SUITABILITY OF BASESTOCKS FROM MEDIUM CHAIN FATTY ACIDS FOR HYDRAULIC FLUIDS

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Abstract: Basestock properties are crucial for hydraulic fluids, because the additive amounts are low. The formulated fluids must endure long service life under high humidity levels, elevated temperatures, exposure to various metals and intensive friction in vane pumps. Ester-based fluids have enjoyed success in higher technology hydraulic systems due to reduced operating temperature. Their basestocks are synthesized from petrochemically isomerized C9–C13 monocarboxylic acids, which are esterified to polyols, such as trimethylol propane. In this study, Medium Chain Fatty Acids (MCFA) of C10–C14 have been esterified with TMP and tested under thin film simulation study. Their stability, fluidity, volatility and other properties were comparable to those of mineral and synthetic basestocks. Environmental benefits of MCFA were clearly evident, because they can be produced not only from palm oil, but also from industrial crops crambe and camelina.

Keywords: Vegetable oil, Hydraulic fluid, Basestock.

1. INTRODUCTION

With rapidly accelerating spread of electrical vehicles, long-term future of engine oil market becomes uncertain. So far engine oils represent more than 50% of all automotive and industrial lubricants by volume with Hydraulic Fluids (HF) being the distant second at 20–25% share of the market. However, the anticipated decline in engine oil market is likely to affect the whole lubricant technology, including hydraulic fluids. Large industry players do not anticipate the demand for engine oil basestocks, such as poly alpha olefins (PAO), to grow significantly and it is unlikely that they would commit to the development of new lubricants for passenger cars. Possible reduction in basestock selection, additive availability and other research resources would negatively affect the technological progress in HF, gear oils and most other lubricants as well.

One segment of oils, which is less affected by the above transformations, is biodegradable basestocks [1]. Internal combustion or diesel engine oils have not yet been considered as viable target applications for vegetable oil or other environmentally safe lubricants. After extended period in the crankcase engine oil acquires high level of contaminants from partial combustion and wear debris. Their abundance reduces biodegradability dramatically, therefore, nearly all attempts to utilize biodegradable engine oils on broad commercial scale have failed so far. In the meanwhile, HF applications have enjoyed steady increase of biodegradable basestock volumes. Potential environmental benefits were not the only advantages as compared to mineral oil or PAO. For example, vegetable oils, such as Low Erucic Acid Rapeseed oil (LEAR) showed much higher flash point due to high molecular weight, better Viscosity Index (VI) due to linearity of molecular structures, better inherent Anti Wear (AW) properties due to ester linkages and many other improvements. Combination of the latter two would often lead to more than 10 °C reduction in hydraulic system temperature of operation, which would translate into extended service life of pumps, hoses, joints and other components.

Therefore, many HF users chose to fill their systems with biodegradable products, despite problems in oxidative stability, low temperature fluidity and other issues. Nevertheless, technical disadvantages have to be resolved sooner or later, especially when new types of fluids, produced from renewable

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resources, are finding application in many technical areas. Mineral oil HF are replaced with LEAR in lower end applications, while more demanding HF use oleates and saturated esters of polyols or similar derivatives.

Saturated esters have much better oxidative stability than those with double bonds, such as those in LEAR or other vegetable oils. Therefore, high performance HF often are based on esters from lauric or other Medium Chain Fatty Acids (MCFA), which are fully saturated. Most frequently palm and coconut oils are used for MCFA manufacture, however, alternative crops have recently been considered as well. Camelina and crambe are non-food crops, which can be cultivated in most parts of Europe in order to produce oilseeds with 40% or higher oil contents [2]. Camelina oil has substantial amount of gondoic acid, which is a C20 linear fatty acid with cis- double bond between 11 and 12 C atoms. Crambe oil is rich in erucic acid, whose double bond is located between 13 and 14 C atoms. When applying metathesis method using ethylene (i.e. ethenolysis [3]), these acids can be converted into MCFA and alpha-decene, see Fig. 1 for MCFA from Crambe oil.
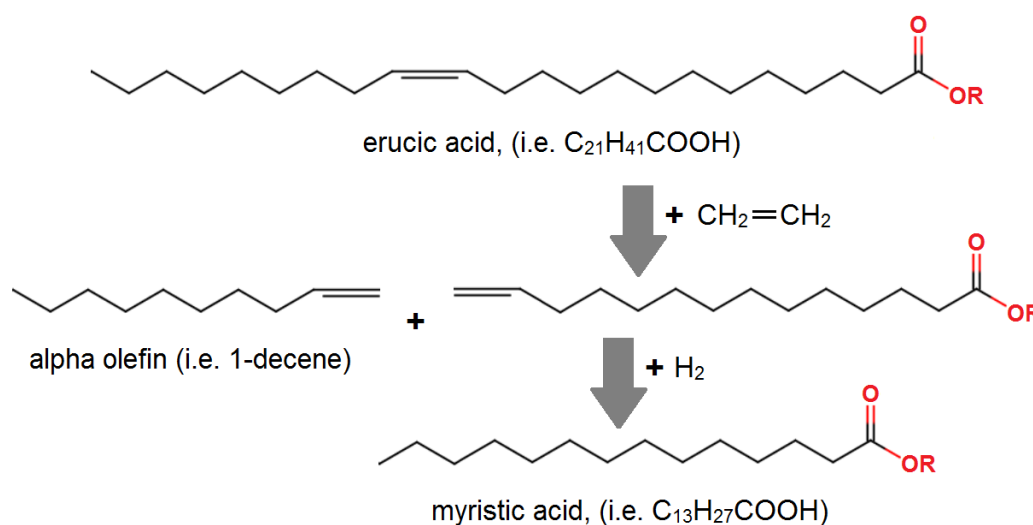

