THE FUTURE OF HYDRAULIC FLUIDS: BIODEGRADABLE?

Hydraulic fluids are used in various types of applications and environments. They represent a powerful mechanical solution for actuation over electrical systems and have a market share between 8-10% of the total lubricant tonnages. The market for base oils themselves had a value of approximately 25 billion USD in 2019, with 50% of this value being Group I base oils by volume. The automotive sector accounted for 44% of the base oil market in the same year, with other notable applications being process oils, hydraulic oils, and industrial oils [1]. Base oils are categorized into five groups by the American Petroleum Institute based on their different properties and components. Group I oils are the major group currently used, but it is expected that Group II and III oils will become more dominant given the changing automotive industry demands [2]. However, hydraulic equipments require fluids that are most efficient in a certain temperature range, viscosity range, etc. Therefore, it is important when deciding on a type of fluid to use to take into account the fluid's chemical characteristics and properties so machinery can run properly and efficiently.

Figure 1 shows the temperature ranges that the mentioned product line fluids would work best in and their respective viscosity ranges. Using these fluids is most suitable within a temperature range of 30˚C-60˚C, and fluid life reduction is typically seen within a temperature range of 80˚C-90˚C.

Hydraulic fluids are used in various types of machinery worldwide, and these fluids must meet certain requirements so the machinery can work well. Oil pressure and sump temperature are continuously increasing to improve efficiency and cost-performance ratios. Another option to increase operating efficiency is the reduction in viscosity and the use of base stock with lower compressibility (viscosity-pressure coefficient). To promote better performance under these conditions, highly functionalized viscosity index (VI) improvers or base oils with high intrinsic VIs are necessary to note. Contamination with water or metal particles can result in the base oils creating byproducts like sludge, reducing the lubrication properties of the oils. Even though hydraulic oils have no contact with combustion gases, as engine oils do, water contents represent the most important thread for hydraulic oils, especially when esters are being used.

Contamination with particles is the second concern. Some base stocks interact with water or metals, creating byproducts like sludge and rendering the liquid inefficient in lubricating. Choosing a fluid that would provide the greatest payoff to companies is a challenging process as many factors need to be kept in mind. On the other hand, hydraulics are still the undisputed leader in actuation. Electrically actuated brake calipers, or flaps and control surfaces in aircraft, did not achieve a breakthrough in the market or persisted in limited applications.

Product line	Min. vicosity (intermit.) mm^2/s [SUS]	Max. temperature (intermit.) °C [°F]	Recommended viscosity mm^2/s [SUS]	Max. cold start viscosity mm^2/s [SUS]	Min. temperature °C [°F]
H1B	5 [42.38]	115 [239]	12-80 [66.03-370.3]	1600 [7406]	-40 [-40]
H1P					
Series 15 Open circuit	12 [66.03]	85 [185]		860 [3981]	-20 [-4]
Series 20	7 [48.79]	95 [203]		1000 [4629]	-40 [-40]
Series 40		105 [221]		1600 [7406]	
Series 42		115 [239]			
Series 45	9 [55.51]	105 [221]		1000 [4629]	
Series 51	7 [48.79]	115 [239]		1600 [7406]	
Series 90	7 [48.79]	115 [239]			-40 [-40]
TMP/TMM					
LV/LC/KV/KC		105 [221]			
Hydrostatic steerings	10 [58.91]	90 [194]		1000 [4629]	-30 [-22]
Proportional valves	4 [39.17]			460 [2129]	
Electrohydraulic valves	12 [66.03]	82 [180]		440 [2037]	
Spool valves	6 [45.59]				
Orbital motors	12 [66.03]* 20 [97.69]**	90 [194]	20-80 [97.69-370.3]	1500 [6944]	

* For OMR, OMH, OMS, OMT, OMV, TMT

** For OML, OMM, OMP

Figure 1. Viscosity and temperature ranges of hydraulic fluids of different product lines [3].

