Characteristics of Lubricants for Low GWP Refrigerants and ENEOS's Fundamental Research

○Tomohiro TAKAKI*, Takafumi KIMURA, Masaki KAWAGUCHI, and Yuya MIZUTANI

Lubricants R&D Department, ENEOS Corporation, 8, Chidoricho, Naka-ku, Yokohama, 231-0815, Japan

ABSTRACT

The Kigali Amendment to the Montreal Protocol stipulates a gradual reduction in hydrofluorocarbon (HFC) refrigerants. Both HFC and hydrofluoroolefin (HFO) blended refrigerants will likely be used from now on. This report introduces the technology behind refrigeration oils applicable to low-GWP refrigerants such as R454C and R479A, which have a GWP below 150. In response to the ongoing refrigerant transition, we have actively conducted various foundational studies, some of which are summarized in this report.

Keywords: Refrigeration Oil, R454C, R479A, Tribology, Pump-down, Foaming, COP

1. Introduction

The Kigali Amendment to the Montreal Protocol stipulates a gradual reduction in hydrofluorocarbon (HFC) refrigerants with high global warming potential (GWP). Both HFC and hydrofluoroolefin (HFO) blended refrigerants will likely be used from now on. For the time being, it is expected that multiple refrigerants will continue to be used concurrently. At the previous conference, we introduced refrigeration oils compatible with multiple refrigerants such as R410A, R32, and R454B [1]. HFO blended refrigerants such as R454C and R479A, each exhibiting a GWP below 150, are considered as potential alternatives to R32 for use in room air conditioners. This report introduces the technology behind refrigeration oils that are applicable to low-GWP refrigerants such as R454C and R479A. Although various types of refrigeration oils are available, we focus on polyol esters (POEs), which offer excellent stability with HFO refrigerants and superior supply reliability.

In addition to the development of products compatible with next-generation refrigerants, we are engaged in fundamental research on refrigeration oils and ester compounds. In parallel, we have been exploring collaborative research opportunities with universities and industry partners to further advance innovation and practical applications in this domain. For example, in collaboration with the Miyazaki group, our efforts include the evaluation of the coefficient of performance (COP) in refrigeration cycles using R454C [2]. In addition, we have demonstrated a high-efficiency oil for household refrigerators using R-600a [3,4]. This report also outlines selected aspects of our fundamental research.

2. Refrigeration oils compatible with low-GWP refrigerants

To ensure reliability in the event that trace amounts of water and/or oxygen enter the refrigeration cycle, refrigeration oils are required to exhibit excellent stability. In general, compounds containing carbon-carbon double bonds (C=C) tend to have a lower oxidative stability. Accordingly, HFOs may exhibit a higher susceptibility to degradation compared to HFCs. Therefore, refrigeration oils must demonstrate enhanced stability under conditions involving HFO blended refrigerants. In an evaluation using R32 and R1234yf as refrigerants, it was found that, under identical pressure conditions, the viscosity of the oil-refrigerant mixture decreases as the proportion of R-1234yf increases. This reduction in viscosity may adversely affect the anti-wear property [5]. These two challenges can be effectively addressed by modifying the base oil and additive formulation designed for refrigeration oils.

2.1 Enhancement of stability through additives

Two test oils were prepared using POE, which is widely used as a refrigeration oil, with different additive formulations. Oil-A1 contains additives primarily developed for HFC refrigerants, whereas Oil-A2 is a modified formulation intended for HFO blended refrigerants. The stability of the test oils was evaluated using autoclave tests in accordance with JIS K 2211. After filling autoclaves with the refrigerants and test oils, we heated them under the specified conditions shown in Table 1. After that, the stability was evaluated by measuring the acid number of the test oils. The acid number is a major indicator of deterioration in lubricating oils. A higher value indicates more degradation.

The test results are shown in Fig. 1. In the stability test with R32, Oil-A1 exhibited a low acid value. On the other hand, in the stability tests with R454C and R479A, Oil-A1 showed a slight increase in acid value. In contrast, Oil-A2, which was formulated with improved additives for HFO-blended refrigerants, exhibited a lower acid value.

