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A Comparative Study of Traditional and Non-traditional Polyol Ester Lubricants for Carbon Dioxide (R-744) Applications

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ABSTRACT

Carbon dioxide (R-744, CO₂) has received increased recognition as a non-ozone depleting and ultra low global warming potential refrigerant for automotive and commercial heating and cooling applications. The lubrication requirements for transcritical CO₂-based equipment are different from equipment using hydrofluorocarbon (HFC) refrigerants due to both the higher system operating pressures of CO₂ and molecular structure differences of CO₂ vs. HFCs. In particular, the high solubility of CO₂ in the traditional commercial polyol esters (POEs) used with HFCs results in significant viscosity reduction in the compressor which can result in insufficient lubrication of bearings and improper sealing of clearances. The lubricant must possess good load carrying and lubricity properties in the presence of CO₂ over the total range of operating conditions of the compressor.

This paper presents a comparison of traditional POEs to non-traditional POEs in bench tests; both alone and in combination with CO₂. The miscibility of the lubricants in CO₂ was measured over the temperature range of -40 °C to 25 °C at a concentration of 10 wt% lubricant in refrigerant and provides an indication of refrigerant/lubricant compatibility at low temperature; a requirement for good oil return. The viscosity of lubricant/CO₂ mixtures was measured as a function of temperature and pressure over a range of typical conditions encountered in CO₂ refrigeration applications. The results show the enhanced viscosity retention of non-traditional POEs vs. traditional POEs in the presence of CO₂. The frictional properties of the pure lubricants were evaluated using the Mini Traction Machine (MTM) at 40, 80 and 120 °C. Coefficient of friction measurements as a function of entrainment speed illustrate how friction varies for each lubricant over the full range from boundary lubrication (metal-metal contact) to hydrodynamic lubrication (full fluid film). Measurements of the traction coefficient under elastohydrodynamic lubrication conditions provide an assessment of the relative energy efficiency of the lubricants. The combined results of the miscibility, viscosity and frictional property measurements highlight the challenge in designing a lubricant with the best overall balance of good compatibility and lubricity/load carrying performance in the presence of CO₂.

1. INTRODUCTION

Carbon dioxide (R-744, CO₂) has received increased recognition over the last 21 years as a non-ozone depleting and ultra low global warming potential (LGWP) refrigerant for heating and cooling applications (Kim, *et. al.*, 2004). However, the decrease in coefficient of performance at high ambient temperatures and the higher operating pressures required relative to the competing HFC-based refrigerant technologies has to some extent limited its broad commercial application (Brown, *et. al.*, 2002). But despite these deficiencies, CO₂ is used commercially today in Northern climates in both subcritical and transcritical cycle supermarket refrigeration (Matthiesen, *et. al.*, 2010). In addition, commercial transcritical CO₂ applications include hot water heaters, beverage vending machine and beverage dispensing systems (Jacob, *et. al.*, 2006, Rohrer, 2006).

The lubrication requirements for transcritical CO₂-based equipment are different from equipment using HFC refrigerants. Traditional polyol esters (POEs) used with HFCs such as R-134a and R-410A are typically much more

soluble in carbon dioxide which results in significant viscosity reduction of the working fluid; especially in the lubricant rich compressor environment. The combination of high operating pressures and high CO₂ solubility in the lubricant can lead to insufficient lubrication of bearings and improper sealing of clearances. For this reason, the commercial POE lubricants recommended for use with CO₂ are typically several ISO viscosity grades higher than would normally be used with an HFC and in most cases contain anti-wear and extreme pressure additives to compensate for the decreased lubrication performance of the lubricant/refrigerant mixture. But additives may be consumed over time and possibly form undesirable deposits on the internal components of the refrigeration system, most notably expansion devices such as thermal expansion valves or capillary tubes. A challenge exists to design a lubricant with CO₂ solubility characteristics that allow for sufficient lubricity and load carrying in the compressor environment while at the same time ensuring good oil return as well as high overall efficiency of the refrigeration cycle.

