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To what extent do synthetic esters contribute to better sustainability of greases?

S. Lucazeau, *Product Manager Industry & Automotive, NYCO - Paris*

1. Sustainability, a complex notion

Sustainability is a wide, complex notion that is now mentioned and used commonly, but it would deserve clarification as to how it is defined, and what it actually covers.
Sustainability refers to social, economical and environmental consequences of human activity. This notion analyses how durable and equitable a given activity is likely to be when taking in consideration its potentially negative effects:

- harm to the environment – pollution, toxicity to plants and animals, reduced biodiversity
- harm to people – health and wealth, living and working conditions
- depletion of resources

Such an evaluation approach is very broad, either in time by anticipating future effects on the long run, or geographically, or even socially, as not only the actors of the assessed activity will be looked at – but also all the other people that may be impacted.

Sustainability does include some political aspects, especially when it comes to thinking about equitability of human activity.

2. Sustainable lubricants

Current concerns about lubrication revolve mainly around its impact on human health and environment (i.e. European Ecolabel, Vessel General Permit…). However, some other broader aspects are clearly gaining visibility:

- Fossil resources depletion: use of petroleum derived materials;
- Competition with food resources: use of fatty acids originating from controversial palm oil extensive growth;
- Energy saving through friction reduction, which is strongly linked to CO_2 emissions – and global warming;
- Durability, i.e. extended lifetime of lubricants that reduces waste generation and downtimes.

Extending the notion of "environmentally friendly" lubricant to that of "sustainable" lubricant would therefore require examining not only the impact of the use of lubricant itself, but also the impact of its production, transport and disposal, and this should also be considered for its raw materials. Also, immediate users of lubricants may not be the only people that may be impacted. Such a thought process is used in the Life Cycle Analysis.

Life Cycle Analysis uses various impact categories[1]: climate change, stratospheric ozone depletion, human toxicity, respiratory inorganics, ionizing radiation, ground-level photochemical ozone formation, acidification (land and water), eutrophication (land and water), ecotoxicity, land use, resource depletion (minerals, fossil and renewable energy resources, water).

The relative importance of each category probably remains a judgement call. Therefore, a fair proposal for the definition of a sustainable lubricant could be "a lubricant that minimally degrades the quality of both the environment and people's lives, whilst conserving resources on the long run, in a responsible way".

3. Standards and legislation

There are numerous standards and labeling programs, most of which being voluntary schemes or simple guidelines. They help clearly define assessment criteria and they also encourage the development and use of products in a more sustainable approach.

- ISO 14000: environmental management, in particular ISO 14040 (Life Cycle Analysis) and ISO 14031 (environmental performance).
- ISO 26000: social responsibility.
- ASTM E2986: sustainable manufacturing.
- EN 16760: biobased products, Life Cycle Analysis.
  EN 16751: biobased products, sustainability criteria.
- European Commission, JRC/IES – ILCD: Life Cycle Assessment.
- ISCC: sustainability certification system covering agricultural crops and derivatives.
- OECD: Green Growth strategies.
- RSPO/Green Palm: certification/trading system covering sustainable palm oil.

According to Ecolabel Index[2], 463 Ecolabels are reported across the world.

The standards, labels and legislations that specifically deal with lubricants are:

- European Ecolabel, Nordic Swan, Swedish Standards, Blue Angel...: certifying label schemes covering environmentally acceptable lubricants;
- Vessel General Permit: mandatory use of Environmentally Acceptable Lubricants;
- OSPAR: international convention for the protection of marine environment;
- US Biopreferred: USDA labelling initiative for biobased products.

They actually set targets and limits on:
- Environmental impact, through aquatic toxicity, biodegradability, and bioaccumulation;
- Innocity of products, through toxicity and risks associated to exposure;
- Fossil resources depletion, through renewable carbon content;
- Performance and durability, through technical specifications.

Whilst environmentally acceptable lubricants have long been considered low performance products, it is certainly not the case any more thanks to the inclusion of performance requirements in standards.

Amongst them, the European Ecolabel appears to be the labelling program that comes closest to sustainability considerations: innocuity, renewability, performance and durability.

However, Ecolabel and similar programmes in Europe are voluntary schemes, whereas OSPAR and Vessel General Permit requirements are mandatory.

The OSPAR has been translated into mandatory requirements in the UK, Netherlands and Norway waters, aiming at protecting marine environment. The Vessel General Permit requires ship operators to use Environmentally Acceptable Lubricants in all oil-to-sea interfaces, in the US waters.

4. Synthetic esters

Synthetic esters are base fluids that belong to group V. They are used, in particular, to formulate high performance lubricants. Synthetic esters combine a number of specific features:

a. Their remarkable thermo-oxidative stability extends the lifetime of lubricants and provides excellent cleanliness on equipment.

   Increased power density in engines generate better energy efficiency, but also causes more fouling and deposit formation, and costly maintenance operations and downtime. It may also decrease lifetime of lubricants and shorten drain intervals.