Figure 1. Scheme of Crambe → MCFA process utilizing ethenolysis and hydrogenation reactions to yield myristic acid from erucic acid.

Erucic acid is the most abundant fatty acid in Crambe oil. Ethenolysis leads to regrouping of the p-electrons via molecular cleavage of the double bond, resulting in α-olefin and ω-unsaturated linear carboxylic acid. Further processing involves removal of α-olefin, which is much more volatile than the acid, followed by hydrogenation of the latter into C14 saturated MCFA, i.e. myristic acid. The same process can be utilized for Camelina oil, which contains significant amounts of gondoic acid in addition to oleic acid, Fig. 2.
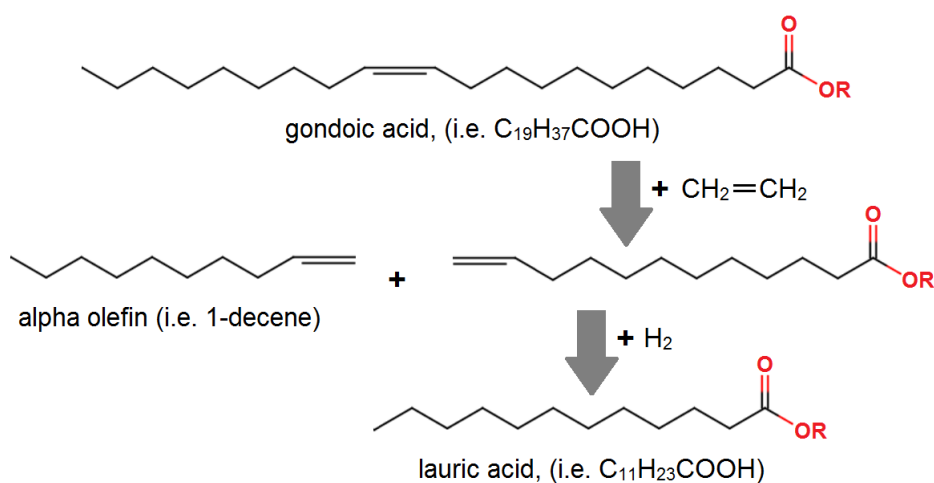

Figure 2. Scheme of Camelina → MCFA process, utilizing ethenolysis and hydrogenation reactions to yield lauric acid from gondoic acid.

Resulting lauric acid and other MCFA, as well as mono-unsaturated acids (erucic, gondoic, oleic, etc.) can be utilized in synthesizing polyol esters for lubricant applications. In HF application, basestock usually comprises around 90–100% wt. of lubricant with remaining 0–10% wt. taken up by additives to impart necessary rheology, low friction, anti-wear properties, low temperature fluidity, corrosion resistance, elastomer compatibility, oxidative stability, water rejection, foam inhibition, air release, microbial resistance, odor, color and many other characteristics. Although many HF parameters are highly sensitive to the additive use, some key properties, such as low volatility, long term cold storage and biodegradability cannot be significantly improved by using additives. Many other properties are mostly defined by the basestock with only partial capability of the additives to change them. Viscometric properties, low temperature fluidity, volatility, oxidative and hydrolytic stabilities and solvency of the lubricants are primarily determined by the basestock.

