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An Investigation of the Filterability of Synthetic Biodegradable Hydraulic Fluids

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Abstract

The purpose of this research is to evaluate the filterability of prototype synthetic ester based hydraulic fluids in order to determine if their filterability differs from conventional mineral oil based hydraulic fluids. The experimental procedure followed is specified by the International Organization for Standardization; ISO 13357-1:2002 Petroleum Products - Determination of the filterability of lubricating oils, is limited to a viscosity up to ISO VG 100 . This standard test method specifies test equipment, conditions, procedures, and precision for wet filterability of hydraulic fluids. The procedure includes a sample preparation stage where water is added to the hydraulic fluid and mixed into the blend under carefully controlled conditions. This is followed by a four-day aging process at 70˚C after which the fluid is filtered through a 0.8 microns filter membrane in a two-stage process. The wet filterability of lubricants in hydraulic operations is critical because fine filtration is necessary to prevent wear of machine components and water contamination is a common occurrence. Three synthetic ester base stocks were evaluated in this research. Multi-walled nanotubes, methacrylate polymers and sulfur-phosphorus antiwear additives were incorporated into these base stocks. A conventional mineral oil containing fluid was included for comparison purposes. The test results indicate that the wet filterability of these hydraulic fluids depends upon additive composition more than base stock selection. The data obtained from filterability tests will be used in the development of efficient, renewable and long-life hydraulic fluids.
Keywords: Filterability, Synthetic esters, Hydraulic fluids

1. Introduction

This research will investigate the feasibility of synthetic esters as hydraulic fluid base-stocks by studying the filterability of prototype fluid formulations. Synthetic esters have been used on a limited basis in fire-resistant hydraulic fluids formulations for more than 25 years. Environmental concerns and a desire to reduce dependence upon limited petroleum reserves are driving a world-wide conversion from refined mineral based stocks to synthetic ester base stocks. The use of synthetic esters has a singular attractiveness; the renewability of the ester base stock.

The life-cycle of triglyceride derived synthetic esters is depicted in Figure 1; vegetable oil obtained from a natural source, i.e. soybean, canola, rapeseed, palm, etc, is processed and used in hydraulic applications. After the ester has been used, it is burned and carbon dioxide and water are released in the combustion process. Through photosynthesis seed oil plants convert the combustion byproducts into biomass and release oxygen. Hence, synthetic esters derived from vegetable oils are a sustainable alternative to mineral-oil based hydraulic fluids.

