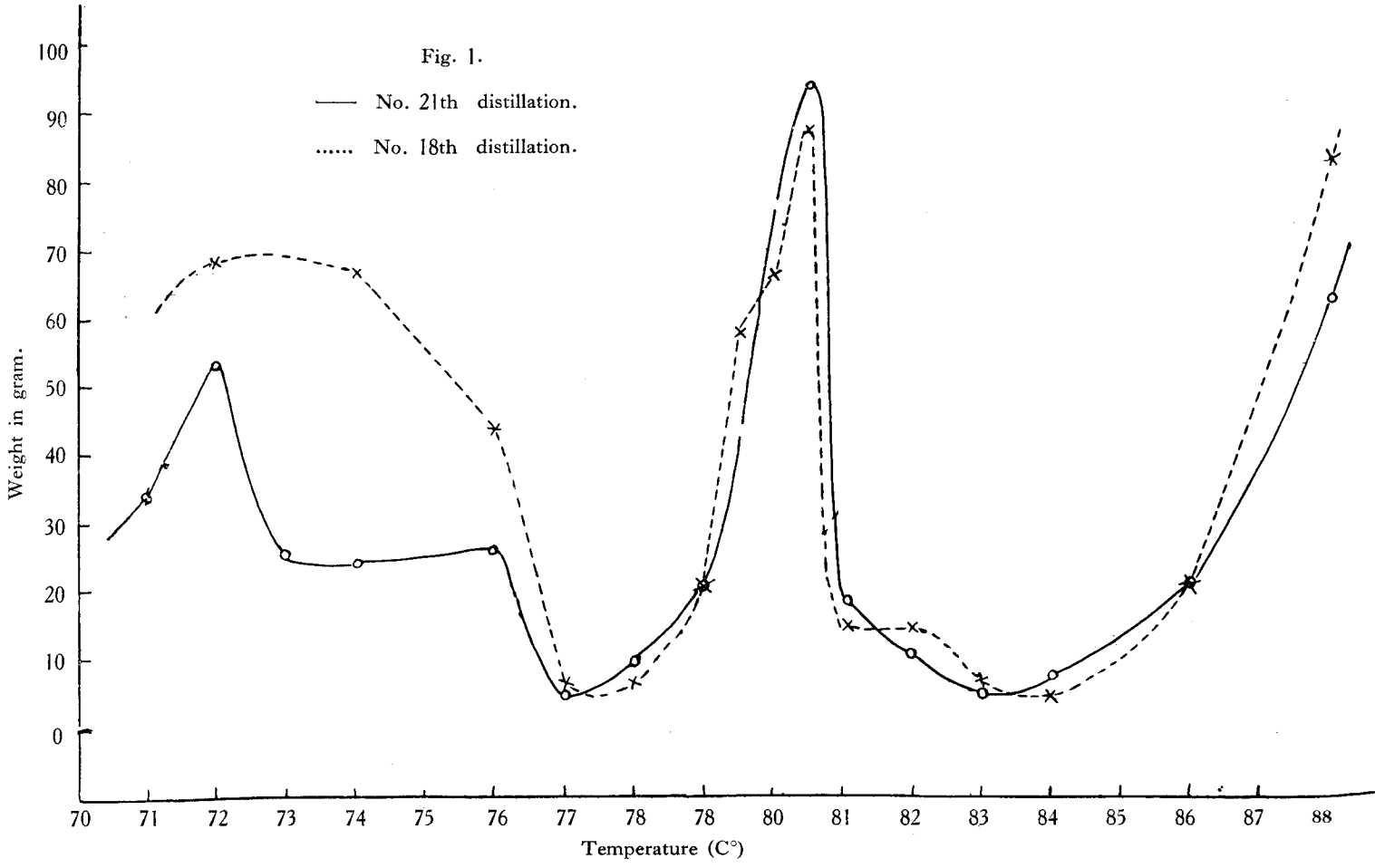


Fig. 1.

— No. 21th distillation.

..... No. 18th distillation.

The results of the 21st. fraction — the weight of each distillate, the ratio of weight to temperature range $\Delta w/\Delta t$, specific gravity, and index of refraction — are given in Table II.

In Fig. I. the actual weight of distillate against the temperature of 18th. and 21st. distillations is plotted.

The temperature — weight curve of the 21st. distillation (Fig. I.) shows two maxima, one at 80—81°, and the other at 72°, and there appeared to be a maximum in the neighbourhood of 90°. As seen in Table I, the major portion of the oil boils at 70—90°, distills at 80—81°, and this fraction shows the largest index of refraction 1.414, and the highest density 0.765; and the fraction B. p. 71—72°, corresponding to the other maximum in the curve, indicates $d_4^{25} = 0.7295$, $n_D^{25} = 1.3965$.

TABLE II.