2. EXPERIMENTAL

2.1 Lubricant/CO₂ Miscibility Measurement

The miscibility of the lubricants with CO₂ as a function of temperature was determined using a 28 mL stainless steel test cell fitted with sight glasses and a valve with an overall pressure rating of 17 MPa. Measurements were conducted in the temperature range of -40 to 25 °C at 10 wt% lubricant in refrigerant based on charge with no adjustment for carbon dioxide vapor in the unfilled vapor volume. The test cell was first charged with 1.45 grams of lubricant and then connected to a vacuum manifold and evacuated to < 13 Pa. The test cell was then cooled to -20 °C and CO₂ is added to the desired total mass of 14.5 grams of lubricant and refrigerant. After warming to room temperature, the test cell was then visually monitored in a temperature controlled bath as the temperature was decreased from 25 °C to -40 °C at a rate of approximately 1 °C per minute.

2.2 Lubricant/CO₂ Mixture Liquid Viscosity Measurements

The apparatus for measuring the viscosity and composition of lubricant/CO₂ mixtures as a function of temperature and pressure consists of a temperature controlled circulation loop as shown in Figure 1 (Seeton and Hrnjak, 2006).

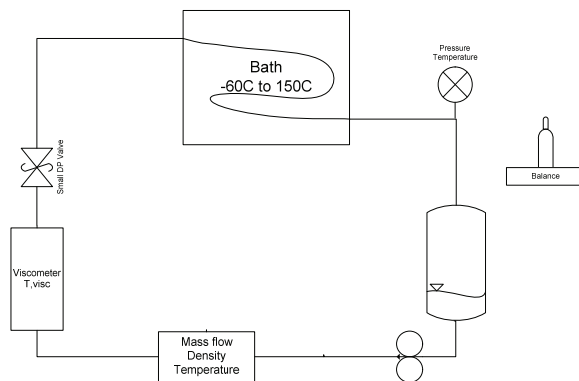


Figure 1. Thermophysical Properties Test System Schematic

The circulation loop contains a pump, vibrating tube densitometer, high pressure oscillating piston viscometer, bulk lubricant/refrigerant reservoir and pressure transducer. Thermocouples are located at multiple locations in the loop as well as directly in the mass flow meter and viscometer. The design of the loop allows for continuous circulation of the liquid mixture as well as providing agitation to achieve rapid vapor-liquid equilibrium. The lubricant was first charged to the system gravimetrically (± 0.02 grams) and the circulation loop cooled to -10 °C. The CO₂ was next charged gravimetrically (± 0.02 grams) from a small stainless steel sample cylinder in an amount necessary to achieve the desired bulk CO₂/lubricant composition. For safety reasons the loop was not filled to capacity and a small vapor space existed at the top of the bulk reservoir, so a vapor space correction was applied to the composition to account for CO₂ in the vapor phase. Once the system was charged, a gear pump was used to circulate the liquid through each of the measurement devices. The bulk mixture pressure was measured to ± 0.020 MPa. The liquid density was measured to ± 0.002 g/cc with the vibrating tube densitometer. The liquid kinematic viscosity was measured to $\pm 1.0\%$ of value using a high pressure oscillating piston viscometer. Incorporated into the viscometer

housing are two high pressure sight glasses to allow observation of the liquid miscibility where, if bulk mixture pressure is within 1% of saturated refrigerant pressure, the mixture can be checked for possible phase separation. Measurements were collected in the temperature range from -10 °C to 120 °C (± 0.5 °C) and compositions of CO₂ in lubricant from 0 to 30 wt%.

2.3 Lubricity Measurements

The fundamental lubricating properties of the lubricants were evaluated using the Mini Traction Machine (MTM) commercially available from PCS Instruments (Figure 2a). The MTM uses a rotating ball on rotating disk geometry (Figure 2b) to evaluate the lubricity properties of fluids under a variety of conditions. Two different types of experiments were performed. In the first experiment, the coefficient of friction (CofF) was measured as the mean entrainment speed was continuously ramped from 0 to 2 meters/second at a fixed slide-roll-ratio (SRR) of 50%. The entrainment speed is defined as the mean speed of the ball and disk, $(V_{\text{disk}} + V_{\text{ball}})/2$. The SRR is defined as $[2(V_{\text{disk}} - V_{\text{ball}})/(V_{\text{disk}} + V_{\text{ball}})] * 100$ (LaFountain, *et. al.*, 2001, Smeeth and Spikes, 1996). In the second experiment, the traction coefficient of the lubricants was evaluated at high mean entrainment speed (2 meter/s) while the SRR was ramped continuously from 0 to 70 %. Both experiments were conducted at 40, 80 and 120 °C and at a fixed load of 30 Newtons.