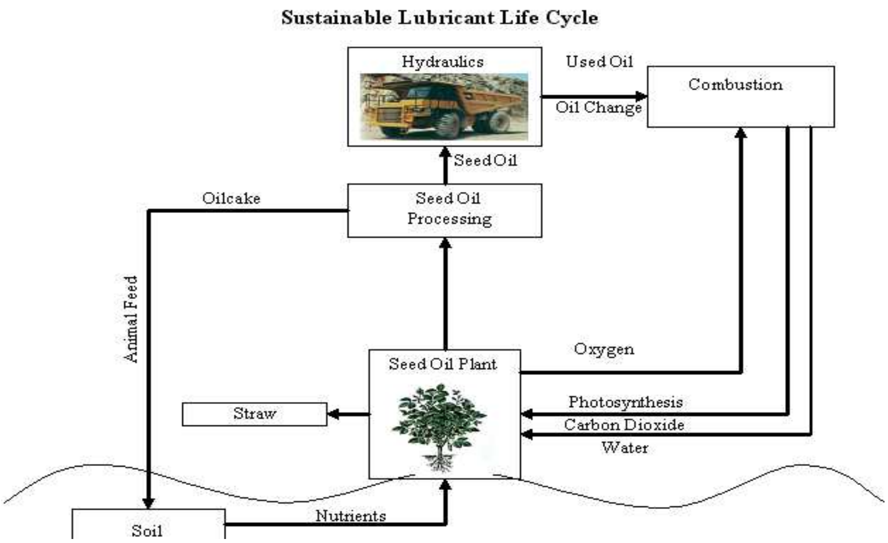
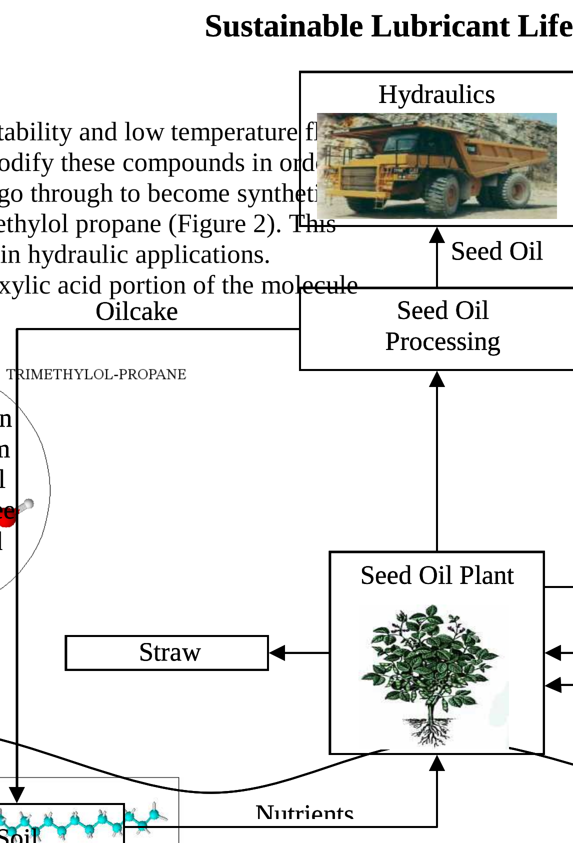
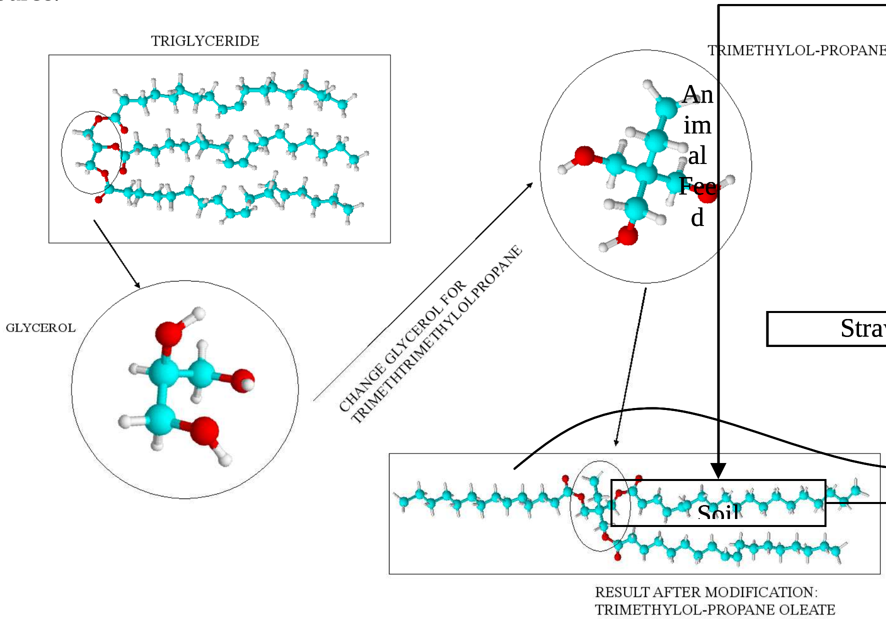


Figure1. Sustainable Lubricant Life Cycle



The chemical and physical characteristics of vegetable oils such as oxidation stability and low temperature fl are not adequate for most hydraulic applications. Therefore, it is necessary to modify these compounds in ord improve their performance. The process that vegetable oils (triglyceride esters) go through to become syntheti esters is fairly simple; glycerol is substituted for by another alcohol such as trimethylol propane (Figure 2). This hindered polyol substitution boosts the fluid's high temperature stability needed in hydraulic applications. Trimethylolpropane oleate (TMP) esters are termed bio-based because the carboxylic acid portion of the molecule has a natural source.



$$Triglyceride\ ester \xrightarrow[]{-glycerol \atop +trimethylolpropane} TMP\ ester$$

Figure 2. Chemical Modification

1.1. component selection

Hydraulic fluid formulations incorporate a mixture of additives and base stocks. The base stocks listed in Table 1 were selected on the basis of their viscosity and potential applicability for hydraulics. The viscosity of a typical hydraulic fluid is 32 to 68 centistokes at 40˚C. The C-18 polyol ester meets these requirements without the incorporation of additives but exceeds the viscosity of typical hydraulics with the incorporation of additives. The other three base stocks can be adjusted to this range through the incorporation of polymethacrylate polymers.

Table 1. Stocks

Base Stock	**Viscosity @40˚C, cSt**	**Description**
C-10 diol ester	14	Diisodecyl adipate
C-8 polyol ester	15	TMP Caprylate
C-30 hydrocarbon	15	Paraffinic mineral oil
C-18 polyol ester	48	TMP trioleate

To use a synthetic ester as a hydraulic fluid, additives have to be incorporated into the formulation to enhance a variety of properties including oxidation stability, prevent foaming, reduce wear and improve high-temperature viscosity properties. The additives evaluated in this study are listed in Table 2.

