

Bio-lubricants advances using tailored molecular structures to address key durability challenges

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Introduction

Bio-lubricants are crucial to the bio-economy because they offer a sustainable alternative to petroleum-based products, enhance environmental protection, support economic growth through innovation, and align with global sustainability goals. Their development and use help build a more resilient, renewable-based economy that values resource efficiency, reduces greenhouse gas emissions, and fosters sustainable practices across multiple sectors. The current bio-based lubricants market has a relatively small share of the overall global lubricants market, with revenue of \$2.13B vs. \$132.44B in 2021 [1].

Improvements to bio-lubricant characteristics often rely on modifications to their inherent chemical structure. The synthesis of these novel bio-lubricants is derived from innovative chemically synthesised

bio-oil feedstocks. Over the years, different routes were explored to either enhance the lubrication characteristics by modifying the structure of the oil molecules by increasing the plant production of estolides, erucic acid, and wax esters, all of which showed a positive effect on the friction and wear-reducing capabilities of the oils [2-5] or by introducing nanomaterials [2-7]. Estolides, a type of bio-oil derivatives, have been gaining attention due to their ability to be tailored by oligomeric length and functional groups to achieve desired characteristics in viscosity and oxidation resistance [6], as seen in Figure 1 [8]. In addition to their high potential in the bio-lubricant industry, estolides are known for their incredible biodegradation and non-toxicity. Recently, improvements have been made to estolides, including novel synthesis methods using a mesoporous aluminosilicate [7].

Enhancing the lubrication properties

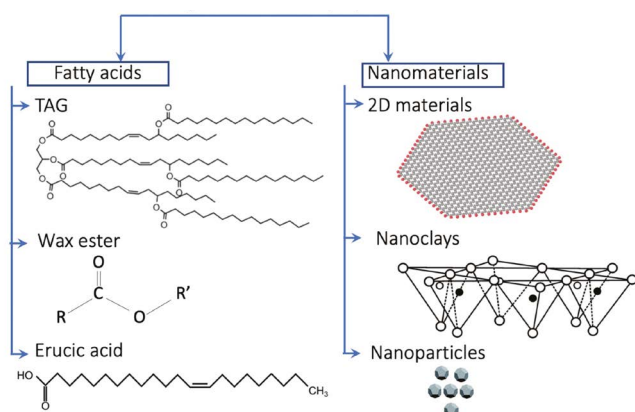


Figure 1: Approaches for improving the lubrication characteristics of plant-based lubricants reviewed below are divided into two groups, affecting the fatty acid structure through introduction of TAG estolides (example of TAG estolide from *Orychophragmus violaceus* seed oil is presented), wax esters or erucic acid and with the use of nanomaterials such as 2D materials, nanoclays or nanoparticles. Reproduced with permission from [8].

Natural, plant-based oils or natural fatty acids are often used as bio-lubricants or in the synthesis of estolides. Therefore, substantial research has been conducted on the properties of efficient bio-lubricants. Research has demonstrated a strong connection between erucic acid and lubrication efficiency [8]. The greater the content of erucic acid found in the plant-based oil, the greater the lubrication efficiency of the oil. Another example of a bio-lubricant that has been seen to improve lubricant efficiency is wax esters. This class of esters is also mainly derived from plants. In both cases, the isolation of the responsible fatty acid or ester led scientists to push the limits of production through novel genetic engineering. Quite recently, scientists have developed possible methods to boost both erucic acid concentrations and wax ester production through genetic modification of both leaves and the seed through *Agrobacterium* [9], [10].

Estolides

Estolides are produced through the formation of a carbocation at the site of unsaturation from a carboxylic acid and a fatty acid [11]. A positive charge is formed at the site of reaction, which

then forms an ester linkage through nucleophilic addition with another fatty acid. These linkages considerably strengthen the estolides' resistance to hydrolysis, which is a desirable trait in bio-lubricants [12]. This characteristic allows the bio-lubricant to resist degradation under high temperatures and the presence of water.

Over the years, researchers have developed unique methods for the mass production of estolides. Some examples include synthesising estolides from oleins (a class of unsaturated hydrocarbons) obtained from sunflower oil, rather than fatty acids, via a sulphuric acid-catalysed synthesis [13], [14]. The objective of the study was to transform low-value byproducts into high-value estolides while observing the effect of reaction time on the estolide kinematic viscosity. Controlling the kinematic viscosity allows for estolides to be used in a variety of lubrication applications. A 100g of olein samples was equilibrated to 50°C and catalysed with concentrated sulphuric acid. The samples were purified and analysed. The results showed a strong, direct correlation with the molecular weight of the estolides formed. Molecular weight directly affects the estolide's viscosity, leading to the conclusion that the degree of oligomerisation (the process of producing estolides) can be controlled through reaction length [14].