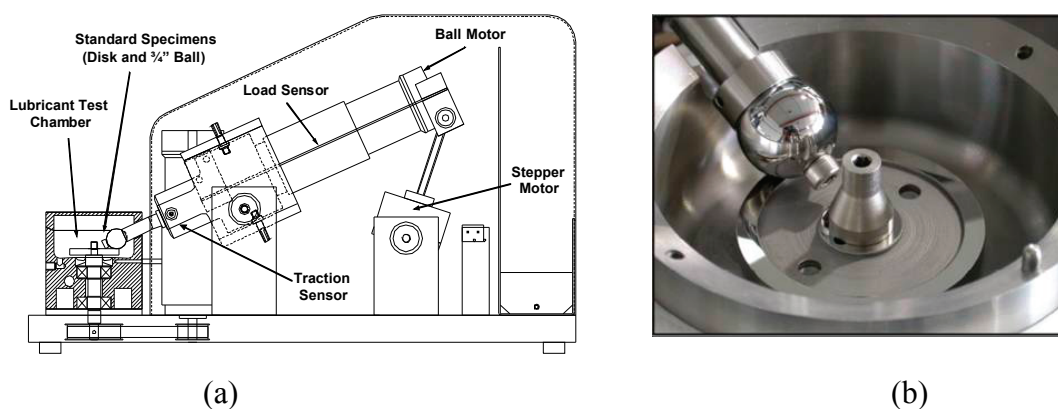


Figure 2. Schematic of (a) the Mini Traction Machine and (b) the Ball-on-Disk Contact Geometry

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties of the POE Lubricants

All of the POEs in this study were ISO viscosity grade of 68 lubricants. The physical properties of the lubricants are summarized in Table 1. Traditional POEs are given the designation TPOE while non-traditional lubricants are designated as NPOE. TPOEs as defined in this study are reaction products of pentaerythritol or dipentaerythritol, or combinations of both, with a mixture of branched and linear C5-C9 saturated fatty acids and are commercially used with both HFCs and CO₂ (Figure 3). The NPOEs are defined as those esters that contain high molecular weight components. The percent of high molecular weight components for each of the NPOEs is provided in Table 1. One distinguishing characteristic of NPOEs is very high viscosity index in comparison to most TPOEs.

3.2 Miscibility of Lubricants with CO₂

The results of miscibility evaluations of the various POEs at 10 wt% in CO₂ over the temperature range of -40 °C to 25 °C are reported in Figure 4. The POEs can be organized into three distinct categories over this temperature range; fully miscible, partially miscible and immiscible. TPOE 1 is fully miscible over the entire temperature range investigated which is typical for POEs designed for HFCs. While high miscibility/solubility of the oil with the refrigerant is desirable for good oil return and high COP, this property can also result in significant viscosity reduction by refrigerant which can negatively impact the ability of the lubricant to provide adequate fluid film lubrication of bearings and sealing of clearances. At the other end of the spectrum, NPOE 1 and NPOE 2 were completely immiscible demonstrating compatibility with CO₂ that is similar to alkylbenzenes, polyalkylene glycols

and poly-alpha-olefins (Li and Rajewski, 2000, Seeton, *et. al.*, 2000). It should be noted that under conditions of lubricant/refrigerant phase separation there can still be considerable solubility of CO₂ in the lubricant (Marcelino

Property	TPOE 1	TPOE 2	NPOE 1	NPOE 2	NPOE 3
Viscosity at 40 °C, cSt.	65	72	67	69	68
Viscosity at 100 °C, cSt.	8.3	9.8	9.9	10.9	10.6
Viscosity Index	99	120	130	150	145
Pour Point, °C	-37	-39	-54	-46	-60
Flash Point, °C	260	265	276	279	210
Density @ 15.5 °C, g/mL	1.000	0.981	0.963	0.986	1.02
Percent Polymer Content	0	0	42	38	68

