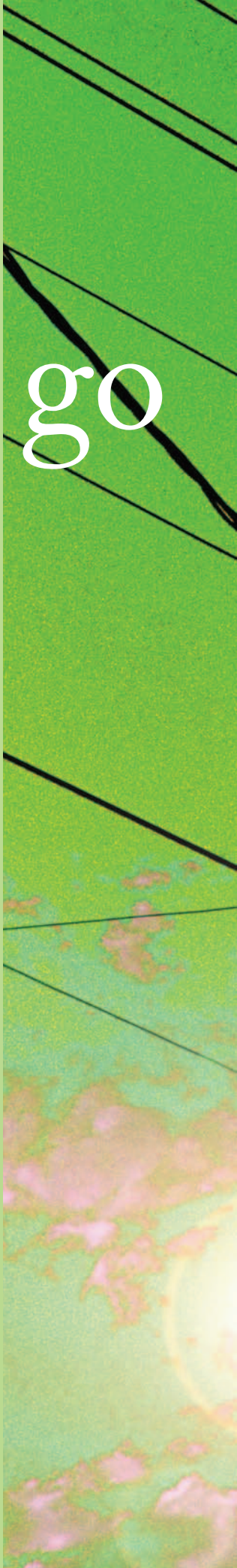
By Ray Bergstra

green means go



The market for vegetable based lubricants continues to attract interest as a viable long-term alternative to petrochemical based products. While vegetable oils are known to have a number of technical shortcomings as lubricants, governmental support, emerging technology, and ongoing uncertainty over crude oil supply are all contributing to the development of new natural-product based oils.

Interest in biodegradable lubricants historically has been in response to environmental concerns, particularly relating to the effects of oil leaking onto the ground and into fresh water. Biodegradable and non-toxic products such as ester based hydraulic oils, gear oils and greases are recommended for use in environmentally sensitive areas where small amounts of leakage are inevitable. Forestry (particularly in northern European countries), water treatment and water management industries are common applications for biodegradable and non-toxic lubricants.

Most major lubricant marketers maintain ester based lubricants in their product offering and these products are typically based on either synthetic or natural esters. Unfortunately, biodegradable ester lubricants come at a premium price, and while a number of successful niche markets have been established, the cost issue has prevented widespread usage.

"It really is a case of the technology push waiting for the market pull," comments Brenda Jones, manager of hydraulics and forestry products with Petro-Canada Lubricants. And the fact remains that in highly cost-competitive markets like agriculture and forestry, individual users can ill afford to increase their lubricant costs.

Biobased Progress As we look to the future, what should we expect to see when it comes to vegetable oil based lubricants? What, if anything, has changed in this market? As is often the case, there are both technical and marketing hurdles to consider — and there have been recent developments in both areas.

In terms of the market, the initial push for biodegradable oils was for reduction of the impact of potential lubricant spills. Vegetable oils are a natural fit (pardon the pun) and

environmental concerns remain as a driver for new product development.

A case in point is the recently launched soy based transformer fluid, Cooper Envirotemp FR3 Fluid, marketed by Cooper Power Systems and made by a subsidiary of Cargill Inc., a leader in developing vegetable oil based technology. The development of this new product application was in response to environmental concerns over leaks and potential costly clean-up operations. However, other benefits were noted as the project progressed. When compared to petroleum based products, FR3 has better compatibility with paper insulators for longer transformer life, and better fire resistance — a highly important safety feature for transformers.

Ironically, environmental considerations, while important for marketing the product, cannot be fully enjoyed by end-users since the EPA considers all oil spills, either vegetable or petroleum, as requiring identical levels of reporting and clean-up. Luis del Valle, global marketing director for Cargill Industrial Oils & Lubricants in Minneapolis, points out that unless the status of vegetable oils within the EPA changes, the primary benefits of using vegetable based lubricants will not be realized.

Another significant driver for the industrial use of vegetable oils is "green chemistry" initiatives by the U.S. government, which promote the development of new biobased products and processes. Related to this is the 2002 Farm Bill, which promotes cooperation between agriculture and other industries towards the use of home-grown chemical resources as alternatives to petrochemicals.

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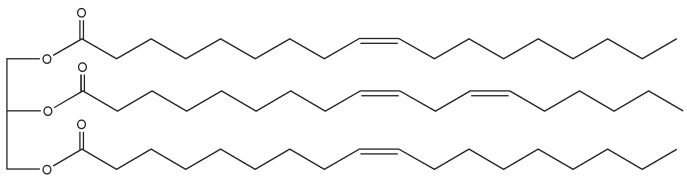
As a result, biobased chemicals and materials are growing fields for a range of industries, including polymers, adhesives, personal-care products, coatings and, of course, lubricants and fuels. In these markets, manufacturing companies use marketing terms such as renewable, biobased, green, environmentally sound, and natural, in order to establish a responsible image to their customers, and increase the value of their products.