2.2 Design of base oils considering refrigerant-dissolved viscosity

As mentioned, a higher kinematic viscosity is preferable for the oil-refrigerant mixture to prevent wear. To prevent a decrease in the kinematic viscosity of the mixture, we attempted to design the chemical structure and prepared three samples in this study.

Fig. 2 shows a schematic illustration of the device for measuring refrigerant solubility and viscosity. All the measurements and calculations were performed following those in previous reports [6,7]. The mixtures of refrigerants and oils were sealed in pressure vessels while measuring the kinematic viscosity of the oils with dissolved refrigerants and the amount of refrigerants dissolved in the oils. Then, the pressure in each vessel was measured after reaching equilibrium under an arbitrary temperature and pressure. The viscosity and density of the oil-refrigerant mixtures were measured using the attached viscometer at the same time as the amount of dissolved refrigerants.

The viscosity of each pure oil and its refrigerant-dissolved viscosity is shown in Table 2. Compared with Oil-B, Oil-C alone exhibited a higher viscosity both before and after refrigerant dissolution. In contrast, while Oil-D alone had a lower viscosity than Oil-B, it exhibited a higher viscosity upon refrigerant dissolution. Accordingly, formulations of refrigeration oils can be customized to fulfill specific user requirements.

Table 1 Conditions of stability test.

Vessel volume	200 mL
Oil amount	30 g
Air	3 mL
Moisture in oil	500 ppm
Refrigerant	R32, R454C, R479A
Refrigerant amount	30 g
Catalyst (50 mm)	Fe, Cu, Al
Temperature	175 ºC
Time	168 hours

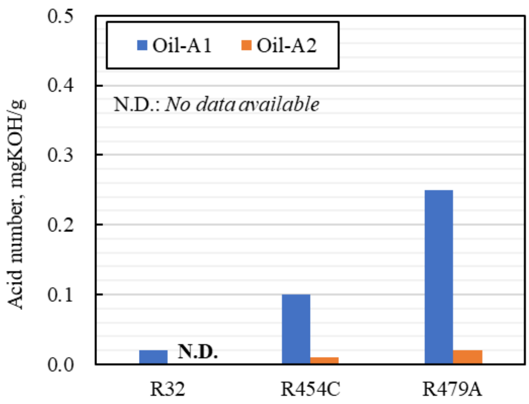

Fig. 1 Analysis result for aged oil.

Table 2 Viscosity results before and after refrigerant dissolution

Test oil		Oil-B	Oil-C	Oil-D
Pure oil (40ºC)	mm^2/s	68	74	56
R454C (80ºC/2.0 MPa.)	mm^2/s	3.4	4.0	3.7
R479A (80ºC/2.0 MPa.)	mm^2/s	3.9	4.2	4.0

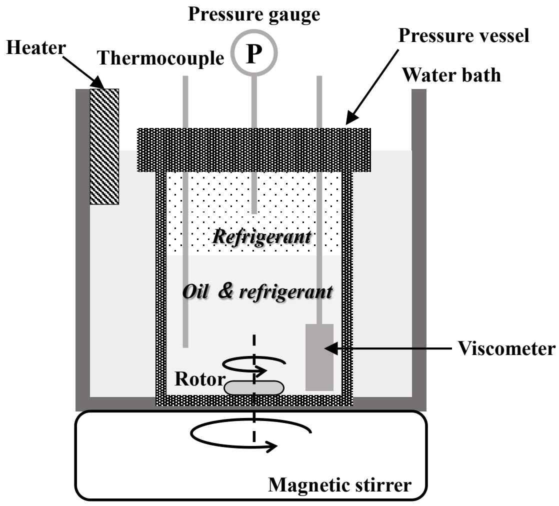

Fig. 2 Kinematic viscosity of refrigerant-oil mixture.

3. Study on tribological properties

The influence of fluorinated refrigerants on lubrication performance has been reported in previous studies [8]. Currently, the industry is undergoing a refrigerant transition, and we have focused on R32 and R1234yf to investigate their effects on lubrication performance and to clarify the lubrication mechanisms [5]. As mentioned in this report, under the specified conditions, increasing the proportion of R1234yf enhances refrigerant dissolution, which in turn reduces the viscosity of the oil-refrigerant mixture. Therefore, designing the viscosity of the mixture is crucial under fluid and mixed lubrication conditions. A block-on-ring test (Fig. 3), simulating boundary lubrication conditions, was also conducted. The wear width of the block after the test was measured to evaluate the anti-wear property, and the results are shown in Fig. 4. An increasing proportion of R1234yf in the refrigerant tended to improve the anti-wear property. According to an electron probe micro analyzer (EPMA) of the friction surface (Fig. 4), fluorine was more strongly detected on the surface exposed to the R1234yf atmosphere than on that exposed to the R32 atmosphere. Therefore, it is considered that R1234yf contributed to the formation of a denser lubricating film that prevents wear.

