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Biobased-Biodegradable, Vegetable Oils, Biobased Esters: How to choose?

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Although biobased and biodegradable lubricants have been around since 1980s, there is still a need to clarify the difference between natural vegetable oils, chemically modified vegetable oils, esters made from vegetable oils and the resulting biodegradable products. There are also new terminologies beyond biodegradability that refer to environmentally friendly lubricants. Terms such as Biobased, Bio-Preferred, Environmentally Aware Lubricants (EAL); and Vessel General Permit (VGP) are relatively new and also need to be explained.

Vegetable Oils

Vegetable oils refer to oils that are extracted from plants, seeds, kernels, nuts, or grains. Based on their economic impact in their respective regions they are divided into Major Oils, Minor Oils, and Non-Edible Oils[1]. Major oils include oils like soybean, palm, rapeseed (canola), sunflower, cottonseed. Coconut, peanut, olive, palm kernel, corn, linseed, and sesame. Minor oils are known for their uses but do not match the larger production levels of Major Oils. They include oils like niger, mango kernel, poppy, cocoa bean, shea, grape seed, and the like. Non-Edible Oils include castor, tung, and tall that are commercially grown for their chemical properties.

Vegetable oils are made of triglycerides. A triglyceride or triacyl glyceride is a lipid molecule or a fatty ester derived from glycerol and three (tri) fatty acids. When considering materials for grease manufacture, not all vegetable oils are the same. Their fatty acid profiles vary considerably; and fatty acid profiles are indicators of stability of the oil when considering use. Because oxidation stability is fundamentally important in the longevity of industrial lubricants, it is important to review their fatty acid profiles and the percentage of some key fatty acid contents. Of the fatty acid constituents of vegetable oils those with more stability are desirable, but they negatively impact cold temperature flowability. For example, stearic acid is a fatty acid with no double bonds which makes it oxidatively stable, but it is solid at room temperature and cannot flow. Oleic acid on the other hand has one double bond that makes it less stable than stearic acid, but it is liquid at room temperature and can provide flowability for use in industrial lubricants, but it still impacts the pour point of the oil negatively. Similarly, Linoleic acid with two double bonds, and much worse Linolenic acid content with three double bonds, provide better fluidity at cold temperatures but impact oxidation stability negatively and exponentially.

Some seed oils have been modified through genetic selection, breeding, or genetic and transgenic modifications. For example, canola oil is a genetic variation of rapeseed with low or zero percent erucic acid content. High oleic soybeans produce oils with high oleic acid content with better oxidation stability. But varieties that have higher percentage of linolenic acid could show a relatively poor oxidation stability even if they have high oleic acid content.

The best-known test of oxidation stability for vegetable oils is the Oil Stability Index (OSI) as used by food processors. Figure 1 shows a picture of the Oxidative Stability Instrument that is used to determine the Oil Stability Index (OSI).

Figure 1: *Oxidative Stability Instrument.*
Picture: Courtesy of Environmental Lubricants Manufacturing, Inc.

A newer test instrument using a similar concept is the Rancimat method that also determines the oxidation stability of natural fats and oils, in their pure form as well as in fat-containing foods and cosmetics.
Table 1 presents the properties of some vegetable oils including the Oil Stability Indices.