Table 1. Physical Properties of the POE Lubricants

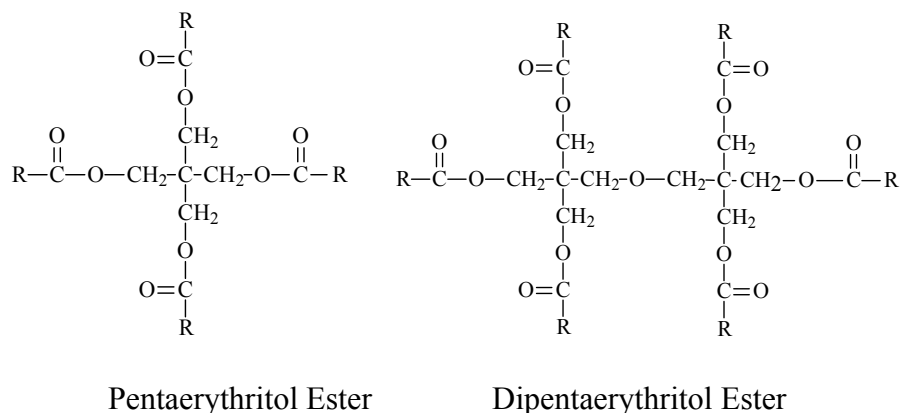


Figure 3. Some Chemical Structures of Traditional POEs

Neto and Barbosa., 2008). Immiscible lubricants, including immiscible POEs, are used today in transcritical CO₂ systems specially designed to ensure proper oil return to the compressor (Lee and Kang, 2008). The system design and operating conditions must also account for the phase inversion that occurs for immiscible POEs below -20 °C. Two of the lubricants in the study (TPOE 2 and NPOE 3) demonstrated partial miscibility behavior. These lubricants were immiscible at higher temperatures but became miscible with CO₂ at lower temperatures.

3.3 Viscosity of CO₂/Lubricant Mixtures as a Function of Temperature and Pressure

A comparison of the solubility of CO₂ in different types of synthetic lubricants has been studied extensively by several groups (Seeton, *et. al.*, 2000, Yokozeki, 2007) but relatively few studies have compared POEs of varying chemical composition (Fandino, *et. al.*, 2008, Bobbo, *et. al.*, 2008). Plots of the kinematic viscosity of CO₂/lubricant mixtures as a function of temperature at 3.5 MPa are shown in Figure 5 and illustrate the impact of CO₂ dilution on the viscosity of the lubricants. The pressure of 3.5 MPa was chosen for this study because it represents a typical low side pressure for applications with an evaporation temperature of 0 °C (e.g., air conditioning and bottle coolers). From a compressor designer's viewpoint, it is highly desirable to have a constant lubricant viscosity throughout the entire temperature operating range of the compressor. Taking 20-55 °C as an example of a typical operating range for a transcritical compressor, it can be seen that oils exhibiting the smallest change in viscosity (i.e., having the flattest viscosity curve in Figure 6) are NPOE 1 and NPOE 2. The POEs that exhibit a more pronounced variation in viscosity, especially at low temperatures, are TPOE 1 and TPOE 2. These observations correlate with the miscibility with CO₂ reported in Figure 5. The more miscible lubricants typically display greater viscosity reduction with decreasing temperature due to higher solubility of CO₂, while the viscosity of the less soluble lubricants is affected to a lesser extent. NPOE 3 represents an example of a lubricant with properties optimized between the two

extremes, having miscibility with CO₂ that is in some cases better than a TPOE while also displaying CO₂ solubility properties comparable to immiscible NPOEs, especially in the temperature range of 20-55 °C.

