

Structure Analysis of Base Oils by X-ray Diffraction Method

Tomoko HIRAYAMA^{*1}, Kazuaki NEMOTO¹, Yuka MITSUNAGA¹, Takashi MATSUOKA¹
¹Doshisha Univ., Kyotanabe, Kyoto 610-0394, Japan

Introduction

Microscopic structure of lubricants has received a lot of attention recently because of its contribution to friction states. As is well known, general oil transforms its structure to glass under high pressure, as realized in continuously valuable transmission mechanics, for example[1,2]. Past studies have focused mainly on macro-characteristics of lubricants under high pressure, such as their viscosity and bulk modulus[3,4]. Based on these studies, some reports have shown that the traction properties largely depend on the molecular structure of the traction oil[5]. In addition, to investigate the molecular structure of the oil under high pressure, some simulation studies with molecular dynamics techniques have been done recently[6]. These studies indicate the growing attention being paid to the microscopic behaviour of machine oils.

The X-ray diffraction method has been used as a traditional method of getting information about the microscopic structure of materials. In this method, structure is estimated by analyzing obtained intensity profiles of X-ray scattering. However, there has been no research directly investigating the microscopic structure of machine oils. We applied the X-ray diffraction method to structure analysis of machine oils, focusing especially on their microscopic behavior under high pressure. Since general machine oil consists of several base oils, we chose two base oils as samples, n-hexadecane and dicyclohexyl; the former is a normal alkane, and the latter is a dual-cyclic alkane.

For this study, synchrotron radiation (SR) X-rays were applied to structure analysis because SR X-rays have a characteristic high brightness and wide energy range. In addition, the SR X-ray enables us to obtain accurate intensity profiles in a short period compared to X-rays in laboratories.

In summary, the final purpose of this study is to analyze microscopic structure of base oils under high pressure using synchrotron radiation X-ray diffraction and to determine exactly the pressure at which the oil transitions from liquid to solid. In this period, we basically investigated microscopic structure of the oils at normal pressure with 'Max80' in the NE-5C beam line in PF-AR, as a first step.

Experimental Procedure

In this study, we used an AR-NE5C beam line with a cubic multi-anvil type apparatus, called 'Max80', to analyze microscopic structure.

Cubic Multi-Anvil Type Apparatus for High Pressure

The cubic multi-anvil type apparatus, which is a single-stage type press, uses six anvils made of cemented carbide to create high pressure conditions. Each anvil has a square edge face to press a sample specimen. These sizes are selected based on sample size. Two of these six anvils are used as the upper and lower presses, and the other four anvils are used as side presses[7].

The optical alignment of this apparatus is shown in Figure 1. The X-ray beam enters through two slits and the gap of anvils, and the sample is irradiated by the beam. Finally, the diffracted X-ray from the sample is detected by the one-dimensional Solid-State Detector (SSD).

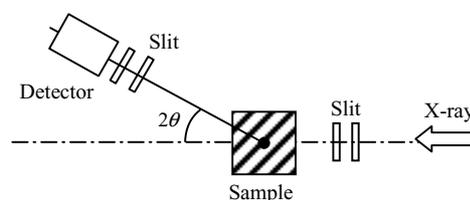


Figure 1: A diagram of optical alignment

Condition of Incident Angles

To obtain accurate information about the structure of the sample oils, we measured the scattering intensity at 13 diffraction angles: $2\theta = 2.5, 3.0, 4.0, 6.0, 8.0, 10.0, 12.0, 14.0, 16.0, 18.0, 20.0, 22.0,$ and 25.0 degrees.

Sample Oil

Two base oils, n-hexadecane ($(\text{CH}_2)_n$) and dicyclohexyl $\text{C}_6\text{H}_{11}\text{C}_6\text{H}_{11}$, were prepared as sample oils. The former is a normal alkane, and the latter a dual-cyclic alkane. We chose these oils because their simple and contrasting structures suited our basic study. The molecular geometries of these oils are shown in Figure 2, and their basic properties are listed in Table 1.