Oil	Oil Stability Index (OSI) (hours)	Total Acid Number TAN	Flash Point (PM)	Flash Point (COC)	Fire Point (COC)	Pour Point (°C)	Cloud Point (°C)	Viscosity @ 40	Viscosity @ 100	Viscosity Index	4 Ball Wear	Pin & Vee Block load (lbs)	Iodine Value*
Apricot Kernel	23.42	0.2844	284.5	324	348	-16	-10.8	36.49	8.202	210	0.615	1732	
Avocado	18.53	0.185	217.5	320	348	-3	-0.2	39.26	8.432	199	0.609	1975	85.656
Babassu	57.8	N/A	261.5	308	327	N/A	N/A	28.65	6.133	170	0.586	1706	
Castor	105.13	0.252	282.7	300	320	-28	N/A	249.5	19.02	85	0.633	1674	93.030
Coconut	75.38	N/A	275.3	306	324	N/A	N/A	27.8	5.947	167	0.504	1738	6.394
Corn	3.73	0.198	180	324	346	-15	-10.2	32.58	7.72	220	0.628	1997	
Cottonseed	4.35	0.13	262	330	350	-6	-3.7	34.23	7.911	215	0.588	1812	
Flaxseed	1.17	0.8399	268	322	348	-12	-7.4	27.35	7.112	243	0.639	1622	173.712
Grapeseed	2.83	0.229	248	324	346	-12	-6.9	33.28	7.858	220	0.623	1736	
Hempseed	0.10	1.6488	248	328	356	-15.8	-28	26.71	6.972	242	0.608	1556	
Jojoba - Refined	42.15	0.13	282.7	304	330	9	9	25.1	6.519	234	0.630	1673	75.152
Jojoba - Golden	38.3	0.752	268.7	304	330	10.7	8	24.82	6.452	233	0.606	1558	
Lard	6.02	N/A				N/A	N/A	N/A	8.543	N/A	0.525	1676	
Macadamia	6.87	0.126	276	328	344	-5	-1.9	39.24	8.441	200	0.594	1797	
Oleic acid	0.10					3	5.9	19.05	4.778	186	0.605	1341	
Olive	5.08	0.132	264	316	342	-6	-5.4	37.56	8.242	203	0.616	1683	74.710
Palm Kernel		N/A	272	322	329	N/A	N/A	31.96	6.606	169	0.461	1622	
Palm	21.52	N/A	287	320	347	N/A	N/A	41.77	8.56	189	0.517	1726	
Poppyseed	17.86	0.151	256	326	356	-18	-15.5	30.52	7.46	226	0.601	1908	
Ricebran	20.82	0.194	248	342	360	-9	-3.9	36.49	8.177	208	0.581	1549	
Ricinoleic Acid	117.1	NA	253	NA	NA	-19	-5.5	NA	NA	NA	0.519	1277	NA
Safflower	17.98	0.1268	244	322	350	-22	0.4	37.9	8.325	206	0.634	1660	84.459
Sesame	5.8	0.136	266	334	342	-9	-5.7	34.1	7.923	216	0.49	1842	
Soybean	17.67	0.1602	292	328	346	-9	-5.1	31.08	7.552	226	0.601	1835	126.839
High Oleic Soybean	35.95	0.2346	248			-12	-9.9	39.12	8.402	203	0.608	1768	
Sunflower	10.23	0.132	272	326	356	-15	-9.9	38.58	8.453	205	0.621	1864	
Walnut	16.48	0.1269	186.7	322	346	-19	-14.5	29.91	7.441	232	0.584	1887	

Table 1: *Properties of selected vegetable oil.*
Source: Environmental Lubricants Manufacturing, Inc.

Researchers at Environmental Lubricants Manufacturing have relied on a more practical test to determine performance of vegetable oils in actual use. Using the ASTM D7043 (formerly ASTM D2271) the oil is tested in a Vickers Vane Pump at 1000 PSI and 79 C for 1000 hours. Figure 2 presents the test stand used to perform the ASTM D7043 hydraulic oil test. 5 gallons of test oil is circulated through the pump with standard vane cartridge and the viscosity of the oil is drawn every 100 hours and tested to determine change. The temperature is maintained at 79°C by the use of a heat exchanger.

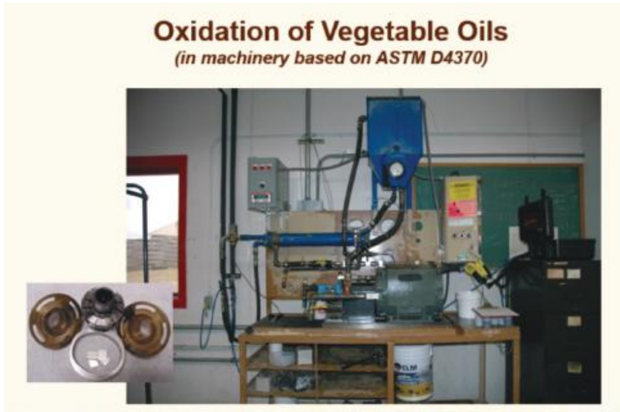

Figure 2: *Test stand set up based in the ASTM D 4370.*
Picture: Courtesy of Environmental Lubricants Manufacturing, Inc.

