[Contribution from the Chemical Laboratory of Tokyo Imperial University]

NAPHTHENIC ACIDS DERIVED FROM JAPANESE PETROLEUM

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Introduction

Up to the present, our knowledge of the naphthenic acids has been confined to their lower homologs, considerable difficulty being encountered in the isolation of the higher homologs in a sufficiently pure state to make possible a determination of their composition and structure. The literature on the higher naphthenic acids is not in good agreement.

Japanese petroleum, especially Akita oil, is of the naphthene series, and T. Yoshimura[1] isolated tridecanaphthenic acid from it.

The object of this paper is to describe an investigation upon the petroleum acids recovered from a waste lye produced at the Akita Refinery of the Nippon Petroleum Company in the refining of a petroleum distillate of 25–26° Bé. ("neutral distillate" from Akita-Kurokawa crude oil).

Experimental Part

The waste lye was a deep brown liquid with an offensive odor; $d_{4°}^{15°}$, 1.0413. Upon acidification, a mixture of acid substances separated as a thick, deep brown oil in 18.6% yield; $d_{4°}^{15°}$, 0.9853; acid value, 68.8; sulfur content, 0.89%. It emulsified with water, owing chiefly to the presence of alkyl sulfuric acids, and formed a copper salt whose ether or petroleum ether solution had an intense and peculiar green color, thus showing the presence of naphthenic acids. It was found to be a complicated mixture of water, naphthenic acids, hydrocarbon oils, alkyl sulfuric acids and esters, phenols (?), other sulfur compounds and inorganic substances.

To remove the hydrocarbon oils and other neutral impurities, the alkali salts of the acids were dissolved in dil. alcohol and extracted with a petroleum ether volatile below 70°. The presence of alcohol (15–40% of the total solution) was found to be necessary to prevent the formation of emulsions on extraction with petroleum ether. The following data are typical: crude petroleum acids (acid value, 68.8), 1000 cc.; 5 *N* potassium hydroxide solution, 250 cc.; absolute alcohol, 500 cc.; water, 1000 cc. This mixture was extracted 18 times with 1000cc. portions of petroleum ether. The acid mixture obtained upon acidification was washed with saturated sodium chloride solution, dried over calcium chloride and warmed in a vacuum to expel petroleum ether. The product was a heavy, viscous, deep brown oil; $d_{4°}^{15°}$, 1.0148; $n_D^{15°}$, 1.4924; acid value, 208. This oil contained naphthenic and alkyl sulfuric acids, and possibly phenols. The petroleum ether removed most of the sulfur compounds other than the alkyl sulfuric acids.

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[1] Sekiyu Jiho, *Petroleum Times of Japan*, March, 1921.

When this was heated above 100° there was considerable carbonization due to the sulfuric acid liberated by the decompositon of the alkyl sulfuric acids; hydrogen sulfide and sulfur dioxide were also evolved. The optimum conditions for distillation were obtained by adding a metallic oxide, such as 1.5% of cupric oxide, whereupon the naphthenic acids distilled unchanged and the alkyl sulfuric acids readily decomposed. The distillation was carried out under 9 mm. pressure and a slow stream of dry carbon dioxide was bubbled through the liquid.

The distillate up to 235° was converted into the potassium soaps and extracted with petroleum ether (volatile at 55°). This soap solution, possibly containing also some potassium phenolates, gave the crude naphthenic acids upon acidification with dil. hydrochloric acid, as a thick, pale yellow oil of faint, peculiar odor, and containing only traces of sulfur; $\mathrm{d}_{4^\circ}^{15^\circ}$, 0.9936; $n_{\mathrm{D}}^{15^\circ}$, 1.4875; acid value, 230.4. No emulsion was formed with water and no change occurred on heating to 110°.