Pour point and kinematic viscosities at 40 °C and 100 °C are usually considered the most important for basestocks. For example, Society of Automotive Engineers (SAE) established certifications for engine oils, whose denominations are composed of a number to reflect low temperature fluidity (e.g. SAE 10W-xx must remain pumpable at –30 °C) and another number to reflect viscosity (e.g. SAE xxW–30 must have viscosity between 9.3 and 12.5 cSt at 100 °C. Specifications for HF also have strict requirements for pour points and viscosity at 100 °C, although their denominations are based on viscosity at 40 °C. It must be pointed out, however, that for the basestock alone strict compliance with HF specifications might not be necessary. Final formulations contain polymers as additives, which affect viscosity and solidification patterns quite significantly. Therefore, simplified low-volume tests can be used to measure kinematic viscosity and pour points, as the most important parameters for the basestock selection.

2. EXPERIMENTAL

Polyol esters were synthesized using conventional methods, which were established previously [4]. Commercially acquired fatty acids were esterified with neopentyl glycol (NP), trimethylol propane (TMP) and pentaerythritol (PE), all acquired from Sigma Aldrich, and purified using distillation under reduced pressure. Oleic acid of 70% purity was acquired from Chempur with reported Iodine Value 85–95. Lauric acid of 98% purity was purchased from Sigma Aldrich. Derivatized alcohols were also utilized for esterification with MCFA or oleic acid, leading to esters with the codes 5P8, L26 and Z26. The latter three represented light amber-colored oils with clear homogeneous appearance.

Paraffinic mineral oil 350N was supplied by Shell Oil Company as HVI 350 with reported API gravity of 29.2°API, viscosities of 67 cSt at 40 °C and 8.32 cSt at 100 °C, sulfur below 0.02%, flash pt of 475°F, pour point 10°F and acid number of 0.01 mgKOH/g. Poly alpha olefin PAO8 was received from Ineos Oligomers as Durasyn 168 with reported viscosity ranges of 45–49 cSt at 40 °C and 7.7–8.0 at 100 °C, flash point above 245 °C, NOACK volatility below 4% and pour point below –50 °C. Sample of LEAR was purchased from Inex Oy and complied with food grade requirements.

2.1. Fluidity measurements

In this report fluidity is considered as viscosity and pre-solidification rheology of the sample. Sample viscosity was determined by using ASTM D445 "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids". Instead of ASTM D97 "Standard Test Method for Pour Point of Petroleum Products", low temperature fluidity of the samples was evaluated by measuring pour points using an in-house low volume method, Fig. 3.

Low-volume method needs only 5 to 20 mL sample, in contrast to the range of 36 to 47 mL required in D97. Ultrafreezer Sanyo MDF193 was used, with a styrofoam insulation sheet on the bottom, which was thicker than 10 mm. The samples were placed into the jars of 25 mm ID and 90 mm high, capped with the lid with a thermometer. The typical quantity of a sample was 10 mL, which was sufficient to fully submerse the glass reservoir of thermometer indicator fluid. Thermocouple use was permitted as well. A control jar with a coolant, acetone or other low-freezing liquid was also added to monitor the temperature changes. The jars were placed more than 50 mm away from the walls of the ultrafreezer chamber. Initially the sample was preheated for at least 2 h at 50 °C or higher temperature. The