   In compressor oils, for instance, the use of synthetic esters improves cleanliness and extends lifetimes of oils to over 10,000 h (Figure 1).

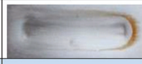
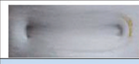
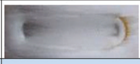
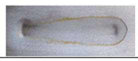
	ISO VG 46 compressor oil PAO based	ISO VG 46 compressor oil Ester based	ISO VG 100 compressor oil PAO based	ISO VG 100 compressor oil Ester based
MCT 200-250				
Deposit temperature °C	224,00	242,00	230,00	> 250
Average merit	8,99	9,66	9,32	10
				
MCT 230-280				
Deposit temperature °C	< 230	230,00	230,00	230,00
Average merit	7,19	8,17	7,72	8,52
				

Figure 1. *Micro-coking test (GFC Lu-27-A-13) on fully formulated compressor oils*

b. Their natural lubricity reduces wear and friction losses, thus improving energy efficiency. This is due to the affinity of esters with metal surfaces, making them friction modifiers.

   It is estimated that one third of the total energy produced globally is lost through friction[3]. The use of synthetics in general, and esters in particular, does result in improved energy efficiency (Figure 2).

Property	Unit	PAO	Gr III	Alkyl Naphthalene	Diester	Neopolyol ester	Complex ester
Viscosity at 100°C	mm²/s	3.95	4.25	4.82	3.22	4.40	5.73
Viscosity at 40°C	mm²/s	17.3	19.7	28.7	11.6	19.7	28.0
HFRR -5N – 60°C – 75 mn Friction coefficient	--	0.492	0.311	0.296	0.225	0.230	0.220

Figure 2. *Friction coefficients of various basestocks (HFRR)*

c. They also display low volatility features, which translate into low flammability/fire resistant properties.

   The polarity of esters increases intermolecular forces and reduces volatility. In addition to extending durability of the lubricant, this feature makes for added safety through fire resistance properties.

   Flash points of over 300°C may be obtained on synthetic esters at ISO VG 46, and up to 320°C at ISO VG 100.

d. The vast majority of synthetic esters is harmless to human health, animals or aquatic organisms, as demonstrated by extensive testing related to REACH registration procedures.

e. They have the potential to biodegrade. A great number of esters falls into the "readily or inherently biodegradable" category according to OECD 301B test method, an ultimate biodegradability test.

Biodegradability of synthetic esters may reach 90%. This is structure dependent. However, the source of fatty acids used (petroleum, vegetable) has no impact.

Whilst it is commonly accepted that viscosity is a limiting factor for biodegradability, synthetic esters may be highly viscous and still demonstrate high levels of biodegradability, as illustrated below:

ISO VG 100: 63%
ISO VG 320: 67%
ISO VG 1000: 79%

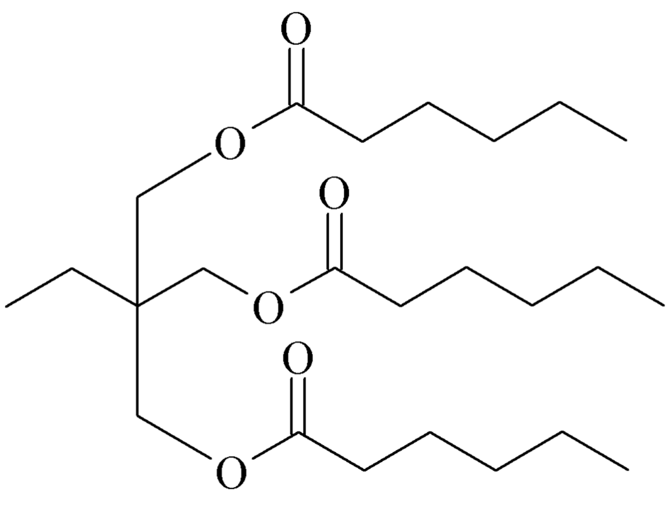
f. The molecular diameter of synthetic esters is greater than 1.5 nm, for the vast majority of esters used in lubrication: C-C single bond indeed is 0.12 to 0.15 nm long.

Moreover, REACH related testing has shown that their Bio Concentration Factor (BCF) is usually well below 100 l/kg.

These 2 factors make synthetic esters products that are very unlikely to bioaccumulate, according to European Ecolabel criteria.

g. Their chemical structures may be chosen to include raw materials made from renewable carbon sources. Renewability content can reach 100% on some esters.

Alcohols are generally petroleum derived, so renewable material will be coming from fatty acids, derived from rapeseed or canola oil, tall oil, tallow, palm and palm kernel oil, coconut oil, castor oil, sunflower oil, soybean oil... amongst other oils.



The above compound is the reaction product of trimethylopropane (petroleum derived) with hexanoic acid (vegetable based). As a result 6 carbon atoms are petroleum derived and 18 are vegetable derived, out of a total of 24. Hence this product contains 75% renewable carbon.

For a given chemical structure, the origin of the raw materials may impact the performance of the resulting ester.