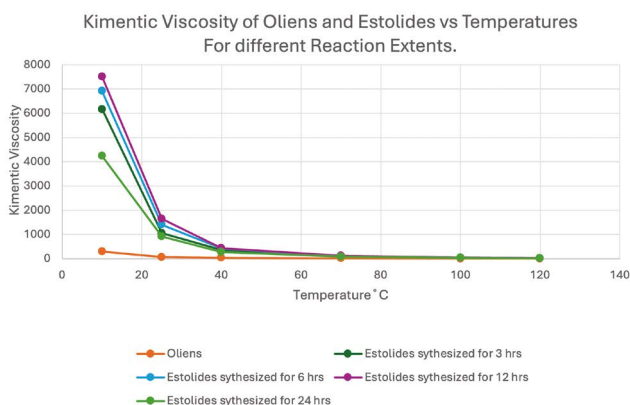


Figure 2: A graph characterising the effect of temperature on the Kinematic Viscosity of different Estolide samples and the Olein sample [14].

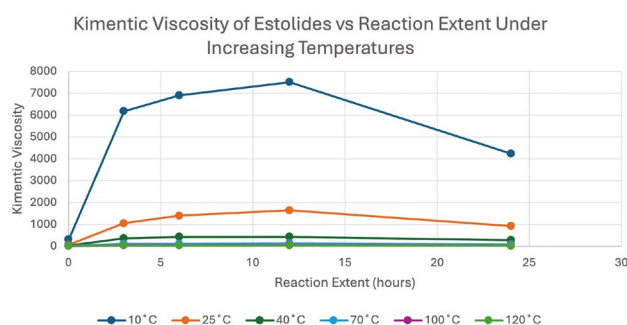


Figure 3: This graph demonstrates the effect of reaction extent on Kinematic viscosity under different temperatures [14].

As seen in Figures 2 and 3, the extent of the reaction had the most significant impact during the first 3 hours and adversely affected the kinematic viscosity between 12 and 24 hours. However, it is not enough to consider the kinematic viscosity. The data in Figure 3 show an increase in kinematic viscosity with reaction extent, suggesting that viscosity can be controlled by reaction extent. However, the desirable characteristic of bio-lubricants is a high viscosity index, or the lubricant's ability to maintain viscosity under high temperatures. The reported viscosity index of the estolides produced with oleins was 178 ± 5 , which is considered on the lower end. In fact, it was 7% lower than the oleins. Although estolides produced from oleins are not as effective on their own, they can act as powerful viscosity modifiers, significantly improving the efficiency of other bio-lubricants. Although creating an estolide bio-lubricant from oleins was unsuccessful, the experimental studies established fundamental techniques for estolide synthesis. They revealed additional possibilities for estolides in the field of bio-lubricants [14].

More recently, researchers have been focusing on a cleaner approach to estolide synthesis, prioritising the biodegradability of the produced estolides and using more environmentally friendly feedstocks. Researchers A. Dalai et al. developed a novel formulation that transforms canola biodiesel into biodegradable estolides through a mesoporous aluminosilicate-

catalysed reaction [7]. The benefits of facilitating this reaction on the mesoporous aluminosilicate are that the catalyst boasts an extremely high surface area, optimal acid conditions, and is compatible with the construction of large organic molecules. Additionally, the catalyst's heterogeneous nature makes it easy to separate from the product and reuse it in subsequent formulations. The resulting estolide was produced with a 96% yield and was tested and characterised as shown in Table 1.

Characteristic	
Viscosity Index	215
Pour Point	$-28 \pm 2.3^\circ\text{C}$
Lubricity or Wear Scar Diameter	$106 \pm 7.4 \mu\text{m}$
Biodegradability	$92 \pm 4.6\%$ in 28 days

Table 1: Key Characteristics of the resulting Estolides [7].

The product was confirmed to be an estolide through H-NMR characterisation. The viscosity index (VI), an essential indicator of thermal stability, of the product was exceptionally high compared to the previously discussed VI of estolides (around 178 ± 5) [15]. This indicates that the produced estolide is a strong candidate as a bio-lubricant. The pour point of $-28 \pm 2.3^\circ\text{C}$, is favourable for bio-lubricants. The pour point is the lowest temperature at which the estolide will flow, given the influence of gravity. The low temperature indicates that this bio-lubricant will still perform at low temperatures. The lubricity, or the measure of how effective the estolides are at lubrication, is measured with wear scar diameter (WSD). The lower the WSD, the better the lubricant reduces friction. Compared to pure diesel WSD of $600 \mu\text{m}$, the produced estolide offers significantly greater friction reduction as its WSD sits around $106 \mu\text{m}$. The biodegradability of the produced estolides achieved $92 \pm 4.6\%$ aerobic mineralisation within 28 days. The proposed synthesis strategy is optimal and highly effective, offering flexibility in a variety of weather conditions, biodegradability, and a clean feedstock option, as well as high yield [7].