ultrafreezer temperature was set at –18 °C until the sample cooled down to –6 °C. Periodically the sample jars were taken out and inverted up to 90° to observe the meniscus movement confirming fluidity. Then the ultrafreezer temperature was reduced to –33 °C in less than 30 min. Once the sample cooled down to –24 °C, the ultrafreezer temperature was reduced to –51 °C in less than 30 min. After specimen cooled down to –42 °C, the ultrafreezer was set to –69 °C. Formally, ASTM D97 does not give instructions on measuring pour points for the samples, which remain liquid at that temperature. However, the measurement range of the low-volume pour point method was extended by setting the ultrafreezer to –85 °C once the sample cooled down to –60 °C. No attempt was made to determine the actual solidification below –85 °C. Pour point was recorded as the last reading of the sample thermometer, under which the test jar was tilted 90°, but the sample meniscus would still move away from its original circumference within 5 s. In those cases when the central part of the sample surface itself was moving without shifting the meniscus away from the glass/liquid circumference, the sample was considered frozen.
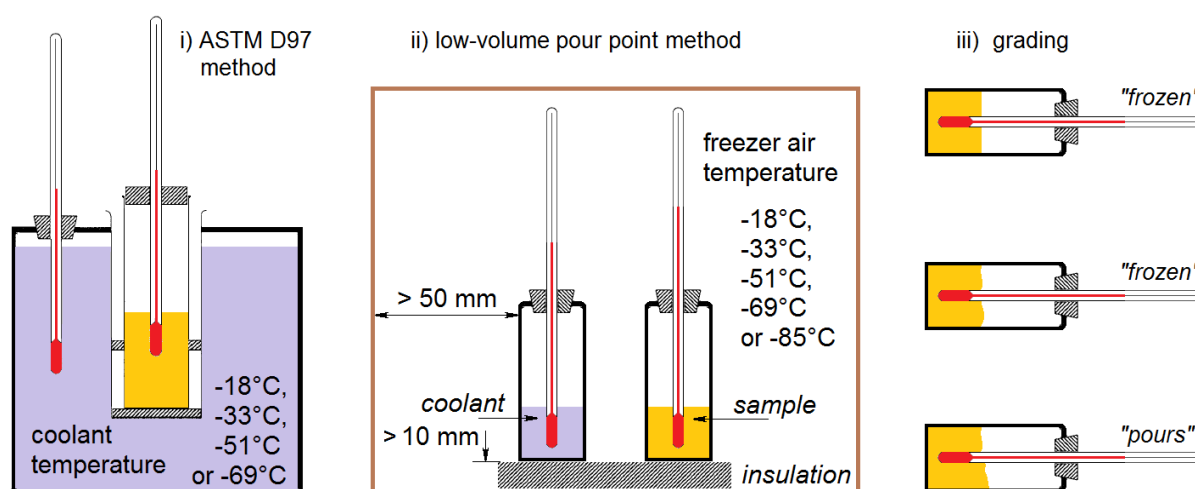

Figure 3. Schematic setup of i) the standardized pour point test equipment, which requires ~50 mL sample, and ii) equipment for low-volumes (e.g. 5 mL) of HF basestocks. The sample was considered pouring, if the meniscus moved away from the original circumference on the glass wall within 5 s, as shown in iii) grading illustration.

The sample jar was taken out for fluidity inspection after every 2–3 °C of temperature reduction. In some cases supercooling with subsequent heat release was observed due to sample crystallization. As a result, initially the sample would reach lower temperature with evident fluidity, but then it would solidify at higher temperature. The higher temperature was considered as an upper pour point per ASTM D97 guidance for black oils, while the lower temperature with suspected supercooling was recorded as the lower pour point.

2.2. Theoretical estimations of material properties

Molecular weight of the samples was calculated for the predominant molecule based on weight fraction. For example, LEAR mostly contains triglycerides of fatty acids, among which oleic acid is the most prevalent. Therefore, mol.wt. of triolein (885 g/mol) was used. Biobased contents was calculated by establishing the number of C atoms from petrochemical resources and biobased (renewable only) resources. The percentage of biobased C number in the total C number was set as the biobased contents. In those cases when some components can be commercially acquired from both petrochemical or biobased sources, the lowest and highest possible values were indicated.

Iodine value was calculated based on the assumption that every aliphatic double bond consumes one I_2 molecule. The final number represented grams of I_2 consumed in 100 g of sample. The length of branching was determined by linearizing the most distant organic backbone in the molecule and counting C atoms in the shortest side branches. For example, in triolein the linear backbone contains 39 C atoms and the shortest side branch contains 18C atoms. Only the most predominant molecule was considered in determining branching, mol. wt. and ester linkages.

3. RESULTS AND DISCUSSION

Specifications for engine oils and HF are based on viscosities, measured at 100 °C and 40 °C respectively. This introduces a certain degree of confusion, when trying to optimize the target molecular structure for the best applicability as lubricant basestock. High VI is a great advantage for engine oils and HF. However, if the mid-value of ISO VG46 grade is targeted, VI over 200 would result in SAE 20 specification, while VI below 100 would produce SAE 30, see Table 1.

Table 1. Comparison of viscosities in the middle of HF and engine oil specification intervals by calculating their values to 40 °C and 100 °C for Viscosity Index (VI) of 100 and 200.