For further purification, the methyl esters were made by treating them with an excess of absolute methyl alcohol and dry hydrogen chloride. The supernatant ether layer was separated, washed with dil. alkali solution and dried over calcium chloride, and was then a pale yellow liquid of fruity odor; $\mathrm{d}_{4^\circ}^{15^\circ}$, 0.9613; $n_{\mathrm{D}}^{15^\circ}$, 1.4715.

The mixture of naphthenic acids obtained by saponification with alcoholic potash and subsequent acidification with dil. hydrochloric acid was a light yellow, viscous liquid; $\mathrm{d}_{4^\circ}^{15^\circ}$, 0.9918; $n_{\mathrm{D}}^{15^\circ}$, 1.4824; acid value, 254.3; mean mol. wt. (calc.), 221; no iodine number. It is significant that the esterification increased the acid value and lowered the refractive index.

By means of a series of 30 fractional distillations the mixture of methyl esters was separated into 3 fractions, and these proved to be the methyl esters of trideca-, tetradeca- and pentadecanaphthenic acids. All were colorless liquids with a fruity odor.

TABLE I

PROPERTIES OF METHYL ESTERS

	$C_{12}H_{23}COOCH_3$	$C_{13}H_{25}COOCH_3$	$C_{14}H_{27}COOCH_3$
$\mathrm{d}_{4^\circ}^{15^\circ}$	0.9622	0.9644	0.9659
$n_{\mathrm{D}}^{15^\circ}$	1.4663	1.4686	1.4728
B. p. (8.9–9.0 mm.)	124–126°	135–137°	147–149°
B. p. (760 mm.)	262–263°	277–278°	296–297°
Analysis: Calc. C	74.3	74.9	75.5
Found H	11.6	11.8	11.9
C	74.1	74.7	75.5
H	11.0	11.2	11.3
Mol. wt. Calc.	226	240	254
Found	233	242	250

The esters were saponified with 2 *N* alcoholic potash solution and extracted with petroleum ether (b. p., 55°) to remove unsaponified material.

The soap solutions upon acidification precipitated the corresponding naphthenic acids as oils. These were washed, dried and then heated to 70° in a vacuum to expel the solvent. All were colorless, odorless liquids.

Table II

Properties of Free Acids

	$C_{12}H_{23}COOH$	$C_{13}H_{25}COOH$	$C_{14}H_{27}COOH$
$d^{15°}_{4°}$	0.9916	0.9930	0.9941
$n^{15°}_{D}$	1.4784	1.4807	1.4848
B. p. (8.9–9.0 mm.)	167–169°	178–180°	191–192°
Neutralization value. Calc.	264.3	247.9	233.4
Found	262.2	249.5	236.5
Mol. refraction, Calc.	61.56	66.16	70.80
Found	60.64	64.82	69.26

These acids have no iodine number and do not become discolored upon exposure to the air. They form various metallic salts, esters, acid chlorides, acid amides and acid anilides.

A somewhat modified Claisen flask was used for the fractional distillation. In the lower part of the distilling column, which was longer and wider than in the ordinary type, was inserted a platinum basket upon which small aluminum rings 6 mm. in diameter were piled to a height of 4 cm. This modification was intended to bring about a better fractionation and to prevent a mist from passing into the condenser. The flask was electrically heated and the pressure was maintained at 8.9–9.0 mm., by an electrically regulated Gaede oil pump.

It is to be noted that the specific gravities recorded in this paper are higher than those given in the literature for products of other origin,[2,3] but are approximately the same as those given by T. Yoshimura.[1]

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Summary

The crude naphthenic acids derived from a kerosene distillate of a Japanese petroleum (Akita-Kurokawa oil) have been purified and the corresponding free C_{12}, C_{13} and C_{14} naphthenic acids and their methyl esters are described. Their properties differ slightly from those of naphthenic acid obtained from other sources.

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[2] Kraemer and Böttcher, *Ber.*, **20**, 595 (1887).

[3] V. Kozicki and v. Pilat, *Petroleum*, 11, 310; *Chem. Centr.*, [I] **1916**, 1145.