Wax esters

Wax esters are organic compounds consisting of an ester formed between a long chain of fatty acid and a long chain fatty alcohol [10]. In past years, wax esters were obtained from now-banned whaling methods, specifically from sperm whales. Currently, methods for securing spermaceti oil remain unsustainable or difficult to implement. Methods range from cultivating the desert plant jojoba to chemical processes using petroleum derivatives. Ultimately, these processes fell out of favour due to high energy costs or difficulty in execution. However, methods using synthetic biology have been investigated to modify plants to produce wax esters rather than the usual triglycerides. Researchers K. Demski et al. focused on genetically engineering the tobacco plant, *Nicotiana benthamiana*, using a mix-and-match approach [10]. Through this process of trial and error, the researchers were able to formulate a pathway to synthesise wax esters like spermaceti oil to act as a bio-lubricant. To achieve this, the plants were modified using *Agrobacterium*, following a 4-step process.

The first step of this enzymatic pathway is catalysed by Fatty Acyl-ACP Thioesterases (FAT), which control fatty acid chain length by removing fatty acids of the desired length. Different FAT enzymes were used to prioritise fatty acid lengths of 12-16 carbons. Then, enzymes from the codling moth and navel orange worm are added to introduce specific areas of unsaturation into the fatty acid, in the Z or E configuration. Fatty Acyl-CoA Reductases (FAR) enzymes are used to convert fatty acids to fatty alcohols. Finally, the wax ester is assembled with a wax synthase [10]. The desired products were first isolated from the tobacco leaves with thin-layer chromatography, and then the wax esters were decomposed and characterised in gas chromatography. Ultimately, the results indicated that the produced wax ester resembled that of spermaceti oil. The engineered wax esters closely resembled the composition of natural spermaceti oil.

The composition of the C12-C16 carbon chain-length chains species vary; however, it is more important that we can accurately design wax ester compositions. This was achieved successfully in this experiment. Although the composition of the target compounds (12:0–16:0 fatty acid and fatty alcohol) moieties was not reported, it was found that they achieved the highest content of the target compounds. It remains unclear whether this process is ready for mass production; this sets a precedent for future chemical production via crop transformation. This process has laid the foundation for genetic engineering targeted in chemical synthesis through synthetic biology. Interestingly, this method has shown potential for synthesising insect sex pheromones, with possible uses as environmentally sustainable crop deterrents [10].

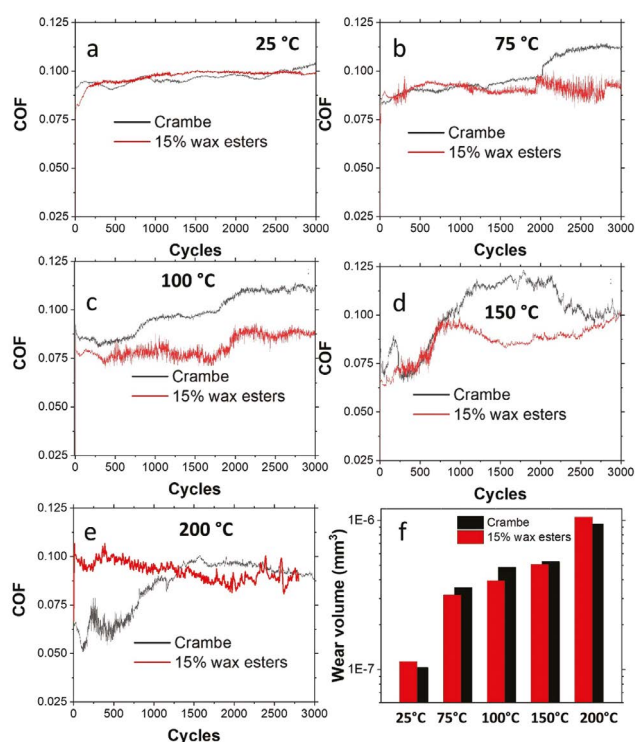


Figure 4: Coefficient of friction behavior for Crambe oil and Crambe oil with 15 wt.% wax esters at (a) 25°C, (b) 75°C, (c) 100°C, (d) 150°C, and (e) 200°C. Reproduced with permission from [9].