Fraction.	Temp.	Weight.	%	$\Delta w/\Delta t$	d_4^{25} *	n_D^{25} *	M.R.
1	66—70°	66	9.4	14	—	—	
2	70—71°	34	4.8	34	0.7213	1.3930	
3	71—72°	54	7.7	54	0.7295	1.3965	
4	72—73°	25	3.5	25	0.7347	1.4000	
5	73—74°	25	3.5	25	0.7432	1.4035	
6	74—76°	27	3.8	13.5	0.7446	1.4045	
7	76—77°	5	0.7	5	0.7449	1.4050	
8	77—78°	10	1.4	10	0.7480	1.4072	
9	78—79°	21	3.0	21	0.7521	1.4090	27.54
10	79—79.5°	43	6.1	86	0.7567	1.4125	27.83
11	79.5—80°	76	10.8	152	0.7595	1.4130	27.36
12	80—80.5°	94	13.3	188	0.7652	1.4145	27.43
13	80.5—81°	19	2.7	38	0.7615	1.4130	27.36
14	81—82°	11	1.6	11	0.7568	1.4080	
15	82—83°	5	0.7	5	0.7526	1.4075	
16	83—84°	8	1.1	8	0.7437	1.4042	
17	84—86°	21	3.0	10.5	0.7413	1.4020	
18	86—88°	63	8.9	31.5	0.7201	1.3920	
19	over 88°	99	14.0	—	—	—	

Two portions correspond to methylcyclopentane and cyclohexane and they show a slight difference in density and index of refraction, compared with the same compounds obtained by other chemists, indicating the presence of some aliphatic hydrocarbons as an impurity. The purification of these fractions, however, was not continued as our apparatus was insufficient for the purpose.

CYCLOHEXANE.

The hydrocarbon B. p. 80—81°, isolated from Japanese petroleum, was also compared with respect to its physical constants with hexahydrobenzene prepared from pure benzene by the method of Prof. P. Sabatier, passing with pure hydrogen over reduced nickel heated at 180°, and purified by distillation¹.

TABLE III.

Observers.	B. p.	Density	Index of refraction.
Authors			
from petroleum	80—81°	$d_4^{25} = 0.765$	$n_D^{25} = 1.414$
„ benzene	80.3—81°	$d_4^{25} = 0.7738$	$n_D^{25} = 1.4195$
Markownikoff	80.5—81°(760 m.m.)	$d_4^{20} = 0.7727$	—
Zelinsky	81—82°	$d_4^{20} = 0.7764$	$n_D^{20} = 1.4258$
Baeyer	79—79.5°		
Fortey, from			
american petroleum	80.55—80.65°	$d_4^{20} = 0.7722$	
galician „	80.8°	$d_4^{20} = 0.7903$	
Rosenthal	80.85°(760 m.m.)	$d_4^{20} = 0.7764$	$n_D^{18} = 1.43197$
R. Kissling	80.8°(760 m.m.)	$d_4^{20} = 0.7788$	$n_D^{20} = 1.4266$

It gave, on analysis, the results shown in Table IV. which agree fairly well those required for cyclohexane.

¹ C. R., **132**, 210, 566 (1901).

² Ber. D. Chem. Ges., **28**, 577 (1895); **30**, 1225 (1897); Lieb. Ann., **302**, 1 (1898).

³ Ber. D. Chem. Ges., **28**, 1205 (1895); **30**, 390 (1897).

⁴ Ibid., **26**, 229 (1893); Lieb. Ann., **278**, 88 (1893).

⁵ J. Chem. Soc., **73**, 932 (1898).

⁶ Organische Verbindungen. 17, (1914).

⁷ Chemische Technologie des Erdöls, 31.

TABLE IV.

Fraction.	Temp.	Substance.	CO ₂	H ₂ O	C%	H%
9	78—79°	0.1459 ^{grm.}	0.4540 ^{grm.}	0.1916 ^{grm.}	84.86	14.62
”	”	0.1311	0.4082	0.1719	84.92	14.60
mean					84.89	14.61
10	79—79.5°	0.1029	0.3211	0.1360	85.11	14.72
”	”	0.1148	0.3578	0.1484	85.37	14.40
”	”	0.1132	0.3537	0.1487	85.21	14.63
mean					85.23	14.58
11	79.5—80°	0.1034	0.3234	0.1326	85.29	14.29
”	”	0.1031	0.3223	0.1341	85.27	14.49
”	”	0.1042	0.3257	0.1374	85.25	14.69
mean					85.27	14.49
12	80—80.5°	0.1371	0.4297	0.1757	85.43	14.27
”	”	0.1149	0.3610	0.1493	85.69	14.40
”	”	0.1010	0.3166	0.1316	85.49	14.51
mean					85.54	14.42
13	80.5—81°	0.1280	0.4000	0.1635	85.23	14.22
”	”	0.1311	0.4105	0.1700	85.39	14.44
”	”	0.1032	0.3231	0.1354	85.39	14.62
mean					85.34	14.43
14	81—82°	0.1392	0.4350	0.1816	85.23	14.53
”	”	0.1179	0.3689	0.1545	85.31	14.59
mean					85.27	14.56
Calc. for C ₆ H ₁₂					85.62	14.38

According to Prof. P. Sabatier, reduced nickel heated at 300° serves as a catalyst for the dehydrogenation of cyclohexane which loses all the six hydrogen atoms of the ring and yields hydrogen and benzene. At a lower temperature, the reverse change occurs, the passage of hydrogen and benzene over reduced nickel heated at 180° resulting in the hydrogenation of benzene. The catalytic transformation of cyclohexane under the influence of reduced nickel into benzene, thus offers a convenient method for identification of the hydrocarbon as observed by N. Zelinsky¹ in russian petroleum using heated palladium black as a catalyst.