To further investigate the lubrication mechanism, the adsorption activity of the refrigerant on the nascent iron surface was measured [9,10]. Adsorption properties were evaluated using the apparatus developed by Mori et al. [11,12], which consists of a vacuum chamber connected to a mass spectrometer. Details of this experiment can be found in Ref. [11,12]. A brief overview of the experimental procedure is provided below. The specimen metal is cut to expose a nascent surface while introducing the sample gas. The introduced gas is adsorbed onto the nascent metal surface, and the exhaust gas is measured using a mass spectrometer. The adsorption activity can be calculated using changes in fragment intensity measured by a mass spectrometer. For reference, propane (R290) and propylene were also evaluated, and the test results are shown in Fig. 5. These results indicate that the C=C double bond in the chemical structure affects adsorption behavior.

Furthermore, adsorption behavior was investigated using the molecular simulation software Matlantis^{TM}. This simulator is based on a neural network potential (NNP) obtained by machine learning with a huge number of density functional theory (DFT) calculation results as teacher data and possesses the same level of accuracy as the DFT method while working tens of thousands of times faster [13,14]. The results of adsorption energy calculations, which serve as indicators of adsorption strength and stability, are also shown in Fig. 5 [10]. The adsorption energy showed a similar trend to the experimentally obtained adsorption activity, indicating that R1234yf and propylene exhibit high adsorption properties. These findings indicate that HFOs are more likely to influence tribological characteristics on nascent iron surfaces.

In addition, a comparative study on adsorption and lubrication performance was conducted with the H. Sakai & K. Sakai group using a simplified ester model of POE. In this study, quartz crystal microbalance with dissipation monitoring (QCM-D) was used to evaluate interactions with iron oxide surfaces [15,16].

4. Effect refrigeration of oil on compressor explosions during pump-down

Explosions of outdoor units have occasionally occurred during pump-down operations. The Hihara group conducted a study simulating an explosion during the pump-down of an air conditioner and investigated the influence of refrigeration oil [17-20]. Examples of refrigeration oils include POE, polyalkylene glycol (PAG), and polyvinyl ether (PVE). Higashi et al. reported that POE was less prone to explosion and safer than PAG on the basis of experimental results [17, 18].

In practice, due to the refrigerant solubility and viscosity requirements for the oil, it is sometimes difficult to modify the type or composition of the base oil. Therefore, the possibility of suppressing combustion through the use of additives was investigated. Saitoh et al. [19] and Ito et al. [20] evaluated oxidation inhibitors, stabilizers, and anti-wear agents in combination with refrigerants R22, R32, R1234yf, and R290. These studies were conducted in collaboration with us, and several compounds exhibited effects such as reducing the maximum pressure during diesel combustion and narrowing the flammable concentration range of the refrigerants. Fig. 6 [20] summarizes the effects of 1 wt% additive on the upper flammable limit of each refrigerant. The results suggest that the additives contribute to improved safety.

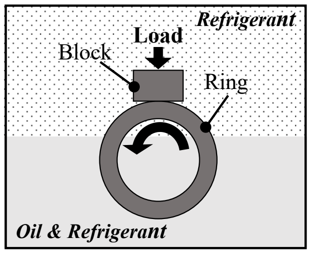

Fig. 3 Schematic illustration of block-on-ring test.

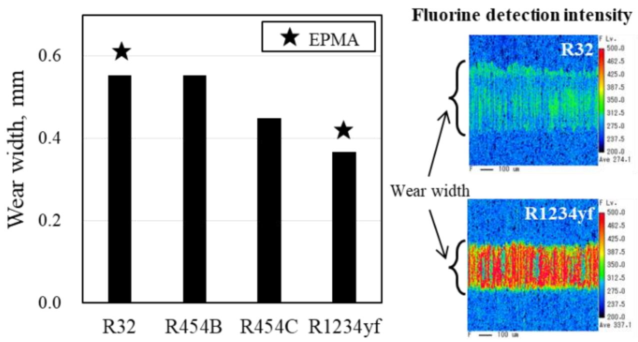

Fig. 4 Results of block-on-ring test and EPMA.