As a result, synthetic esters do contribute to improved sustainability, as they deliver added human safety, they exhibit excellent environmental profiles, they may decrease dependency on fossil resources, and they contribute to fuel economy improvement and reduction of CO_2 emissions. This is a unique set of properties combining performance and good environmental profile.

For instance, synthetic esters are excellent candidates for the formulation of European Ecolabel certified, Vessel General Permit compliant, OSPAR listed lubricants like hydraulic fluids, stern tube oils, subsea fluids... and greases.

5. Ester based greases

Producing greases on the basis of synthetic esters may require some adjustments in the manufacturing process, especially with high viscosity esters. Resulting greases are expected to show most of the benefits listed for ester base fluids.

ASTM D942 – oxidation Pressure drop	Unit	99°C 100 h	99°C 500 h
GREASE A	kPa	22	80
GREASE B	kPa	10	41

GREASE A : bentonite grease, group I mineral base fluid
GREASE B : bentonite grease, synthetic ester base fluid

The remarkable thing about these fluids is that their biodegradability is not necessarily limited by viscosity. Biodegradable esters are available in a very wide range of viscosities, from ISO VG 15 to ISO VG 1000. High viscosity esters may be used to formulate marine greases used for ropes, metal cables, winches, open gears or bearings, and complying with environmental standards.

A specific European Ecolabel category is defined for greases: they must content over 75% of biodegradable components and over 45% of carbon from renewable origins. Their aquatic toxicity must exceed 1000 mg/l on algae, daphnia, and fish – amongst other criteria.

An NLGI 2, multi-purpose grease was formulated using an ISO VG 150 synthetic ester, thickened with Lithium 12-hydroxystearate, and suitable additives (figure 3). Such grease shows good overall features and is European Ecolabel certified.

6. Going further into sustainability

Extending the above sustainability notions on greases means taking in account raw materials and grease production and transport, costs, lubrication lifetime, equipment maintenance, energy savings, and lubricant disposal through a thorough Life Cycle Assessment.

Properties	Unit	Typical Result	Test method
Appearance	-	Homogeneous paste	Visual
Base oil viscosity at 40°C	mm²/s	150	ISO 3104
Dropping point	°C	198	ISO 2176
Penetration Unworked Worked 60 strokes 100 000 strokes	1/10 mm	277 274 315	ISO 2137
Oil separation (30 h at 100°C) Oil separation (168 h at 40°C)	% mass	2.9 2.7	ASTM D6184 NFT 60-191
Evaporation loss (22 h at 100°C)	% mass	0.2	ASTM D972
Copper corrosion (24 h at 100°C)	-	1b	ASTM D4048
Oxidation test at 99°C after 100 h after 500 h	kPa	14 34	ASTM D942
Wear scar diameter – 1h, 40 kg	mm	0.62	ASTM D2266
Water washout at 80°C	% mass	0.75	ASTM D1264
Weld Load – 4-ball test	kg	315	ASTM D2596
Load-Wear Index	daN	41	ASTM D2596
Low temperature torque at -30°C Starting torque After 60 min	Nm	0.06 0.03	ASTM D1478
Bearing corrosion, EMCOR method Distilled water	-	0/1	ASTM D6138

Figure 3. *Main properties of European Ecolabel certified, NLGI 2 ester based Li grease*

One element that might be put forward against the use of esters in sustainable greases is the controversial, extensive use of palm oil as feedstock for the production of fatty acids of renewable origin. However, a majority of palm oil derivatives producers are RSPO (Roundtable for Sustainable Palm Oil) certified, which should make for a more responsible approach to extensive palm growth.

Also, whilst we can state clearly that synthetic esters do show excellent environmental profiles, we are not in a position to compare their carbon footprint with that of other base fluids. This brings us to the notion of judgement of the relative importance of criteria.

As an illustration, marine pollution from stern tube oil spills is estimated to reach 80 million liters per annum[4]. Switching from mineral oil based lubricants to European Ecolabel certified, ester based lubricant does make a huge difference for the marine environment. Should reduced CO_2 emissions be favoured over marine pollution?

7. Conclusion

Synthetic esters demonstrate a unique combination of high performance features and excellent environmental profile.

Greases complying with existing standards can be produced using such base fluids. These greases are of particular interest in areas where potential release to the environment is a concern: marine applications, water catchment areas, total loss lubrication...

Extending this notion to sustainability requires a heavy, complex study including a Life Cycle Analysis.

However, some level of personal appreciation remains when it comes to evaluating the "level of sustainability" of a grease.

LINK
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[1] *ILCD Handbook, ISO 14040-44*
[2] *http://www.ecolabelindex.com*
[3] *Stachowiak, G.W.; Batchelor, A.W. Engineering Tribology. Tribology Series, 24; Elsevier Science: Amsterdam, Netherlands, 1993*
[4] *The Challenge of Stern Tube Bearings and Seals - Mr. John Thornhill BSc (Hons) CEng FIMechE, General Manager of Seals, Wärtsilä UK Ltd*