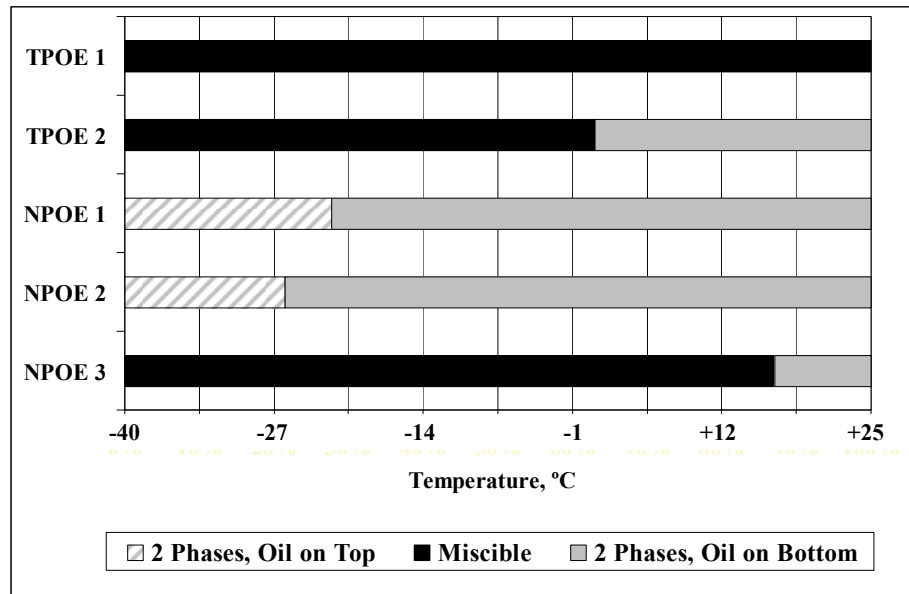


Figure 4. Miscibility of the POEs with CO₂ at 10 wt% in CO₂

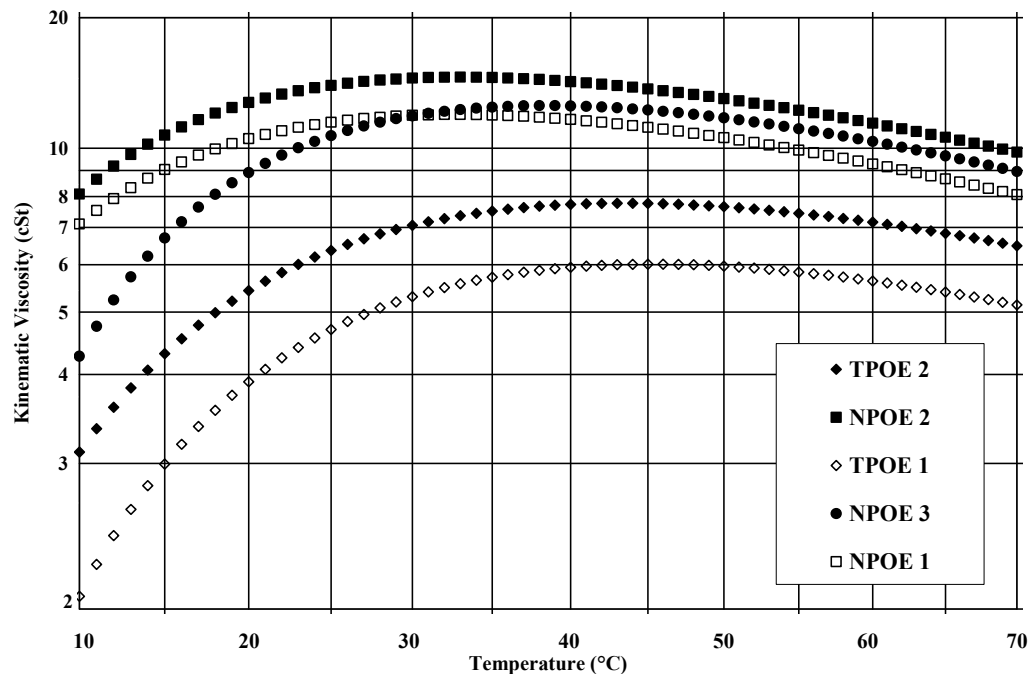


Figure 5. Kinematic Viscosity of Lubricant/CO₂ Mixtures as a Function of Temperature at 3.5 MPa

3.4 Lubricating Performance of the POEs

The lubricating properties of the POEs in the absence of CO₂ were evaluated using the Mini Traction Machine. A plot of the coefficient of friction (Coff) as a function of entrainment speed at 40 °C (Figure 6) shows how friction varies as the rate of oil entering the contact region increases. The shape of the curves can be related to the classic