The oil within this test is exposed to metal surfaces, friction generated heat, atmospheric moisture, light and oxygen. Oxidation can be determined by an increase in viscosity and changes in the Total Acid Number of the oil. Experimentally, field test observations have shown that changes of viscosity of less than 10% in the 1000-hour test could be desirable for moderate use hydraulic system. Table 2 shows the viscosity of selected test oils at the start of the test and after 1000 hours of testing.

Oil Sample	Viscosity @ 0 hr: in cSt.	Viscosity after 1000 hrs: in cSt.	Viscosity Difference in cSt.	% of change in Viscosity from 0 to 1000 hours
High Oleic Sunflower Oil	39.34	113.3	73.96	188%
High Oleic sunflower oil with antioxidant	39.19	105.7	66.51	170%
High Oleic Canola Oil	37.51	115.6	78.09	208%
High Oleic Soybean Oil	42.1	68.96	26.86	60%
Fully Formulated High Oleic Soybean Oil Based Industrial Hydraulic Oil	43.18	46.11	2.93	6,8%
Fully Formulated Soybean Oil-Based Universal Tractor Transmission Hydraulic Fluid	44.24	41.92	-2.32	-5%
Fully Formulated Biobased Derived Synthetic Ester Industrial Hydraulic Oil	44.06	44.54	0.48	1%

Table 2: *Summary of Viscosity Changes in Vickers VQ-20 Vane Pump Tests: ASTM D-7043 (formerly ASTM D 2271 Vickers 104C Vane Pump).*

Chemical Modification of Vegetable Oils

The most common chemical modification of vegetable oils has been partial or full hydrogenation that has been in use for frying food. Fully hydrogenated vegetable oils are solid at room temperature and are used in food products and in frying applications. When stability and liquidity is desired, as in cooking oil, then the vegetable oil is partially hydrogenated. Hydrogenation of vegetable oils is known to result in creation of trans fatty acids with negative health effects. As a result, genetic enhancements of oil seeds have gained popularity to produce oils that are naturally stable enough that eliminate the need for hydrogenation. But, the resulting oils have been helpful for making more stable lubricants without the need for reduced need for additives or for hydrogenation.

Other chemical modifications include esterification that results a more stable oil with known physio-chemical properties and offer more consistency than the natural vegetable oils whose properties could change as a result of changes in soil or growing conditions. Simply described, esters are produced by reacting an alcohol with a vegetable oil and removing the glycerol component. If, for example, methanol is the choice alcohol in esterification, then the ester would be methyl ester. Esters could be produced to have different viscosities. Complex esters, Estolides, and other chemical processes are used to produce known and consistent esters for use in industrial applications. For many industrial applications where the oil has long residency in the machine, like hydraulic oils, the use of select esters is preferred. Chemical modifications and esterification of vegetable oils increase their cost; and based on the complexity of the modification the cost could range from 1.5x to 3x that of vegetable oils. This necessitates the need to match the base oil that performs the best and is economical for the end use.

Synthesising to form esters allows the oil to 'calibrate' to perform in very high temperatures or in very cold temperatures far above or below the vegetable oils could in their natural form. Examples of synthetic esters include simple/monoesters, diesters, polyol esters, complex ester, and aromatic esters. Table 3 shows a list of esters with their respective properties.

Synthetic Ester	Chemistry	Viscosity @40 ℃(cSt)	Viscosity @100 °C(cSt)	Viscosity Index	Flash Pt. (℃)	Pour Pt. (℃)
Lubricit 2-EHO	Monoester	8	3	190	215	-40
Lubricit DINA	Diester	11	3	140	220	-60
Lexolube 3I-310	Polyol	14	3	120	230	-65
Lubricit TMP C9	Polyol	21	5	140	285	-30
Lubricit DTDA	Diester	22	5	150	245	-55
Lubricit NGDO	Polyol	24	6	200	270	-60
Lexolube 2X-109	Diester	27	5	140	260	-60
Lubricit PE 49	Polyol	33	6	150	315	-45
Lubricit TMP THCFA	Polyol	37	7	155	300	-15
Lubricit TMP C18	Polyol	46	9	190	325	-45
Lubricit PE 418	Polyol	66	12	185	340	-35
Lexolube PQ-68	Polyol	68	9	105	250	-30
Lubricit 9526	Complex	330	45	185	320	-40
Lexolube CP-460LC	Complex	460	46	150	290	-25
Lexolube CG-3000	Complex	3000	290	230	320	-20