Natural vs. Synthetic This brings us to synthetic vs. natural esters. Fully synthetic ester base oils are generally of two types — diacid esters and polyol esters. Both are biodegradable and non-toxic and highly amenable to environmentally sensitive applications. Synthetic esters are manufactured from selected alcohols and acids, and are well known to offer superior and unique levels of lubricant performance in terms of cold-flow properties, thermal stability and resistance to oxidation, as shown by their use in aviation gas turbine, refrigeration, and severe compressor applications. Since most commercial acids are vegetable based, many synthetic ester also can claim a significant level of renewable content.

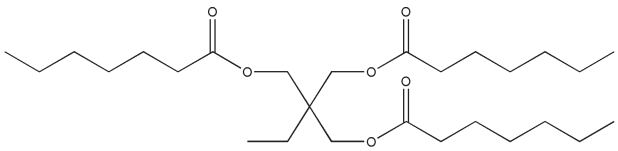
On the other hand, the components for synthetic esters may also be animal fat or petrochemical based, which is why synthetic esters typically are not claimed to be biobased. But, the main market hurdle for synthetic esters is the price. Their high performance is directly related to the selection and purity of the acids and alcohols used to make them, and that processing leads to higher costs. Nonetheless, synthetic esters are well established in selected markets, particularly forestry and freshwater management applications, because they have excellent performance under severe conditions coupled with ready biodegradability and low toxicity.

By contrast, vegetable oil based products, such as those produced from canola, soy, palm and sunflowers, are referred to as natural esters since they are used following extraction and purification that does not involve chemical changes to the oil. The chemistry of different vegetable oils is fairly similar in that they are triglycerides (esters derived from glycerine and a range of fatty acids from C_{12} to C_{18}).

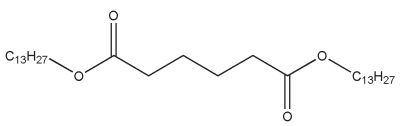
Canola and soy are among the more common vegetable oils applied as lubricants, and they are both made up mainly of oleic and linoleic acids. Both oleic and linoleic have points of unsaturation, or carbon-carbon double bonds. These double bonds



A Triglyceride Ester



A Timethylolpropane Ester



An Adipate (Diacid) Ester

are reactive to heat and oxygen, and are a main source of vegetable oils' poor oxidative stability, one of the key performance issues. Vegetable oils can be hydrogenated, which converts the carbon-carbon double bonds to single bonds (and makes a saturated fat), and this will improve the stability. Unfortunately, as we all know, hydrogenation also raises the pour point, which is why hydrogenated vegetable oils become spreadable, like butter, at ambient temperatures.

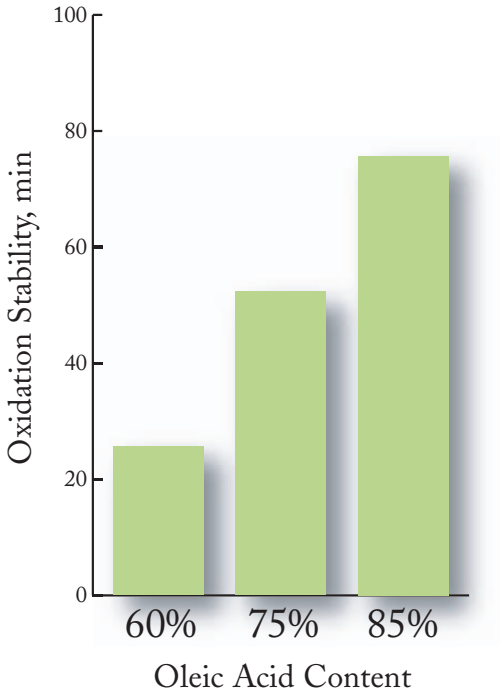
Strategic Moves So what is being done to make vegetable oils more attractive as lubricant base oils? There are three methods by which vegetable oil based products have been improved so that they can be used in more severe applications.

The first involves simply blending natural vegetable oils with fully synthetic esters. This may seem like a trivial approach but in fact, there are a number of important results achieved through blending vegetable with synthetic oils. When compared to fully synthetic ester lubricants, blends with natural esters will be less costly. And compared to pure vegetable oils, performance may be improved in terms of oxidation stability and low-temperature properties.

Further, in markets where legislation may require a defined minimum of natural content, or simply for green marketing purposes, blending natural vegetable oils with synthetic esters is a simple yet highly effective formulating method to meet those needs.

A second development for use of vegetable based lubricants is that edible oil production has evolved towards hybrids of higher oleic acid contents and lower linoleic content. Dietary health recommendations today favor mono-unsaturated fats (those with more oleic acid) over polyunsaturated fats (those with linoleic acid). Since linoleic acid has poorer oxidative stability for industrial purposes, reducing its content subsequently improves the overall stability of the vegetable oil.