Stribeck curve (LaFountain, *et al.*, 2001) and provides important information on the frictional properties of the lubricants under conditions of near boundary, mixed film and thick film (hydrodynamic) lubrication. At lower entrainment speeds there is direct metal-to-metal asperity contact (near boundary lubrication conditions), but as the

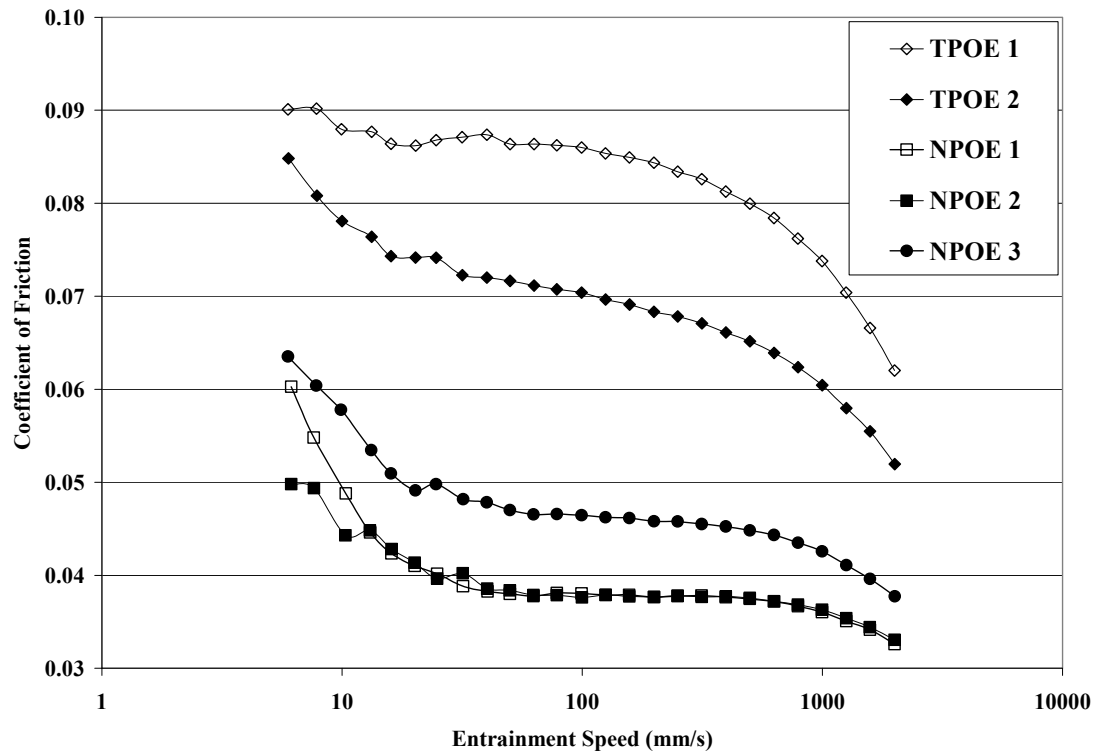


Figure 6. Coefficient of Friction as a Function of Entrainment Speed at 40 °C

entrainment speed increases there is a pressure buildup between the contacting surfaces due to increasing oil entrapment in the contact inlet. The increasing pressure in the contact inlet results in a progression from near boundary, to mixed film, to complete fluid film (hydrodynamic) lubrication. Under conditions of near boundary and mixed film lubrication, also termed the elastohydrodynamic lubrication (EHL) regime, the high pressure in the contact produces local elastic flattening of the surfaces and increases the viscosity of the lubricant. In such contacts, the CofF is determined by the molecular structure of the lubricant and contact temperature (Gunsel, *et al.*, 1999). The NPOEs demonstrated lower CofF over the entire range of lubricating regimes from near boundary to full fluid lubrication. Tests conducted at 80 °C and 120 °C (not shown) displayed a similar trend.

The traction coefficient of the pure lubricants was measured in a separate experiment with the Mini Traction Machine. Traction coefficient is measured at high entrainment speed (2 m/s) as a function of slide-roll-ratio (SRR) of the ball-on-disk contact. The plots shown in Figure 7 illustrate that the traction coefficient reaches a limiting value at high SRR (usually above an SRR = 50%). Low values are associated with high energy efficiency (Bovington, 1999). A higher limiting value of traction coefficient can be directly related to increased energy consumption under conditions of fluid film lubrication. As with the lubricity experiments described above, the NPOEs displayed significantly lower limiting traction coefficients when compared to TPOEs. Tests conducted at 80 °C and 120 °C displayed the same trend (Table 2).

