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Measurement and correlation of thermophysical properties of waste lubricant oil

C.T. Pinheiro, R.F. Pais, A.G.M. Ferreira, M.J. Quina, L.M. Gando-Ferreira *

CIEPQPF-Research Centre on Chemical Process Engineering and Forest Products, Department of Chemical Engineering, University of Coimbra, Portugal

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ABSTRACT

Measurements of viscosity, density and surface tension of waste lubricant oil (WLO) were conducted at different temperatures. The dataset was constituted by nine WLO samples from different producers. The main objective of the work is the investigation of the temperature dependence of viscosity, including the glass transition, T_g, and dynamic crossover, T_x, temperatures. In addition, different correlations were evaluated to predict viscosity and surface tension starting from a property easily obtained such as density. WLO show rapid decrease of viscosity with shear rate, followed by an extensive and well defined Newtonian plateau. The temperature dependence of viscosity at the Newtonian plateau of WLO deviated from the Arrhenius behavior, and was accurately described by four different models: Williams–Landel–Ferry (WLF), MYEGA, power law and Ghatee. The minimum and maximum absolute average relative deviation (AARD) were 0.08% and 0.9%, respectively. T_g predicted by WLF equation varied between T = 170.5 K and T = 198.7 K, while MYEGA tends to predict lower T_g (about T = 20 K). The power law and Ghatee models estimate T_x nearly with the same accuracy. A ratio T_x/T_g of about 1.28 ± 0.03 was obtained for WLO, which agrees with the literature. Waste oil is a moderately fragile glass forming fluid with a fragility parameter, m, ranging from 47.8 and 64.5. New correlations were developed for the prediction of viscosity and surface tension from density at different temperatures. AARD of 7% was observed for viscosity and 2% for surface tension.

1. Introduction

Lubricants are products designed to form a protective film that reduces friction and wear of machinery moving parts, cool surfaces, protect against corrosion and reduce energy consumption. During operation, lubricant oil undergoes chemical changes due to oxidation and contamination, decreasing its effectiveness up to a point that no longer meets quality specifications and needs replacement. The resulting waste lubricant oil (WLO) is a hazardous waste that requires proper disposal and treatment to reduce the risk of water, soil and air contamination [1,2]. Among the existing treatments, regeneration has become the preferred route, whereby base oil is produced by removing contaminants, oxidation products, and additives from the waste oil. Regeneration of WLO can prevent negative environmental impact, besides the inherent economic advantages [3,4]. The amount of crude oil required to produce a certain volume of lubricant is nearly nine times higher to produce the same volume from waste oil [2]. Various methods have been employed to carry out the waste oil regeneration, involving the removal of contaminants by distillation, acid treatment [5,6] solvent extraction [7], clay treatment, hydrogenation [8], or a combination of these processes.

The determination of thermophysical properties for quality control is essential throughout all stages of the lubricant supply chain, including the selection of the proper treatment route. According to national legislation, the decision of sending WLO to one of the recycling destinations is made after checking the conformity of certain technical specifications [9].

Properties of lubricant oil such as density, viscosity index, among others, are typically determined to assess its market value compared with the standards provided by the Society of Automotive Engineers. Udonne [10] evaluated different methods of recycling WLO (acid/clay treatment, distillation/clay, acid treatment and activated charcoal/clay treatment methods) by comparing density and viscosity of WLO with the final base oil. Isah et al. [10] performed a similar study using viscosity and density as probe properties. Kannan et al. [11] recycled WLO collected from automobile service stations which was subjected to dehydration, vacuum distillation followed by solvent extraction and finally the addition of additives to the re-refined oil. All these studies involved determinations of viscosity at 40 and 100 °C and density at 15 °C.

* Corresponding author.
E-mail address: lferreira@eq.uc.pt (L.M. Gando-Ferreira).

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However, it would be convenient to have determinations in wider ranges of temperature for engineering and efficient application of regeneration techniques. Few studies have been performed on the temperature dependence of WLO properties such as viscosity and density. Low-temperature fluidity is also an important property in lubricant rheology that is rarely addressed in the literature.

The surface tension is another property seldom mentioned in the literature although it can play an important role in the efficiency of regeneration [12]. After the work of Winchester and Reber in 1929 [13] on the temperature dependence of surface tension of fresh oil, this topic has been little investigated. The surface tension of mineral and aeronautical lubricant oil was assessed by Ross [14]. Jones and Wedeven [15] reported surface tension measurements for synthetic paraffinic, naphthenic and paraffinic mineral oil. To the best of our knowledge, only recently Kaldonsky and co-workers [16] evaluated the lubricity and surface properties of synthetic perfluoropolyether (PFPE) oil, comparing them with standard automotive oil. Studies have reported that changes in the surface tension of the oil can be the earliest sign of contamination, sludge potential and oxidation [17]. It is important to note that surface tension is intimately connected with the foaming tendency of lubricant oil [18]. It affects not only bubble formation and size but also the rate of liquid return to the void by bubble collapse or detachment [15]. Moreover, surface tension also influences oil cooling capacity by affecting spreadability. Poor wettability may reduce heat-transfer due to vapor phase formation [19].