Table 2. Additives

Additive	**Functionality**	**Composition**
A	Viscosity index improver	Polymethacrylate
B	Pour point depressant	Polymethacrylate
C	Anti-wear / antioxidant	Sulfur-phosphorus
D	Friction modifier / viscous drag reduction	Carbon nanotubes

1.2. carbon nanotubes

Carbon nanotubes have exhibited the potential to reduce friction in dry sliding contacts with plain carbon steel. These nanometer-diameter helical tubes of graphitic carbon have been found to reduce sliding friction and significantly decrease wear in polyacrylate and epoxy resin composites[1,2]. As an additive at a concentration of 0.01%-0.1% m/m in commercial engine oil, milled carbon nanotubes were reported to reduce wear rate by 57%[3]. Carbon nanotube dispersions tend to be unstable due to their propensity to form mechanically entangled aggregates[4]. These aggregated bundles or ropes can be dispersed into fluid suspensions by a variety of techniques, including the selective use of dispersant additives[5]. US Patent App 2005124504 identifies succinates and other dispersant polymers as useful for suspending nano-size particles of graphite in crankcase oils. This patent claim relates to engine oil additives containing nanomaterial dispersions that exhibit enhanced thermal conductivity[6]. Valvoline™, the patent holder described above, provided carbon nanotube dispersions for use in this research. Figure 3 depicts carbon nanotubes prior to dispersion in oil.

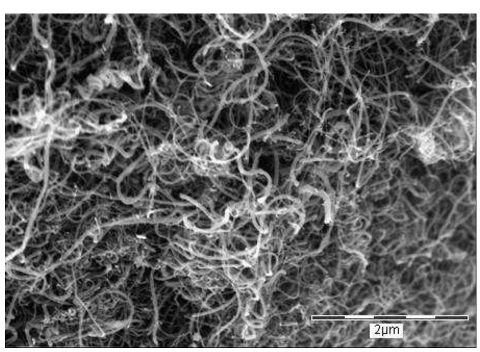


Figure 3. Carbon nanotubes [7]

1.3. polymethacrylate viscosity index improver

Viscosity index (VI) is a dimensionless number that describes the viscosity-temperature relationship of hydraulic fluid and lubricating oils[8]. Fluids with a lower temperature-dependence have a higher VI. Polymethacrylate viscosity index improvers are used in hydraulic applications because they have good shear stability. These additives raise the viscosity of the base fluid to which they are added and reduce the viscosity fluctuation with temperature. This widens the fluid temperature operating window[9].

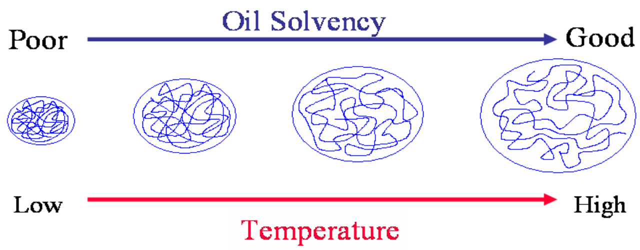


Figure 4. Viscosity Index Improver molecule behavior

1.4. filterability

The filterability characteristic of a fluid can be defined as its ability to pass through a filter without giving rise to undue pressure drop. Excessive pressure drop is undesirable because it can lead to abbreviated filter life. Normally, flow degradation occurs over a period of time as filters accumulate dirt, sludge and wear debris. When filters become blocked by additives that precipitate out of oil as a result of a chemical reaction with water or other liquid contaminants, filter usage and machine wear can increase dramatically.

Several test methods have been developed for evaluating the filterability of lube oils. Filterability tests generally consist of filtering a specified quantity of fluid through a standard medium. The results are typically reported in terms of a ratio between flow rates with and without water in an attempt to compensate for the effect of viscosity on filterability[10].

2. Methodology

2.1. sample preparation

Base stocks and additives were weighed into a 500 ml beaker on an analytical balance to the nearest 0.02 gram. The combined ingredients were then blended on a magnetic stirring hotplate at 70˚C for 1 hour. Since the polymer additives are extremely viscous, a glass stirring rod was used to scrape the sides of the beaker. Below is Table 3 showing the formulations that were prepared.