In a recent study, Shirani et al. [9] demonstrated that the lubrication performance of conventional Crambe oil can be significantly improved by incorporating

wax esters derived from genetically modified Crambe seeds (Figure 4). Although no noticeable enhancement was observed at ambient temperature, substantial reductions in friction and wear occurred under elevated temperature conditions. Their findings indicate that adding 15 wt.% wax esters to Crambe oil enhances thermal stability, as confirmed through tribological testing, quartz crystal microbalance (QCM) measurements, and fourier-transform infrared spectroscopy (FTIR) analysis. QCM results revealed that above 100°C, the wax ester component dominates the mixture's behavior, providing greater thermal stability and reduced sensitivity to temperature fluctuations. This leads to slower viscosity changes and improved mechanical resistance during heating, making the modified oil more effective as a high-temperature lubricant.

Erucic acid



Figure 5: *Brassica carinata* being grown in a home garden [16].

Erucic acid, a 22-carbon monounsaturated fatty acid, is valued for its varied uses in the bio-lubricant industry and as a high-quality wax ester feedstock [8]. Similarly to the process described earlier, researchers M. Tesfaye et al. [17] focused on producing erucic acid and wax esters in a plant setting through genetic modification of plant seeds. Compared to the previous method, this method is far superior in the industry setting, as the two metabolic pathways introduced into the

oilseed crop *B. carinata*, pictured in Figure 5, become permanent; therefore, the cultivation process following the modification is suitable for industrial mass production [17]. Not only is this developed method suitable for industry demands, but it also produces highly valued erucic acid. Erucic acid bio-lubricants have desirable properties such as a high viscosity index and thermal stability. The long carbon chains allow for durable lubrication membranes to form [18].

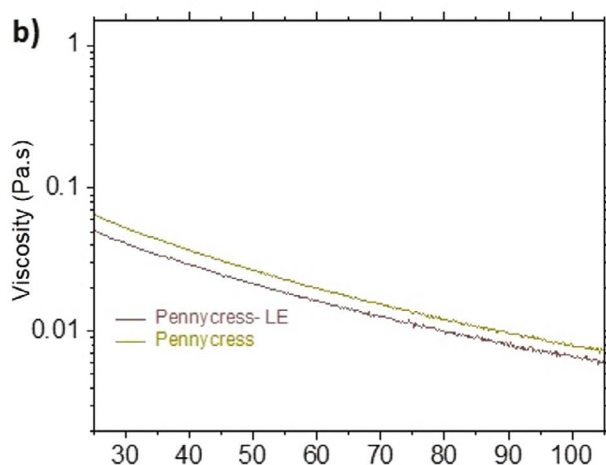
Feedstocks with high erucic acid content are sought after for their ability to synthesise drop-in biofuels and high-quality wax esters. Despite erucic acid bio-lubricants being characterised as biodegradable and non-toxic, high erucic acid is undesirable in food-grade oils. Associations with cardiovascular health raise concerns have limited the use of erucic acid in edible oils [8]. However, in the context of bio-lubricant applications, this characteristic alleviates concerns regarding competition with food uses. A major topic of discussion is the food vs. fuel debate: since erucic acid bio-lubricants are not suitable as edible oils, there is no genuine concern about what the oil's use will be. Additionally, from an economic perspective, cultivating crops designed for erucic acid production reduces purification costs by half for every 10% increase in erucic acid concentration. Results from this experiment yielded highs of 52.7%, a 29% increase compared to unmodified or wild *B. carinata* [17]. The modifications not only significantly improve the yield from each acre of land occupied but also reduce costs in the purification and isolation of erucic oil.

By comparing pennycress oil with high (Pennycress) and low (Pennycress-LE) content of erucic acid (Figure 6), Al Sulaimi et al. [10], demonstrated that viscosity and the oxidation initiation time (OIT) decreased almost 2 times (OIT reduced from 41 minutes to 26 minutes) when the presence of C22:1 changed from 35.7 mol% to 1.8 mol%. These results suggested the positive effect of erucic acid on the oxidation stability of plant-based oils.

a)

Mol% Composition		
Fatty Acids	Pennycress-LE	Pennycress
C16:0	3.5	2.5
C16:1	0.1	0.1
C18:0	1.2	0.6
C18:1 cis	40.8	15.5
C18:1 trans	2.5	1.2
C18:2	29.8	18.7
C18:3	17.6	9.6
C20:0	0.3	0.3
C20:1 cis	1.4	9.7
C20:1 trans	0	0.7
C20:2	0.2	1.5
C22:0	0	0.2
C22:1	1.8	35.7
C22:2	0	0.6
C24:1	0.7	3
C18:1-OH		
C20:1-OH		
C20:2-OH		

b)



c)