Effects of Hydraulic Fluids on the Environment

Hydraulic fluids are often exposed to nature through tube bursts and inevitable leakages, which accounts for a significant loss of the fill per year. Water and soil environments are an important area to focus on because spilled or leaked hydraulic oils directly enter the environment and other small bodies of water. The effects of lubricating oils on water quality are well known. Storm and wastewaters not linked to sewage systems pollute lakes, rivers, wetlands, and seas. Sheening unmasks any spill or release of oils into waters and is not necessarily petroleum-based. Hydraulic oil can leak if the protective seals are worn or defective and large amounts may be discharged to nature during maintenance and repair. A major concern of this is that oil on water surfaces decreases natural oxygen transfer. Shifts towards more sustainable and environmentally friendly hydraulic fluids should be considered to limit the number of alterations that the environment will face [4].

Evolution of Biodegradable Hydraulic Fluids

ASTM published in December 1996 D6046, discussing the "classification of hydraulic fluids with environmental impact" and in October 1997 D6006, discussing a "guide for assessing the biodegradability of hydraulic fluids". The market share of biodegradable hydraulic oils and non-toxic to aquatic species was over decades in U.S. marginal. Esters, polyglycols and bio-olefins fall into the class of synthetic lubricants and their prices are prohibitive. Independent from policies, end-users adopt biodegradable oils only when economically feasible and strictly environ¬mentally necessary. Their usage was boosted by the second issuance of the General Vessel Permit (VGP) [5], effective by December 2013, as they became mandatory for water-sea interfaces because VGP was coupled with enforcement by the U.S. Coast Guard.

Historically, the starting point for biodegradable lubes was around 1988 by a recommendation of the international water protection commission for Lake of Constance. Lake of Constance represents a water reservoir for around 10 million people in Germany, Switzerland, and Austria. Out boarders from recreational activities especially polluted the waters. The hydrocarbon exhaust emissions of two-stroke engines were significantly reduced, so only synthetic esters could meet this. Second, the two-stroke engine oil should be non-hazardous to waters [6]. The first ecolabels German "Blue Angel" were released in:

a. 1988, saw chain oils (RAL UZ-48),

b. 1991, mold release agents (RAL UZ-64) and

c. 1996, hydraulic oils (RAL UZ-79).

In 2010, these three ecolabels were harmonized into one ecolabel "RAL UZ-178". The Hanseatic city and state of Hamburg had already applied a simple solution for prescribing biolubes by using civil law in 1994. By decree of the senator for the environment, effective on January 1, 1995, construction companies were eligible to obtain city contracts for buildings or public institutions only if all construction machines working under the contracts used bio-no-tox fluids. A list of suited fluids was provided. The superregional impact of this measure is clear. The German Association of Mechanical Engineering Industry (VDMA) specified in 1994 with VDMA 24568 first the minimum technical requirements for environmentally acceptable hydraulic fluids and was superseded by ISO 15380 in 2002.

Globally, the ministries for Agriculture misinterpreted the term "biodegradable" as being limited to vegetable sources (soybean, rapeseed, sunflower) to generate an additional income for farmers. This misunderstanding is why esters, more specifically vegetable esters, were politically promoted and funded. Unfortunately, due to the presence of double bonds in their molecular backbones, these esters were very limited in thermo-oxidative stability. Additionally, with the high cost that esters presented, this clientele policy had damaged the reputation of the early bio-lubricants. Today, the OEMs prescribes saturated esters (HEES), which are based on fossil up-streams or can be synthe¬sized by using vegetable resources and assure a content of renewables. Furthermore, HETG (triglycerides) are still popular for lower oil reservoir temperatures due to their lower costs [7].