4.0 CONCLUSIONS

The miscibility with CO₂, viscosity of lubricant/CO₂ mixtures and frictional properties have been determined for two structurally different classes of polyol esters. Traditional polyol esters (TPOEs) display excellent miscibility with CO₂ while non-traditional polyol esters (NPOEs) are partially to completely immiscible. The high solubility of

TPOEs with CO₂ translates to more severe viscosity reduction of the lubricant/CO₂ working fluid under conditions typical for the compressor environment in CO₂ applications. However, it is possible to design NPOEs that possess a balance of properties, displaying limited viscosity reduction in lubricant rich mixtures under conditions typically observed in the compressor environment but also having suitable miscibility with CO₂ in refrigerant rich working fluids for good oil return to the compressor.

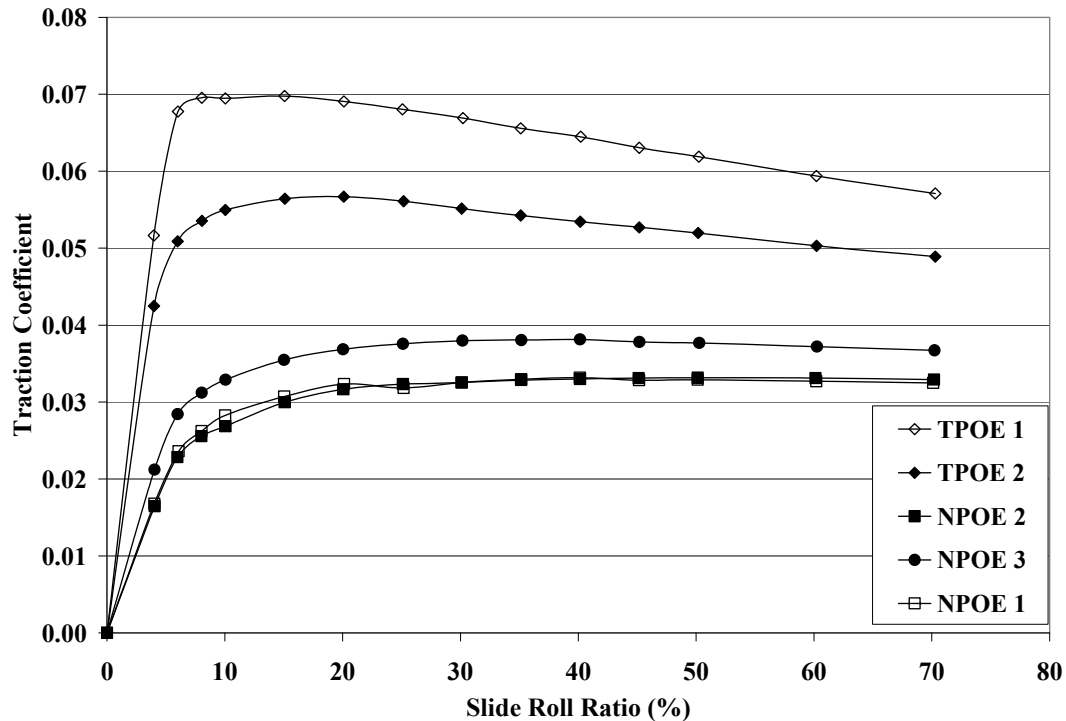


Figure 7. Traction Coefficient as a Function of Slide-Roll-Ratio at 40 °C

	40 °C	80 °C	120 °C
TPOE 1	0.0697	0.0559	0.0423
TPOE 2	0.0567	0.0447	0.0352
NPOE 1	0.0328	0.0250	0.0161
NPOE 2	0.0327	0.0252	0.0159
NPOE 3	0.0387	0.0287	0.0182

Table 2. Limiting Traction Coefficient at 40, 80 and 120 °C at a Slide-Roll-Ratio of 70% and a Mean Entrainment Speed of 2 m/s

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