In general, density measurement involves simple, fast and low-cost equipment. On the contrary, measurement of viscosity and surface tension is more complex and time-consuming, requiring more sophisticated and expensive instruments. Thus, if relationships between density, viscosity and surface tension are known, by measuring the former property the other two may be easily obtained.

Within this context, this work aims to investigate the temperature dependence of viscosity of waste lubricant oil, including low-temperature dynamics, from a glass transition and dynamic crossover standpoints. In addition, correlations between viscosity and density, and between density and surface tension at different temperatures are explored.

2. Materials and methods

2.1. Waste oil samples

A set of nine waste lubricant oil samples were collected in Portugal from different producers (garages, industry, and others) across the country. The samples were taken during the pumping of WLO to tank trucks. These trucks transport WLO to specific plants that are part of the integrated waste oil management system implemented in the country. About 0.5 L of sample were collected in each case in airtight plastic bottles and then stored at room temperature in the dark to maintain their integrity until analysis. Physicochemical characterization of the dataset was performed in a previous work presented elsewhere [9]. Nevertheless, some key properties for the present study were determined, namely the aromatic, naphthenic and paraffinic carbon content by FTIR based on the Indian Standard Method 13155:1991. This test method accounts for the carbon-hydrogen vibrations at different wavenumbers. The sum of aromatic, naphthenic and paraffinic percentages is 100%. The water content was determined by Karl Fischer titration following ASTM D6304. The results are listed in Table 1. Variation intervals of dynamic viscosity, η, density, ρ, and surface tension, σ, which were measured at different temperatures, are also listed in Table 1. The individual values at each temperature of these thermophysical properties are given in Table A1 in the Appendix and the experimental procedures are described in Section 2.2.

2.2. Experimental methods

2.2.1. Temperature dependence of viscosity

Dynamic viscosity was measured using a HAAKE RheoStress 1 rheometer within a temperature range from 298.15 K to 343.15 K. The stirring action of the rotating spindle, plus the small sample volume helps to keep the temperature gradient across the sample to a minimum. A Julabo F12-ED thermostatic bath with water as circulating fluid was used in the circuit of the sample chamber which was held constant to ±0.2 K. A cylinder rotor Z34 DIN 53019 series 1 was used and shear rates, $\dot{\gamma}$, varying from 0 to 1000 s^{-1} collecting 100 points in 300 s for each measurement. Prior to viscosity measurements, the rheometer was calibrated with a Brookfield viscosity standard at 298.15 K with given viscosity 49.9 mPa.s. This standard is a silicon oil with Newtonian behavior, certified by methods traceable to the U.S. National Institute of Standards and Technology (NIST). We have measured η = (49.9 ± 0.8) mPa.s. Therefore, the uncertainty of the measurement relative to viscosity standard is about 1.6%. Taking into account the uncertainty of temperature, the relative combined uncertainty is estimated to be $u_c(\eta)$ 2%.

2.2.2. Temperature dependence of density

Experimental densities were measured using a densimeter Anton Paar DMA 60 digital vibrating-tube, with a DMA 512P measuring cell in a temperature range from 298.15 to 343.15 K. The temperature in the vibrating-tube cell was measured with a platinum resistance probe with uncertainty ±0.01 K. The probe was previously calibrated over the range 273.15–373.15 K against a platinum resistance thermometer ERTCO-Eutechnics High Precision Digital Thermometer certified in the ITS90. A Julabo P-5 thermostatic bath with silicone oil as circulating fluid was used in the thermostat circuit of the measuring cell, which was held constant to ±0.01 K. An NI PCI-6220 data acquisition board (DAQ) from National Instruments (NI) was used for the real-time registration period, temperature, and pressure values. For this task, a Labview application was developed. Modules of temperature (NI SCC-FT01) and pressure (NI SCC-CI20) were installed in an NI SC-2345 carrier and connected to a DAQ board. Water and toluene were used as reference fluids to fit the calibration equation proposed by Lampreia and Nieto de Castro [20]. The combined standard uncertainty of the density measurements estimated taking into account the influence of uncertainties associated with calibration equation, temperature, period of oscillations (six-digit frequency counter), viscosity, and density data of calibrating fluids was about $u_c(\rho)$ = 0.45 kg·m^{-3}. The expanded uncertainty with confidence level 95% (coverage factor k = 2) was estimated to be U(ρ) = 0.90 kg·m^{-3}.

2.2.3. Temperature dependence of surface tension

Surface tension measurements of WLO within 303.15 K to 343.15 K were performed by PC controlled KSV Sigma 70 tension balance using the Wilhelmy plate. The platinum plate was thoroughly cleaned by immersion in a concentrated solution of nitric acid during several hours. Then it was rinsed with acetone, carefully flamed, washed again with acetone and dried. The temperature inside the vessel was maintained and controlled within ±0.1 K using UltraTherm P Selecta bath. Temperature was measured with a platinum resistance thermometer ERTCO-Eutechnics High Precision Digital Thermometer certified in the ITS90.

Each experimental point results from a set of 10 measurements with an uncertainty of ±0.1 mN m^{-1}.