Bio Lubricants	Oxidation
Pennycress-LE	26 minutes
Pennycress	41 minutes

Conclusions

The growing field of bio-lubricants offers a cleaner alternative, with many of the advances discussed addressing significant issues, such as performance limitations, sustainability concerns, and a lack of technology and infrastructure. Advances in estolide production have enabled estolides with high yields, high viscosity indices, and high lubricity. Compared with experiments that established the fundamentals of the estolide output, the bio-lubrication properties have significantly improved. Wax ester and erucic acid have both seen advances in synthetic biology, with research focused on the sustainable production of two promising bio-lubricants through genetic engineering of plants. Overall, advances in technology and scientific understanding in the field continue to accelerate the adoption of bio-lubricants, with estolides already demonstrating greater thermal resistance than traditional mineral oils [15]. As bio-lubricants grow in popularity, infrastructure will naturally follow, and technology will be developed to optimise production. Traditional lubricants may have a high bar to meet, but bio-lubricants offer almost limitless potential through the range of possible formulations and organic synthesis methods. Very soon, lithium-based lubricants may increasingly be replaced by a much more sustainable, cleaner, and non-toxic alternative of bio-lubricants.

Figure 6: Comparison between Pennycress-LE and Pennycress a) mol% composition of FA, b) the dynamic viscosity of both bio-oils and c) OIT values. Reproduced with permission from [10].

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Biographies

Dr. Raj Shah, is a Director at Koehler Instrument Company in New York, where he has worked for the last 25 plus years. He is an elected Fellow by his peers at ASTM, IChemE, ASTM, AOCS, CMI, STLE, AIC, NLGI, INSTMC, Institute of Physics, The Energy Institute and The Royal Society of Chemistry. An ASTM Eagle award recipient, Dr. Shah recently coedited the bestseller, "Fuels and Lubricants handbook", details of which are available at ASTM's Long-awaited Fuels and Lubricants Handbook <https://bit.ly/3u2e6GY>. He earned his doctorate in Chemical Engineering from The Pennsylvania State University and is a Fellow from The Chartered Management Institute, London. Dr. Shah is also a Chartered Scientist with the Science Council, a Chartered Petroleum Engineer with the Energy Institute and a Chartered Engineer with the Engineering council, UK.



Dr. Raj Shah

Dr. Shah was recently granted the honorific of "Eminent engineer" with Tau beta Pi, the largest engineering society in the USA. He is on the Advisory board of directors at Farmingdale university (Mechanical Technology), Auburn Univ (Tribology), SUNY, Farmingdale, (Engineering Management) and State university of NY, Stony Brook (Chemical engineering/ Material Science and engineering). An Adjunct Professor at the State University of New York, Stony Brook, in the Department of Material Science and Chemical Engineering, Raj also has over 700 publications and has been active in the energy industry for over 3 decades.

Dr. Diana Berman received her Ph.D. degree in Physics from North Carolina State University in 2012. After graduating, she worked as a PostDoctoral Researcher in Argonne National Laboratory, at the Center for Nanoscale Materials. In 2016, she joined the University of North Texas as an



Dr. Diana Berman

Assistant Professor in the Department of Materials Science and Engineering. Her research focuses on understanding fundamental aspects of friction, wear, and lubrication of materials with a larger vision of how this knowledge can be applied in practice. She has published more than 70 papers in peer-reviewed journals and 2 book chapters. She also holds more than 10 patents (both US and International). Among her awards are TechConnect Innovation Awards, Ralph E Powe Junior Faculty Enhancement Award, Society of Tribologists and Lubrication Engineers Early Career Award, UNT Early Career Professorship Award, UNT Research and Innovation Award, and NSF Early Career Award.

Mr. Clark Ye is part of a thriving internship program at Koehler Instrument Company in Holtsville, NY underneath Dr. Raj Shah. Ye is also a student in the department of Material Science and Chemical Engineering at Stony Brook University, where Dr. Shah serves on the External Advisory Board.



Clark Ye

Mr. Gavin Thomas is part of a thriving internship program at Koehler Instrument Company in Holtsville, NY and is a recent graduate of the Chemical and Molecular Engineering program at Stony Brook University. He also works as a process engineer at Mill-Max in Oyster Bay, NY where he becomes hands-on with various production processes to ultimately improve safety, efficiency, and cost-effectiveness.



Gavin Thomas

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