Table 3: *Example of commercially available esters.*
Source: Zschimmer-Schwarz.com
https://www.zschimmer-schwarz.com/

Biodegradability

The term refers to ability of a product to break down in the environment when exposed to the soil or water bacteria or organisms. The well-recognised standard tests are established by Organisation for Economic Co-operation and Development (OECD) and come in series of tests known as OECD 301 Series and include:

301 A: Is an aerobic biodegradation test used for non-volatile and soluble (100mg/L) substances. for ready or ultimate biodegradation.

301 B: Carbon Dioxide Evolution (Modified Sturm Test)

301 C: MITI (I) (Ministry of International Trade and Industry, Japan)

301 D: Closed Bottle Test. Suitable for poorly soluble materials and for volatile and absorbing material samples.

301 E: Modified OECD Screening

301 F: Manometric Respirometry Method. Simply described, in this test method standard bacteria are introduced into bottles containing water and nutrients and the sample to be tested. If the sample is biodegradable it would serve as food for the bacteria and is consumed by them. The growth of bacteria results in consumption of oxygen and creation of vacuum with the test bottles as well as production of carbon dioxide through respiration. The test instrument then allows oxygen to enter the bottle through an oxygen flowmeter technique. It also has a means of absorbing the respirated carbon dioxide. The sample bottles are compared with reference bottles that contain only bacteria and standardised nutrients. The samples that show oxygen consumption equal to 60% of the reference bottles within the first 10 days and maintain such level of oxygen consumption for 28 days are considered biodegradable. Figure 3 shows a biodegradability test instrument using the OECD 301 F.

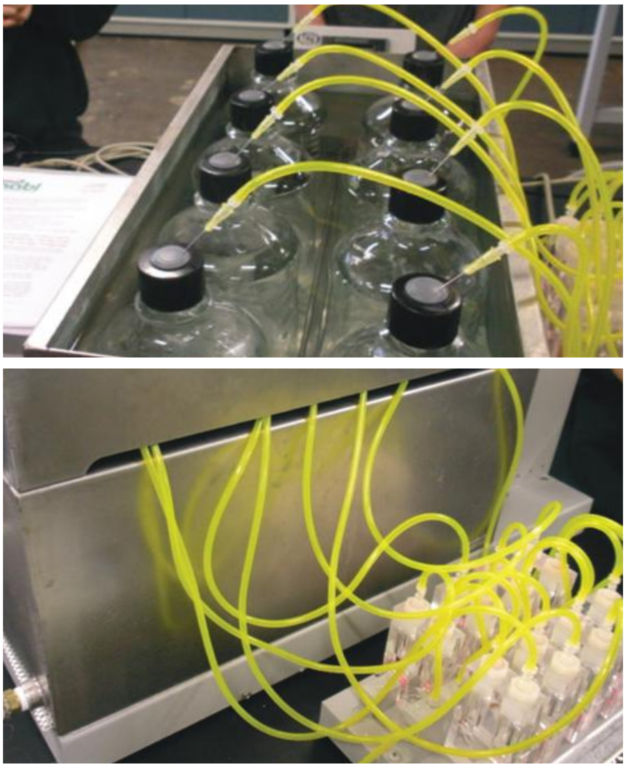

Figure 3: 301 F biodegradability test instrument: (above showing the sample test bottles in water bath with cover removed); and (below) Oxygen flowmeters feeding oxygens to the test bottles).

Picture: Courtesy of Environmental Lubricants Manufacturing, Inc.

Biodegradable: Products that pass the OECD 301 series tests of biodegradability – 60% biodegradable in 28 days – Products could be made from renewable or non-renewable hydrocarbons. For example, some Polyalphaolefins (PAOs) although derived from petroleum can pass biodegradability tests. So, they are biodegradable but are NOT Biobased.

Biobased: Products that are made of RENEWABLE hydrocarbons. Products are described in terms of their Percent Renewable Carbon Content. For example, vegetable oils and most vegetable or animal fat-derived esters are considered Biobased and pass the tests of biodegradability. So, they are considered BOTH biodegradable AND Biobased.