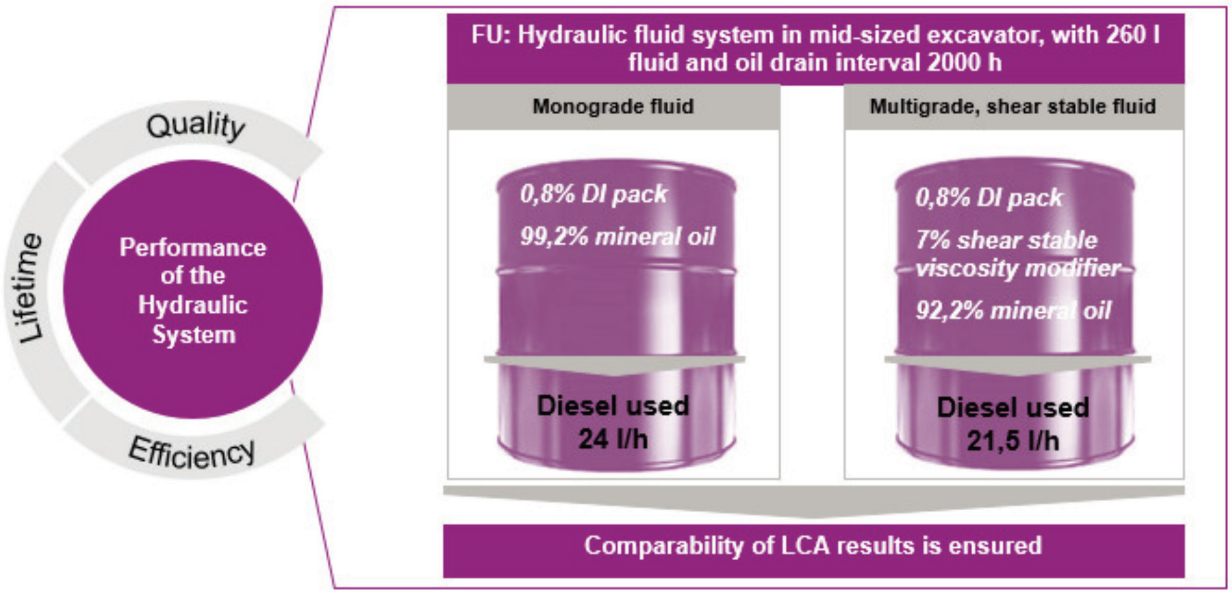

Figure 2. Parameters for the life cycle analysis of hydraulic oils in a medium-sized excavator during 2,000 operating hours (EVONIK) [12].

Environmental Criteria

Environmental criteria of any kind (eco-toxicity and sustainability) are non-functional criteria defined by legislators superposed on technical specifications. Environmental criteria do not improve per se the efficiency and durability of hydraulic equipments. There are several labeling programs with their criteria to determine, if a lubricant is environmentally acceptable based on the base oils and additives that the lubricants are composed of. The three most common base oils that lubricants are composed of are vegetable oils, synthetic esters, and polyalkylene glycols, but recently bio-olefins also appeared.

-Eco-toxicological criteria

More generally, the term "Environmentally Acceptable Lubricants" (EAL) applies to lubricants that are "biodegradable", "minimally-toxic", and "not bioaccumulative". The key criteria specified for EALs are as follows:

a. Ultimate or ready biodegradation of >60% in 28 days.

b. Two or three acute aquatic toxicities (fish, algae, and daphnae) of which each is above >100 mg/L and in case of total loss lubricants above >1,000 mg/L. In some schema, the inhibition growth of bacteria is also requested.

These criteria are consistent with U.N. Global Harmonised System (GHS) adopted by the U.S. [8] and Europe (2008/1272/EC) for the hazard statement GHS 09 "Environmental Hazard". In consequence, U.N. GHS represents the key origin for setting limits and test methods agreed on. Globally, primary degradation as the disappearance of the parent compound is not accepted for EAL ratings or by GHS, as full mineralization as per ultimate or ready biodegradation is the required test. Inhibition of bacteria growth is often the reason for a substance being not readily degradable by being inhibitory to the inoculum. Data on primary biodegradation as per CEC-L-33-A-93, homologue to NF T60-198 or DIN 51828-2, are not considered for awarding an ecolabel or meeting VGP EAL criteria. These test methods for primary biodegradation were withdrawn for decades. CEC-L-33-A-93 was then replaced by CEC-L-103-12.

The U.S. FTC guidelines provide in 16 CFR § 260.8 [9] on biodegradable the following defini-tion: "…competent and reliable scientific evidence that the entire item will completely break down and return to nature (i.e., decompose into elements found in nature) within a reasonably short period of time after customary disposal…" This wording means full mineralization and excludes primary biodegradation.

-Bio-based content

Beside the key criteria of biodegradation, aquatic species, and bioaccumulation, some schemes require a content of renewables. It can be understood as the direct use of vegetable oils or as compounds synthesized from renewable resources. The BioPreferred program (2002) recommended minimum biobased contents starting with 10% for crankcase oils and up to 70% for transformer oils and dielectric fluids [10]. For hydraulic oils, the minimum biobased content is 44%.