Table 3. Formulations

Formulation	TMP	Diester	Mineral Oil	Water	Add B	Add C	Add D	CNT
A	100	x	x	x	x	x	x	x
B	X	100	x	x	x	x	x	x
C	X	x	100	x	x	x	x	x
D	99.34	x	x	0.66	x	x	x	x
E	X	99.34	x	0.66	x	x	x	x
F	X	x	99.34	0.66	x	x	x	x
G	X	x	82.02	0.66	17	0.3	x	x
H	X	82.04	x	0.66	17	0.3	x	x
I	X	81.24	x	0.66	17	0.3	0.8	x
J	X	x	81.24	0.66	17	0.3	0.8	x

K	99.99	x	x	0.66	x	X	x	0.01
L	X	99.99	x	0.66	x	X	x	0.01

2.2. experimental procedure

2.2.1 fluid aging process

Determine the viscosity of the test fluid. Transfer 330mL of the test fluid by means of a graduated cylinder into a 500 ml sample flask. Using a 1ml pipette, add 0.66 ml of distilled water to the 500 ml flask. Place the flask in an oven for two hours at 70˚C. Remove the flask from the oven and agitate the oil-water blend with a laboratory grade mixer at 1800 rpm. Place the mixture in an oven for 70 hours at 70˚C. After the aging process is completed remove the fluid from the oven and allowed it to equilibrate at room temperature for 24 hours.

2.2.2 experimental setup

Assemble the apparatus as shown in figure 3 by connecting components 2 through 4 to a compressed air system. Install a 0.8 micron filter membrane into the pressure vessel 5. Adjust the pressure regulator to an appropriate level based upon the fluid viscosity per ISO 13357.

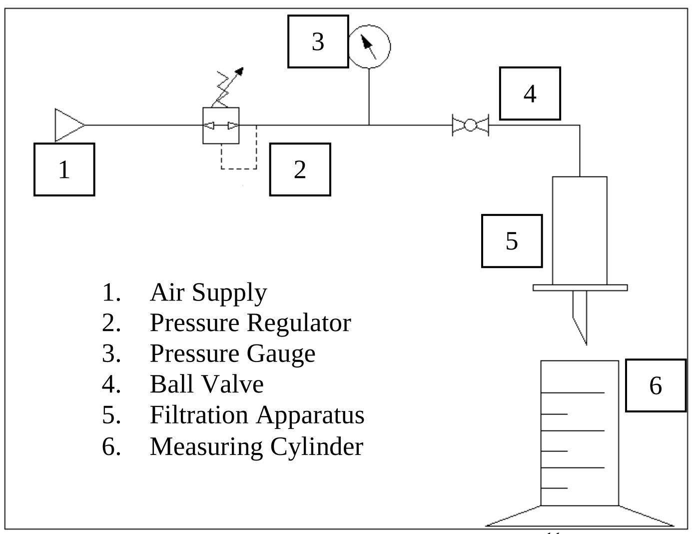


Figure 5. Diagram of experiment setup[11]

2.2.3 run experiment

After the assembly has been prepared, proceed to pour the test fluid into the pressure vessel. Close the pressure vessel and attach the air supply to the inlet. Open the ball valve to allow pressure into the vessel. When the fluid starts passing through the membrane into the measuring cylinder, start the timer and measure the time it takes the fluid to reach 10mL, 50mL, 200mL, and 300mL. After measuring the 50mL mark, calculate T_V, equation (1), the result will be a time measurement, observe the volume of the fluid at the time calculated and label it Vv. This measurement is necessary to calculate Stage I filterability and Stage II filterability.

$$T_V = 6(T_{50} - T_{10}) + T_{10} \qquad (1)$$

3. Data

The capability of any fluid to be filtered through a filter is described as filterability, and this physical property is extremely important in hydraulic applications. In this section, the experimental data will be discussed, it is divided into two categories: Stage 1 filterability and Stage 2 filterability.

3.1. stage I filterability

Stage I filterability determination is based on a comparison of the mean flow rate of a fluid through a test membrane with its initial flow rate. It is defined by equation (2).