To determine the percent of biobased content a standard carbon dating technique is used. To certify as Biobased product by the US Department of Agriculture, products will need to be tested using the ASTM D6866 - 18 – "Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis".

To qualify as Biobased for the purpose of meeting the Purchase Preference requirements by the US Federal Purchasers.

1. Contact the USDA Biopreferred Program
2. Submit a request and send products to certified qualified labs for testing
3. If product meets the minimum biobased content within its category, then the product receives Biobased designation
4. Perform Life Cycle Analysis as per the National Institute of Standard method.

In general, in Europe the environmental emphasis is on biodegradability regardless of renewability; whereas in the US, the emphasis is on Biobased or renewability and petroleum substitution; that often also results in biodegradability.

How to Choose

Vegetable oils in their natural forms and their derivatives offer distinct advantages over conventional mineral (petroleum) oils. Advantages include better lubricity due to their dipolar nature; almost 2X higher Viscosity Index for more stable viscosity at extreme temperatures, higher thin-film strength for better metal-to-metal separation; and higher flash/fire points for better safety. But, if untreated or selected improperly, they lack of oxidation stability could impact long term residency in the machinery like gear boxes or hydraulic systems; they have higher pour points that impact cold temperature performance, their chemical modifications could make them expensive, and finally their compatibility with elastomers, polymers, various metal, and additives need to be understood for proper formulation.

Ideally, it would be best to choose the chemically modified oils or biobased derived synthetic ester for every lubricant application. But history has shown that the very high price of the finished products made with esters would prevent large scale acceptance of biobased products.

So, it is important to choose the right base oil for the right end use application. Leading biobased lubricants manufacturers prepare their products with different base vegetable oils that match the performance to the cost. Products that have shown success using less stable vegetable oils include:

- Dust control agents
- Concreate form release
- Asphalt release agents

Products that require more stable vegetable oils along with added antioxidant packages could include:

- Wire rope lubricants
- Chain and cable lubricants
- Lubricant/Penetrants
- Anti-corrosion lubricants
- Switch plate lubricants

Products that require very stable vegetable oils along with added antioxidant packages could include:

- Food grade hydraulic oils
- Straight oil metal cutting oils
- Transformer cooling oils
- Selected greases:
  - Rail curve grease
  - VGP Wire rope grease
  - Drill rod grease
  - Food grade grease
  - Chassis grease
  - General purpose greases

It should be noted that untreated vegetable oils should not be exposed to processes that exceed 150°C for long periods of time during processing. Experience has shown beyond such temperature the oil oxidation could increase, and polymerisation process could get initiated. If exposure to high temperature continues the polymerisation could be followed by propagation that could continue even after the exposure to such temperatures is stopped, albeit at a slower rate. Recent manufacturing techniques for making grease have utilised microwaves for processing vegetable oil-based greases, which speeds up the process and reduces exposure to high reaction temperatures (200-250C) dramatically and thus resulting in more stable greases.

For most other applications especially if the biobased products have long residency within the machine or require flowability at -40 degrees or lower temperatures, biobased derived esters should be used.

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Biobased lubricants - other factors

There are other factors that should be considered when formulating biobased lubricants and greases. Details are beyond the scope of this paper, but compatibility with packaging polymers, with elastomeric seals and hoses, with some metals, and with other mineral oil-based lubricants should be understood when a product is being formulated.

Some antioxidants cause extreme colour changes in the products. Some food colouring or conventional dyes used for colouring greases could show incompatibility with vegetable oil-based lubricants and greases.

Summary

Biobased and biodegradable lubricants offer great potential to be offered alongside conventional lubricants.

Mineral oil-based lubricants have had years of standardisation and offer consistency and quality with known performance.

Vegetable oils on the other hand have significant amount of variability and range both in stability and price. Ultimately, the end use of the product will dictate which base vegetable oil to use.

The choices range from commodity vegetable oils, genetically enhanced or transgenic varieties that offer more stability, and a variety of chemically modified or esterified base oils that offer consistency and higher performance but could cost 2x to 3x more than vegetable oils or conventional mineral oils. Vegetable oils offer the best performance and price for select lost-in-use applications.

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