Oxidation Stability of Canola Oil



Source: Cargill

Testing by pressurized differential scanning calorimeter (PDSC) has shown that high oleic canola (85 percent oleic acid) can provide a three times improvement in oxidation stability over conventional canola containing 60 percent oleic acids (see graph, at right). The fact that the high oleic oils are preferred for the edible market is good for lubricant applications since oils supplied to both streams can be derived from the same natural source.

A third approach to using vegetable oils for lubricants is to impose a chemical modification to improve the properties of the original vegetable oil. The final oil is no longer "natural," but it is made up of nearly all renewable content. Partial hydrogenation is one method to improve oxidation stability but as already discussed, the benefit is limited since low-temperature properties are compromised. More promising is the process called transesterification.

A recently published example involves transesterification of a natural triglyceride to a new polyol ester fluid. The process begins with palm oil being converted to fatty acid methyl esters which were then transesterified with trimethylolpropane (TMP). The new TMP ester can be considered a fully synthetic base oil, but the main components — all of the fatty acids — are natural based.

This means that a final product that uses an ester synthesized in this way can make a stronger "green" claim. In the case of palm oil, the resulting TMP esters provided a pour point reduction of 25 degrees C from the starting palm oil as well as improved oxidation stability.

Final Hurdles At this time, a range of formulated vegetable oil based products are available from a number of specialty lubricant suppliers. Companies like Cargill, which is fully integrated in vegetable oils, are keeping a careful eye on market demands and trends. "We can provide a number of biobased fluids that are becoming increasingly useful in lubricant applications," states del Valle.

But there is a lot of work to be done, not the least of which is to overcome the cost issue. For many applications, vegetable oil based lubricants should be a perfect fit but they are not yet at the required price point for commodity lubricant markets.

Another major hurdle is the comparative environmental effect of the fully formulated oils as opposed to the base fluids alone. While ester base oils are biodegradable and non-toxic, a full array of non-toxic additives is not yet available to formulators — not the least of which is a viable alternative to zinc dialkyldithiophosphate (ZDDP), the ubiquitous performance additive that is detrimental in toxicity tests.

The market for vegetable oil lubricants is not large but it is growing, and environmental considerations and concerns over crude oil continue to support further investment. As product development chemists and engineers consistently include vegetable based oils in their development processes, new benefits, new applications and new markets are inevitable.

Waiting for the market pull to meet the technology push can be a long process, but right now, it looks like green still means go. ▮

Dr. Ray Bergstra, a consultant to the lubricants and specialty chemicals markets, is the sole proprietor of MTN Consulting Associates based in Edmonton, Alberta, Canada. For information about this article, he can be reached by phone at (780) 436-3993 or e-mail to rjbergstra@shaw.ca.

what does green mean?

When it comes to environmental claims, there is a range of terms used to describe the "green-ness" of chemical base products.

The first is *biobased*. When discussing industrial materials, biobased suggests that the material is sourced from nature, and we tend to differentiate between chemicals and materials that are mined and refined vs. those derived more directly from plants. The latter are often referred to as "green" chemicals as well as renewable. (The reality is of course that most everything is ultimately biobased. Even crude oil comes from long-dead vegetation, but the distinction is that this doesn't happen during a reasonable human time frame.) Products of fermentation processes are one very important type of renewable chemicals.

Biodegradable products are those that will largely biodegrade within a time frame specified by industry standard testing. Such products also are referred to as *readily biodegradable*. This category includes synthetic ester and vegetable oil based lubricants.

Environmentally safe or *environmentally benign* implies a product that contains low or no levels of harmful components (typically defined by aquatic toxicity), and would not pose a significant hazard if small quantities were spilled. An ashless paraffinic hydraulic oil is a good example. These products are sometimes referred to as *inherently biodegradable*, because they will eventually degrade, but not within industry guidelines noted above.

Environmentally friendly is an ambiguous, non-technical marketing term that is used to promote any number of product attributes that can be related to being, at some level, less harmful to the environment. Longer service life, low toxicity, higher efficiency and recyclable are all claims that can have a positive effect on the environmental impact of a product. In every case, clarification is required as to what this claim actually refers to.

Natural products are those chemicals or materials that can be extracted from a living source, i.e. vegetable oils. Through plant breeding and genetic modifications, scientific advances have greyed this area, and many people are not buying into the "natural" status of genetically modified products. (I, for one, question the natural content of things like those crazy hard flavorless tomatoes, but that is another story.) For now, let's just say that if a chemical product is extracted from a plant, it is natural.

Therefore, as we consider how natural, non-toxic and biodegradable a product may be, we need to make sure we're on the same page. Then we can begin to assign various levels of "green-ness."

— *Ray Bergstra*