$$F_I = \frac{(V_V - 10)}{240} \times 100 \qquad (2)$$

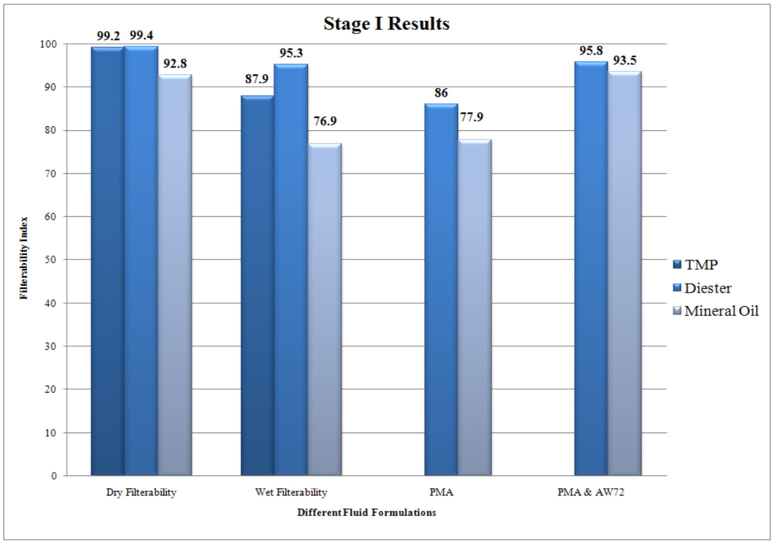


Figure 6. Results of stage I filterability

3.2. stage II filterability

Stage II determination is based on the ratio between initial flow rate of fluid through the test membrane and at the end of the test. It is considered that this part of the procedure is a more severe test, and it is more sensitive to the presence of gels and fine silts in the oil. It is defined by equation (3).

$$F_{II} = \frac{2.5(T_{50} - T_{10})}{(T_{300} - T_{200})} \times 100 \qquad (3)$$

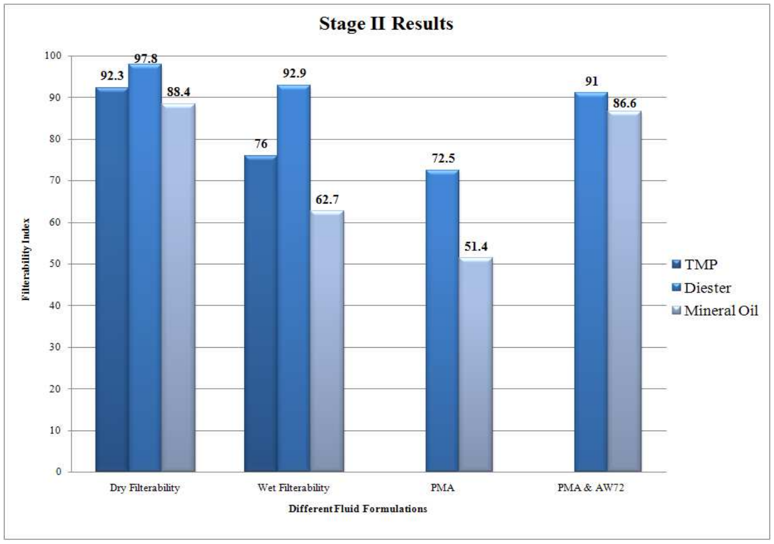


Figure 7. Results of stage II filterability

3.3. difference between stages

Oils with good Stage I filterability and poor Stage II would be unlikely to give filtration problems unless extremely fine filtration is used. Oils with good Stage II filterability are unlikely to give filtration problems even for the most extreme conditions.

4. Conclusion

4.1 additive and base oil filterability

The results on the filterability testing under the conditions specified in ISO 13357 - 1 & 2 indicate that water does not affect the filterability index of base stocks, but it does affect filterability index when additives are present. Evidently, under these test conditions synthetic esters do not hydrolyze or, if hydrolysis occurs, it does not impact filterability. In all cases, the addition of polymethacrylate decreased the filterability of the fluid. Surprisingly, addition of the antiwear additive seems to counteract this effect. Based upon the appearance of the fluid is seems likely that the antiwear additive reduces the size of water droplets suspended in the fluid, thus forming an emulsion. The results show that under the conditions specified in ISO 13357 - 1 & 2 synthetic esters have slightly better filterability properties than mineral oils.

4.2 carbon nanotube filterability

100 ppm carbon nanotubes were added to diisodecyl adipate ester and the wet filterability was evaluated via ISO 13357 – 1. Complete filter plugging occurred. The process was repeated using the dry filterability method. In both cases complete filter plugging occurred. It was observed that carbon nanotubes do not disperse in oils, they are in a suspension state allowing their removal by fine filtration.

5. Future Work

An example of future work made possible by this research is fluid performance testing, to be performed in the Fluid Power Institute™ at MSOE. Also, the effects of synthetic ester based hydraulic fluids on efficiency are to be studied in order to determine the feasibility of synthetic esters as base stocks. Different combinations of additives have to be tested with the base stocks to optimize the formulations proposed by this research. And lastly, to study effective ways to incorporate carbon nanotubes into hydraulic applications since they promise great improvements in efficiency of hydraulic machinery.

6. Acknowledgements

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