¹ Ber. D. Chem. Ges., 45, 3678 (1912).

40 grm. of the substance B. p. 80—81°, were passed over reduced nickel at 300°, and the product possessing an aromatic odour and boiling at 77—81°, was fractionated into two portions. The yield was 24 grm.

	Fractions.	Yield	d_4^{25}	n_D^{25}
1.	77—79°	14 grm.	0.8178	1.4544
2.	79—81°	9 „	0.8288	1.4648

The second fraction showing the same specific gravity and index of refraction as pure benzene, was treated with a mixture of conc. nitric and sulphuric acids, yielding a compound which was purified by distillation. It boils at 210—211°, $d_4^{25}=1.2074$, and gave, on analysis, the following results: C=58.59; 58.52; 58.61; H=3.99; 4.18; 4.42; N=11.26; 11.76; 11.95 (theory requires C=58.51; H=4.10; N=11.39 for $C_6H_5NO_2$).

The physical constants and analytical results agree with those of nitrobenzene. It yields by reduction aniline which was confirmed by forming a double salt with platinum chloride and also other chemical reactions.

METHYLCYCLOPENTANE.

The substance isolated from the petroleum gave, on analysis, the elementary composition and showed the physical constants mentioned on the table V, with those of methylcyclopentane obtained by Markownikoff¹, Zelinsky², S. Young³ and Aschan⁴.

TABLE V.

Observers.	B. p.	Density.	Index of refraction.
Authors	71—72°	$d_4^{25} = 0.7295$	$n_D^{25} = 1.3965$
Markownikoff, synthesized	71.5—72° (742 m.m.)	$d_0^{25} = 0.76$	—
Baku oil	71—72° (755 m.m.)	$d_0^{25} = 0.7664$	—
Zelinsky	71.5—72.5°	$d_0^{25} = 0.7501$	—
Zelinsky and Moser	71° (743 m.m.)	$d_4^{25} = 0.7488$	—
Young	69.98—70.15°	$d_4^{25} = 0.7157$	—

¹ Ber. D. Chem. Ges., **30** 1222 (1897).

² Ibid., **30**, 389 (1897).

³ J. Chem. Soc., **73**, 913 (1898).

⁴ Ber. D. Chem. Ges., **41**, 2431 (1908).

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For identification¹, 20 gm. of the oil B. p. 71–72°, in a flask were subjected to oxidation with 80 gm. fuming nitric acid (sp. gr. 1.51) and the solid reaction product deposited at the bottom of the flask, after 12 hours of reaction, was separated from the mother liquor by filtration. The yield was 3 gm. It melted at 97–120°. By repeated fractional crystallisation from its aqueous solution, it was separated into two compounds, one melting at 184–189° and the other at 98°–100°

The former compound, less soluble in water, was identified to be succinic acid by elementary analysis.

C=40.40; H=5.02, and also by molecular weight determination with $\frac{N}{10}$ NaOH solution, M. W.=117 (theory requires C=40.67; H=5.08; M. W.=118 for C₄H₆O₄).

The latter compound, more soluble in water, was also confirmed to be a mixture of oxalic and glutaric acids, varying carbon and hydrogen contents from 28.5 to 47.7 and from 3 to 5.3 respectively.

The volatile acid found in the mother liquor, was noticed to be acetic acid.

Methylcyclopentane was identified by oxidation with nitric acid, yielding acetic, oxalic and succinic acids with some glutaric acid as noticed N. Zelinsky and Gutt² and also by O. Aschan³.

Thus, by repeated fractional distillation of petroleum, for about four months, we succeeded, as we had expected, in isolating these polymethylenes in fairly pure condition, and the examination of the other portion boiling about 90° will be reported in another article, with that of the fraction boiling below 70°.

April 1923. Laboratory of Organic and Biochemistry.

¹ S. Nametkin: Ber. D. Chem. Ges. **42**, 1373 (1909); C. Engler, H. v. Höfer; Das Erdöl. **1**, 235 (1913); Markownikoff: Ber. D. Chem. Ges., **32**, 1445 (1899); **35**, 1584 (1902).

² Ber. D. Chem. Ges., **41**, 2431 (1908).

³ Ibid., **31**, 1801 (1898).