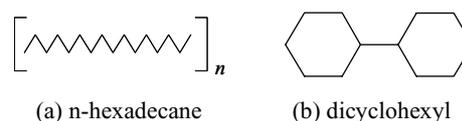


Figure 2: Molecular geometry of sample oils

Table 1: Property of sample oils

	n-hexadecane	dicyclohexyl
Molecular weight	226.4	166.3
MP (centigrade)	18	3-4
BP (centigrade)	287	227

Results and Discussion*Scattering Intensity Profiles*

Some examples of the obtained scattering X-ray intensity profiles from dicyclohexyl are shown in Figure 3, where the vertical axis represents scattering intensity, and the horizontal axis represents energy E . It can be seen that the profiles are peculiar to typical liquid without any sharp peaks from small bottle made by Teflon. In addition, we confirmed that these intensity profiles did not change over three measurements. This indicates that X-ray irradiation did not degenerate the sample oil. We used a similar process to obtain the intensity profiles of n-hexadecane.

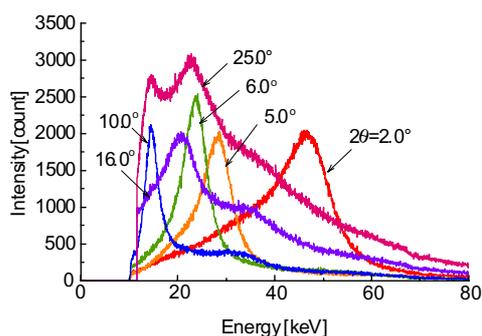


Figure 3: Scattering intensity profiles of dicyclohexyl
Structure Factor

Figure 4 shows the structure factors of the sample oils analyzed with the obtained intensity profiles. The vertical axis represents the structure factor, $S(Q)$, while the horizontal axis represents the scattering vector, Q . As can be seen in the figure, both sample oils have several peaks at almost the same Q values. This is due to the similarities of the structures of these samples. Both n-hexadecane and dicyclohexyl consist of carbon and hydrogen, and the ratio of carbon to hydrogen is 0.32 and 0.35, respectively. As a result, their structure factors are very similar.

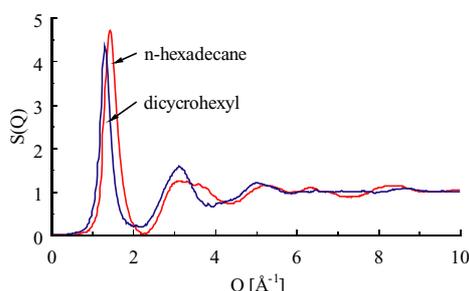


Figure 4: Structure factor of sample oils

PDF and RDF

Figures 5 and 6 show the PDF and RDF of the sample oils obtained by the Fourier transform of the above $S(Q)$ profiles. The vertical axis represents the PDF $g(r)$ or the RDF $4\pi r^2 g(r)$, while the horizontal axis represents a distance r from the referential atom.

In Figure 5 and 6, it can be seen that there are several peaks of the PDF and the RDF. The distance r having a broad peak is dependent on a bond distance and the height of the profile is dependent on the relative amount of the bond. Some typical bond distances are listed in Table 2. The peaks around $r = 1.10$ Å and 1.54 Å correspond to the C-H and C-C bonds of sample oils, respectively. As a whole, we were able to confirm the success of the structure analysis by comparing it with the common bond distance at normal pressure.

Microscopic structures of the oils are much discussed from the RDF in Figure 6. We can see that there are several peaks even at the range of $r \geq 2.0$ Å in the figure. These peaks seem to be caused by two atoms that are not directly connected each other but are in the same molecule. To permit a clear discussion, we numbered all the carbon atoms, as shown in Figure 7.

