SHORT COMMUNICATIONS

*Nuclear Magnetic Resonance of Tar Products. II**

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Tar products consist of chemically similar components of high boiling points, which are very difficult to be distinguished from each other. As the means of analyses of these products, measurements of infrared spectra are usually made, but, other methods seem necessary to be explored. Nuclear Magnetic Resonance (NMR) technique has the advantage that we can analyze the functional groups in any liquid samples under nondestructive condition. Thus, Williams[1] made NMR measurements for saturated aromatic and olefinic components in distilled fractions of petroleum, Richards[2] for the aromatic compounds in various kinds of coals, and Schoolery[3] tried to determine the hydrogen contents of naphthalene derivatives.

The present authors performed the analysis of α- and β-methyl-naphthalenes and reported elsewhere*. This paper will present the preliminary results of NMR measurements for distilled fractions of tar products.

Samples.—Samples used in this experiments are shown in Table I, which were collected from the plant of Yokohama Factory of Tokyo Gas Co., Ltd. at the working condition.

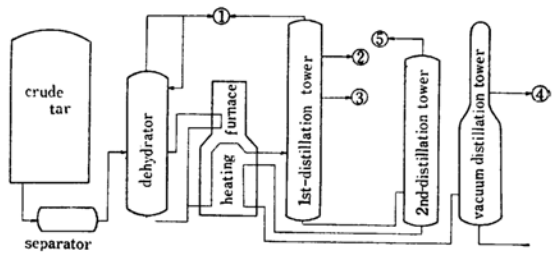
NMR Measurements.—Measurements of the NMR absorption spectra were caried out at 27 Mc./sec., and 40 Mc./sec. by the apparatus constructed by one of the authors (S. F.) and by the Japan Electron Optics Laboratory Co., Ltd., respectively. The concentration of sample is 50% (wt.) in carbon tetrachloride which contains a small amount of cyclohexane as the internal reference. Sample was spun rapidly during measurements.

Results.—The characteristic features of NMR spectra at 27 Mc./sec. were complicated and found to be insufficient for the analyses of functional groups. Even so, we could easily identify the paraffinic, alpha-alkyl and aromatic protons in the spectra. As the preliminary investigations, the results of measurements at 40 Mc./sec. seem satisfactory, which are shown in Fig. 1. Light oil has four absorptions in the aromatic region as well as the absorptions of aromatic hydroxyls of phenol and cresol at 6.3 and 8.6 P./10 M. (benzene=0), respectively. The absorption at 39.1 P./10 M. results from pyridine or picoline. The absorption in paraffinic region is stronger in light oil than in carbolic oil. The absorption of light oil in alpha-alkyl region overlaps those of methyl hydrogens of toluene and xylene. Four absorption bands at 2.4~7.5 P./10 M. observed in carbolic oil were assigned to hydroxyl groups of phenol and of cresol. Carbolic oil is also characterized by three strong absorptions at naphthalene region and a weak one at alpha-methyl region, which is weaker than that in light oil. According to the results of Fig. 1, we can see that naphthalene oil and top oil of the second tower are close to each other in the compositions. Heavy oil showed a broad absorption at aromatic region and other spectra at 37.1, 39.9 P./10 M. which are attributed to β-alkyl hydrogen.

We also examined the fractions obtained by rectifying distillation. The fractions of the

TABLE I

No.	Sample	B.p., °C	S.g.	Tar acid %	Naphthalene %
1	Light oil	85~190	0.919	14	—
2	Carbolic oil	180~200	1.025	46	16.8
3	Naphthalene oil	200~250		9	58.0
4	Heavy oil	225~295	1.079	6	2.5
5	Top oil (2nd tower)	195~270		9	29.6



1) R. B. Williams, A. S. T. M. Special Technical Publication, No. 224, p. 168 (1958).
2) R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, **1960**, 2489.
3) J. N. Schoolery, Lectured at the Chemical Society of Japan, Tokyo, Oct. 1960.
* Report I: *Anal. Chem.*, in press.

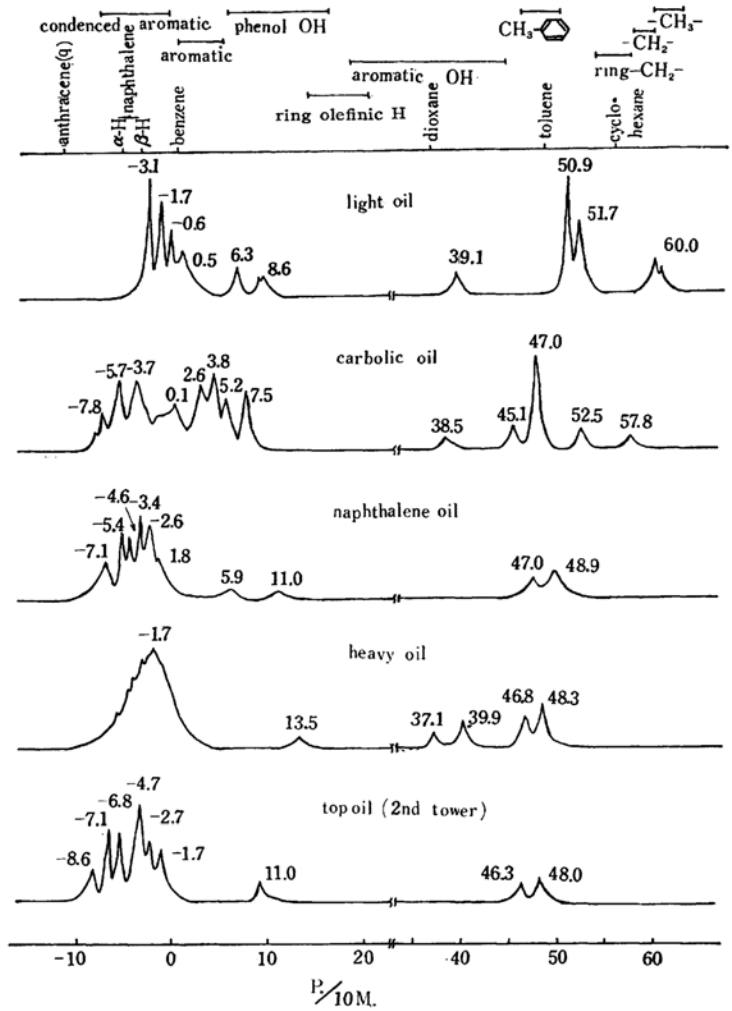


Fig. 1

factory distills which were rectified through the rectifying column were measured by NMR. According to the results of these measurements (not shown here) as well as those shown above, we conclude that the NMR method is quite useful for the analysis of tar products, and useful to figure out the efficiencies of the fractionation processes.

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