The biobased content or content of renewables is determined by the product's contemporary $^{14}C/^{12}C$ content as per ASTM D6866 (methods A, B, or C). The U.S. VGP2013 requires no content of renewables.

The European "bio-lubricants" specification EN16807 tests fully formulated products and requires a content of renewables of >25%. In contrast, the European Ecolabel rates eco-toxicology of individual components. The first and second issuance of the European Ecolabel (2005/360/EC and 2011/381/EU) required a content of renewables >50%, which was cancelled in the third issuance (2018/1702/EC) in favor of more stringent toxicity criteria.

Two companies, Neste and Total Fluides, have signed an agreement to produce NEXBTL, a renewable iso-alkane feedstock in 2015 [11]. Through this, Neste, a renewable fluids production company, and Total fluids, a hydrocarbon fluids production company, have taken a large step towards more renewable hydrocarbon products that can be used worldwide.

Base oil component based on raw materials of biological origin or biomass (recently living organisms, flora, and fauna) of any kind or obtained from biological organisms (algae) can be used as feedstocks in industrial processes to yield hydrocarbons, esters, and PAGs having a content of renewables. They can be broken down into light hydrocarbons of fewer carbon atoms feeding petrochemical processes. PAGs can be polymerized from bio-ethanol converted to ethylene oxide and also from bio-glycerine, a by-product from biodiesel production, converted to propylene oxide.

-Liability and enforcement

Spills ranging from incidental or accidental lubricants leakages to intentional discharges or major accidental oil spills are all subject to penalty imposed by national authorities. The increasing environmental awareness continues to tighten the noose of persecution and surveillance. The fines and countermeasures are not pre-determined or purely based on the amount of oil "spilled", but at least to some degree, by more "emotional factors," and if "Best Available Technology Economically Achievable" (BAT) were used. Environmentally acceptable lubricants (EAL) are established in VGP as BAT. The use of EALs does not authorize their leakage, spill, or discharge, but limits the consequences.

Table 1. Viscometrics of base oils with high intrinsic VIs.

Base Oils	VI	η40 [mm^2/s]	η100 [mm^2/s]	HTHS at 150°C [mPa·s]
PAG (EO/PO-copolymer, non-capped)	192	31.05	7.76	3,01
PAG (EO/PO-copolymer, capped)	225	14.7	4.31	1,94
PAG (EO/PO-copolymer, capped)	230	21.1	5.6	2,62
PAG (EO/PO-copolymer, capped)	224	32.7	7.83	3,36
PPG (PO-homopolymer, capped)	218	18.5	5.0	2,19
PPG (PO-homopolymer, capped)	209	33.9	7.73	3,18
Ester (diisononyl dodecanedioate)	189	24.8	5.6	
Ester (neopentyl glycol dioleate)	207	30.0	7.0	
Blend of two esters (b.o.)	228	21.2	5.6	2,28
Estolide	173	35.30	7.20	
Renewable C31-paraffin	155	18.00	4.30	

EO= ethylene oxide, PO= propylene oxide, PPG= polypropyleneglycol, PAG= polyalkyleneglycol

Shift to synthetics

The low purchase prices of monograde mineral-based hydraulic oils are still promoting their usage; however, sustainability is in future of greater importance. Economy by the higher efficiency of multigrade fluids, eco-toxicity, and sustainability will redefine the decision for purchasing. The vast majority of hydraulic fluids use hydrocarbons.

-Highly functionalized viscosity index (VI) improvers

High viscosity indices can be achieved through polymeric viscosity index improvers. High VIs provide optimum rheology thus offering energy savings over a wide range of working tempera-tures. A primary advantage of multigrade fluids is the omission of oil changes between summer and winter. Figure 2 compares the amount of saved fuel in a field trial of a conventional single-grade reference hydraulic fluid with a highly shear-stable multigrade hydraulic fluid with a high viscosity index. Excavators filled with a monograde hydraulic fluid consumed 24 liters of Diesel per hour and those with multigrade hydraulic fluids consumed 21.5 liters per hour. In consequence, the carbon footprint will also be reduced. The life cycle analysis (LCA) of the field trial over 2.000 hours of operation resulted in 148,508 kg CO_{2eq} for the monograde and in 132,980 kg CO_{2eq} for the multigrade hydraulic fluid. The positive effect of increase in the drainage was not included in the LCA.