First, we focus on the results for n-hexadecane. As can be seen from the RDF, there are two peaks, one around $r = 2.5$ Å and the other around 4.0 Å. The former is due to two carbon atoms jumping over one carbon atom, like C1-C3, and the latter is due to two carbons jumping over two carbon atoms, like C1-C4. The peak around $r = 3.2$ Å is thought to be from two hydrogen atoms connected to each carbon atom, C1 and C3, for example.

The results for dicyclohexyl are similar. As can be seen from the RDF, the wide peak from about $r = 2.5$ to 3.0 Å can be separated into two small peaks. One is due to two carbon atoms jumping over one carbon atom, as with C1-C3, and the other is due to two carbons jumping over two carbon atoms in the same cyclohexane ring, as with C1-C4.

Furthermore, at any $r \geq 4.0$ Å, both RDFs are almost smooth curves without any peaks. This indicates that there is no regularity over a long distance because the sample oils are in a completely liquid phase.

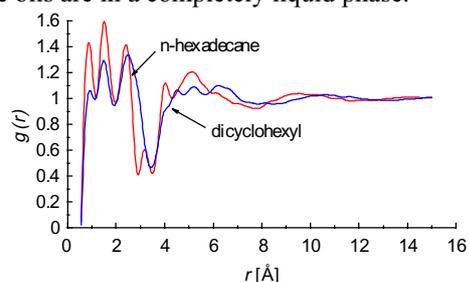


Figure 5: Pair distribution functions of sample oils

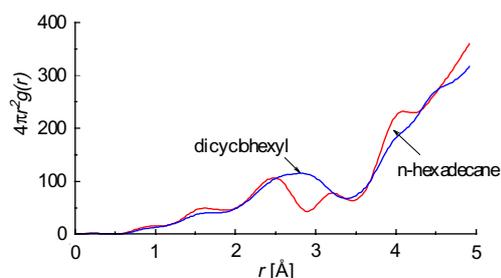


Figure 6: Radial distribution functions of sample oils

High Pressure Science

Table 2: Distance of common bonds in alkane

Bond	Bond distance [Å]
C-C	1.54
C-H	1.10
C=C	1.33

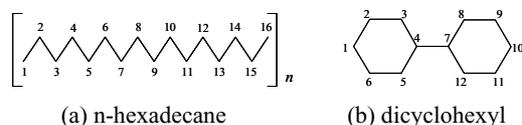


Figure 7: Structural formula with numbering carbons

Conclusion

The microscopic structure of base oils was analyzed using a synchrotron radiation X-ray diffraction method. Conclusions are summarized as: The PDF and RDF of the n-hexadecane and dicyclohexyl were clearly obtained by X-ray diffraction method without any degeneration of the oils. It was confirmed that they correspond to their microscopic structures at normal pressure.

Acknowledgement

We wish to express sincere gratitude to Prof. K. Tsuji (Keio University), and Dr. T. Kikegawa (KEK), Dr. T. Hattori and Dr. Y. Katayama (Japan Atomic Energy Agency) for their sincere cooperation. This work was sponsored by the Ministry of Education, Science and Culture of Japan (No. 18760114).

References

- [1] N. Ohno, J. of Japanese society of Tribologists, 46(5), 349 (2000), *in Japanese*.
- [2] I. Fujishiro, Proc. of International Seminar on Microstructures and Mechanical Properties of New Engineering Materials (IMMM'93), 13(1), 275 (1993).
- [3] Y. Nakamura, Transactions of the ASME, Journal of Tribology, 117(3), 519 (1995).
- [4] Y. Nakamura, J. of Japanese society of Tribologists, 46(5), 368 (2000), *in Japanese*.
- [5] H. Tamura et al., J. of Japanese society of Tribologists, 45(9), 65 (2000), *in Japanese*.
- [6] Y. Tamai, J. of Japan Petrol. Institute, 25(3), 127 (1982).
- [7] W. Utsumi et al., J. of the Crystallography Society of Japan, 42, 59 (2000), *in Japanese*.

* thirayam@mail.doshisha.ac.jp