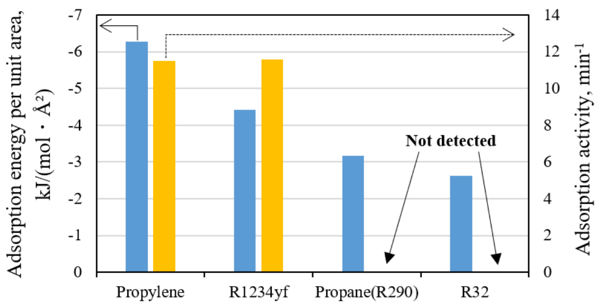

Fig. 5 Adsorption activity and energy (excerpted from [10]).

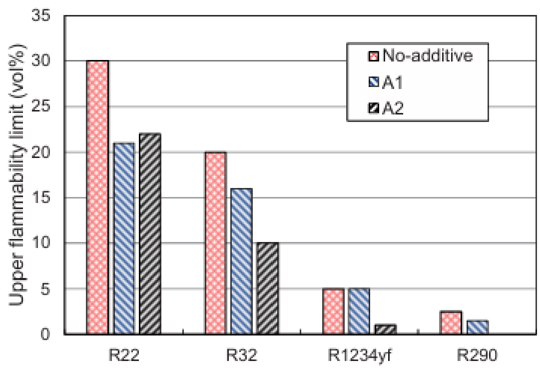

Fig. 6 Effect of 1 wt% additives on upper flammable limit of each refrigerant [20].
(A1: stabilizer, A2: oxidation inhibitor)

5. Foaming characteristics of oil-refrigerant mixtures

Refrigeration oils with dissolved refrigerants exhibit changes in properties such as viscosity and surface tension. Therefore, when an excessive amount of refrigerant is dissolved in the oil and the compressor is started, foaming of the oil-refrigerant mixture may occur. Severe foaming inside the compressor can lead to the discharge of oil together with the refrigerant into the system, resulting in a decrease in the oil volume remaining in the compressor. This may cause internal damage to the compressor and a decrease in COP. Thus, in collaboration with the Fukuta group, we have been investigating foaming characteristics and attempting to clarify the foaming phenomenon using an experimental apparatus that simulates a refrigerant compressor [21, 22].

R410A was used, and two types of POE oils were evaluated. POE-2 exhibited a higher solubility with the refrigerant than POE-1. The oil-refrigerant mixture was stirred using a rotating blade inside a pressure vessel, and the foaming behavior was evaluated on the basis of the height of the generated foam. As shown in Fig. 7 [21], vigorous foaming was observed at a specific refrigerant concentration. Furthermore, POE-2, which has a higher solubility with the refrigerant, was found to be less susceptible to foam formation. It was confirmed that foaming became more vigorous as the mixture pressure approached the saturated vapor pressure of the refrigerant, regardless of the type of oil used.

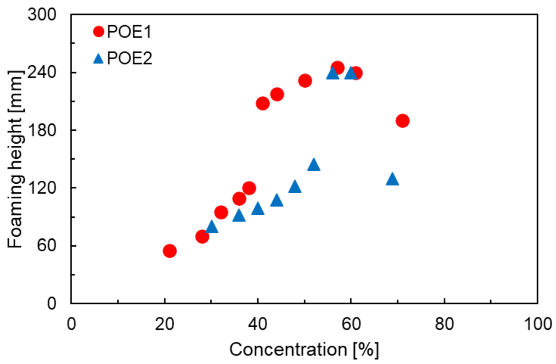

Fig. 7 Foaming height by stirring with different oil [21].

6. Conclusion

This report described refrigeration oil technologies compatible with HFO blended refrigerants. Several fundamental studies were also introduced. It was shown that the lubrication mechanism varies depending on the refrigerant, and that refrigeration oil can influence safety and foaming behavior, suggesting the potential for further improvements.

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