-Base oils with high intrinsic VIs

Viscosity indices above 160 can be considered as very high, because hydrocarbon base stocks, even PAOs, do not exceed in the range of ISO viscosity grades VG 22 to VG 220 this value. Base stocks with high viscosity indices are intrinsic multi-grade formulations. The unique oxygen polarity in the molecular backbones of esters (carboxylic bond) and polyalkylene glycols (ether link in each monomer) increases the viscosity index and favor the lubricity (see Table 1). A lubricant with high VI will yield low viscosities at low oil temperatures and thus reduce friction losses. The impro¬ve¬ments in efficiency come from the lower hydrodynamic drag due to the low viscosity, even at higher oil temperatures, the viscosity, and thus the lubrication film height, is as high as those of homologue hydrocarbons. Ultimately, this is beneficial in transient operation modes of the oil temperature (short operations, frequent cold-warm-cold profiles). Three features describe the base stocks with high intrinsic viscosity indices:

1. Intrinsic lubricity,
2. Low temperature fluidity, and
3. Intrinsic shear stability.

The additive solubility in some synthetics is a point of concerns and limits the choice in additives or forces to identify alternative additives. In conclusion, high intrinsic viscosity indices of base stocks reduce the treat rate of some additives and assure a long retention of viscometrics and friction.

-Biodegradation of hydrocarbons

Low persistence in environment measured as ultimate or ready biodegradation is an immovable property for environmentally friendly lubricants and sustainability as per U.N. sustainable development goals #3 and #12. Hydrocarbon-based lubrication base stocks, like

a. Solvent-refined heavy paraffinic distillates, or

b. Solvent-refined light paraffinic distillates, or

c. Hydrotreated heavy paraffinic distillates

are not readily biodegradable [13,14]. Sufficient data is available to conclude that paraffin waxes are only inherently biodegradable [15].

On the other hand, the molecular masses and/or molecular backbones used as lubricant base stocks for esters [16,17] and PAGs [18,19] can be considered as ready/ultimate biodegradable. PAG, esters and base stocks from biogenic oils or other renewable sources are synthetic base stocks and are currently on the market. Products such as EntradaTM -BASE by Advonex and Estolides by Biosynthetic® Technologies and NovaSpecTM by Novvi [20] are available in the biolubricant market and are hydrocarbon base stocks.

Developments of highly branched iso-paraffins [21,22] synthesized with a two stage "hydrocracking-hydroisomerization" process from Fischer-Tropsch waxes yielded to base oils as with a remarkable ready biodegradation of 54% to 72% according to OECD 301B (set limit >60%) associated with functional combinations of VI 140/PP-55°C and VI 160/PP-25°C.

Esters of estolides, known as secondary esters, represent a new option for integrating a content of renewable materials into base stocks. Unsaturated oleic acids or hydroxy fatty esters, as a vegetable resource, were difficult to use as lubricant base stocks, but converted to estolides, they are ultimately saturated (secondary) esters with oxygen polarities, but have for the most part the characteristics of a hydrocarbon. Estolides are ready/ ultimate biodegradable with >60%.

Farnesene, a methyl-branched $C_{15}H_{24}$ hydrocarbon, is originated from industrial fermentation of sugar cane by genetically modified yeast. The farnesene hydrogenated to farnesane ($C_{15}H_{32}$) is reacted with linear olefins and are ready/ultimate biodegradable with >60%.

Summary

Synthetic and biosynthetic base stocks offer an extended portfolio of properties on a higher price level. Synthetics are in a better position to meet all future combinations of properties. There is clearly visible a competition of solutions of which the selection of synthetic base stocks depends from the canon of "ecotoxicological properties, content of renewable, sustainability" in combination with viscosity index mirrored with the cost/price ratio. The solutions have functional overlaps between each other and their availability in respect of volumes is another selection criteria.

A shift towards biodegradable fluids will greatly reduce the negative impact on the environment that their non-biodegradable and non-toxic counterpart fluids have. With the growing market for base oils and the advancing technology in improved hydraulic systems, synthetic fluids are expected to become a larger percentage of the market value and become more popularized. Hopefully, that the customer or end-user will value this motion.

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