Specification	VG46	VG32	VG22	SAE 20	SAE 16	SAE 12	SAE 8
Spec. at 40 °C, cSt	41.4–50.6	28.8–35.2	19.8–24.2	n.a.	n.a.	n.a.	n.a.
Mid-value 40 °C, VI 100	46.0 cSt	32.0 cSt	22.0 cSt	53.65 cSt	50.4 cSt	38.85 cSt	29.1 cSt
Mid-value 40 °C, VI 200	46.0 cSt	32.0 cSt	22.0 cSt	33.5 cSt	31.8 cSt	25.45 cSt	19.95 cSt
Spec. at 100 °C, cSt	n.a.	n.a.	n.a.	5.6–9.3	6.1–8.2	5–7.1	4–6.1
Mid-value 100 °C, VI 100	6.79 cSt	5.38 cSt	4.32 cSt	7.45 cSt	7.15 cSt	6.05 cSt	5.05 cSt
Mid-value 100 °C, VI 200	9.63 cSt	7.24 cSt	5.45 cSt	7.45 cSt	7.15 cSt	6.05 cSt	5.05 cSt

Viscosity at 100 °C is also very important for HF, especially in heavy duty equipment, whose HF temperature often stays around 90°C for prolonged durations during continuous operations. Frequently even HF cooling systems are installed in such equipment. Therefore, VG32 products with high VI are sometimes used in place of VG46 with lower VI. Basestocks of VG32 are quite appealing, because VG32 of VI=200 nearly matches the specification of SAE 20 and its subdivision of SAE 16. This means that the basestock of VG32 might be applicable both for HF and engine oils, whose viscosities are lower for fuel economy purposes. Therefore, when considering Crambe and Camelina oils as feedstock for lubricant manufacture, VG32 should be viewed as a primary target, if high VI around 200 is expected. If VI values are closer to 100, VG46 is more justified for HF and engine oil applications.

Conventional basestocks PAO8 and 350N are often used in VG46. Vegetable oils are often employed as VG32 basestocks in HF. Fluidity of derivatized polyol esters, synthesized from biobased resources, was compared to that of PAO8, 350N and LEAR in order to identify the main effects of molecular structure.

Table 2. Effect of molecular properties on fluidity of tested commercial basestocks and derivatized polyol esters.

Oil	PAO8	350N	LEAR	5P8	L26	Z26
Pour point	<–50 °C	–15 °C	–24 °C	–33 °C	–21 °C	–30 °C
Viscosity at 40 °C	50.48 cSt	61.4 cSt	46.76 cSt	30.68 cSt	18.43 cSt	24.88 cSt
Viscosity at 100 °C	8.2 cSt	8.46 cSt	10.68 cSt	6.71 cSt	4.29 cSt	5.94 cSt
Viscosity Index	135	109	222	185	145	199
Molecular weight *	629 g/mol	500 g/mol	885 g/mol	733 g/mol	569 g/mol	733 g/mol
Iodine No.*	<5	<5	130	80	<5	80
MCFA or oleate type	n.a.	n.a.	tri-oleate	di-oleate	di-laurate	di-oleate
Branching	C8	random	C18	C3 and C5	C2 and C4	C2 and C4
Biobased contents *	0	0	100	87%	100%	83 to 100%

* theoretical estimate.

As seen in Table 2, oleate esters have much higher VI than laurate. Therefore, if MCFA esters are used in HF, higher viscosity at 40 °C might be beneficial. Laurates also demonstrate higher pour points than those of oleates or even LEAR. This suggests that linear $C_{11}H_{23}$ chains can engage into molecular packing quite easily. In contrast, cis- double bonds, present in oleates, inhibit molecular packing despite much longer linear chains. Iodine Value relates directly to the number of double bonds, but their trans- isomers do not restrict molecular packing as effectively as those in oleates. Possible inclusion of erucic or gondoic acids from Crambe and Camelina into 5P8 or Z26 might still result in pour points approaching those of commercial HF, but their viscosities would be closer to VG32.

Derivatized polyol esters 5P8 and Z26 can be finetuned to match VG32 and formulated to produce HF for commercial applications. This viscosity range can also be suitable for SAE 20 engine oils as well. Increased utilization of non-food vegetable oils for HF and other lubricant applications would increase the agricultural potential of Crambe and Camelina.

4. CONCLUSIONS

1. Although highest share of HF products belong to VG46, when VI approaches 200 it is more reasonable to consider VG32 in heavy duty hydraulic applications, especially at elevated temperatures.

2. Laurate and longer MCFA esters are likely to have low temperature fluidity problems.

3. Inclusion of erucic and gondoic acids into synthesis of derivatized polyol esters can produce exact necessary viscosity.

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