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# Recent developments in Synthetic Lubricant technology

***Dr. Raj Shah*** *and* ***Ms. Rachel Ly****, Koehler Instrument Company*

## Introduction

In 1877, Charles Friedel and James Mason Crafts conducted the first organic synthesis of hydrocarbons to develop synthetic fluids, the base fluids for modern synthetic lubricants. At that time, however, the abundance of cheap mineral oil discouraged the widespread commercialisation of this ingenious discovery. It was not until World War II that the scarcity of mineral oil worldwide paved the way for Germany's first large-scale production of synthetic fluids in lubricants for aviation and high-pressure compressor applications. [1] Looking at 2023, the field of synthetic fluids and lubricants continues to garner more interest worldwide with the Global Synthetic Lubricants Market valued at $42.53 billion and an expected growth rate of 3.3% from 2024 to 2032. [2] Despite the steady dominance of conventional lubricants in the twenty-first century, many researchers are proposing synthetic lubricants as a more reliable, energy-efficient solution for friction due to their superior tribological properties and justifiable greater environmental sustainability as result of that. This paper will present our modern industrial and chemical understandings of conventional and synthetic lubricants, comparative tribological test studies between the two, and the latest breakthroughs in the organic synthesis of synthetic lubricants to highlight their long-term favorability.

## Synthetic Lubricants: Properties and Applications

Synthetic lubricants are produced from man-made synthetic-based fluids containing specific petroleum-derived chemical compounds. The most seen synthetic-based fluids (SBF) are referred to as Group V SBFs, which are categorised into synthetic hydrocarbons, organic esters, polyglycols, phosphate esters, silicones, alkylated naphthalene, and blends of SBFs; the first four fluids listed comprise 90% of SBF usage worldwide. [3]

These compounds in SBFs have relatively low molecular weights with controlled molecular structures to yield desirable and predictable properties for their specialised functions: [3][4]

Synthetic hydrocarbon fluids, like polyalphaolefins (PAOs), are often used in engine oils, gas turbines, and aircraft hydraulic systems due to their hydrolytic stability, low temperature fluidity, and high shear rate viscosity.

Organic esters, like diesters or polyol esters, offer biodegradability, high film strength, and metal-wetting properties at low vapor pressures for compressor lubricants, turbines, and aviation applications. However, diesters could damage paint and seal materials and should be applied carefully depending on the application.

Polyglycols, like polyalkylene glycols (PAGs), are one of the earliest synthetic lubricants created from ratios of ethylene oxide and propylene oxide. They possess exceptional viscosity and thermal properties for applications in hydrocarbon gas compressors from -40°C to 204°C as well as excellent anti-sludging properties.

Phosphate esters, typically found in brake fluids and aircraft hydraulic systems, are characterised by their fire resistance properties. However, they are prone to hydrolytic degradation which could result in the formation of corrosive phosphoric acid that could damage paint and seal materials.

Silicones are chemically inert, providing them with excellent heat resistance and oxidative stability. Despite this, they present insufficient lubricity that limits their applications to only vacuum greases. Alkylated naphthalene displays oxidative and hydrolytic stability in high-moisture environments, seal capability, and improved additive effectiveness in food production, wind turbine, and transmission oil applications. Additionally, it can be blended with other base oils to enhance their overall solubility, cleanliness, and durability. [5]

Blends of SBFs within these categories or with petroleum lubricants are often found in gearboxes, diaphragm pumps, and compressors for effective, synergistic reactions. They can also be used in food production, wind turbines, and transmission oils.

## Comparative advantages of synthetic lubricants against conventional lubricants

Conventional lubricants developed by mineral oil refinement have been the mainstream lubricant to combat frictional barriers since the nineteenth century. Conventional mineral base oils for lubricants originate from vacuum distilled crude oil fractions that undergo sequential refining processes: solvent extraction, dewaxing, and hydrocracking. Firstly, solvent extraction removes aromatics from vacuum distillates, enhancing oil viscosity, oxidation resistance, and sludge-forming resistance. Next, dewaxing processes filter wax crystal formations at low temperatures, resulting in increased turbidity and viscosity. Lastly, hydrocracking exposes mineral base oil to extreme pressures exceeding 100 bar and temperatures ranging from 200°C to 350°C, improving ultraviolet stability and acidity through desulphurisation. [6]

Despite their low prices, conventional lubricants offer many drawbacks compared to synthetic lubricants. Problems linked to conventional lubricants include combustions by low temperature solidifications, oxidation, and viscosity loss caused by extended exposure to high temperature applications. According to Tribology International, mineral oil consists of intricate structures of hydrocarbon compounds with around 30 carbon atoms in each molecule. Moreover, as many as 125 different compounds were found in mineral oil and only 45 of them were precisely analysed, leading to uncertain understandings of the chemical properties in conventional lubricants. Additional inconsistencies in conventional lubricants stem from mineral oil base stocks being solely manufactured based on viscosity, leading to varying chemical compositions obtained from different crude oil and refineries. [7]

On the other hand, synthetic lubricants derived from specific man-made or biological compounds contribute to their well-defined chemical structures and properties. In general, synthetic lubricants are 2-3 times costlier than their conventional counterparts. However, they perform overall better than conventional lubricants with better oxidation resistance, high-temperature stability, low-temperature viscosity, and lower coefficients of friction. These advantages permit synthetic lubricants to be suitable for applications under more extreme temperature and pressure unattainable by conventional lubricants. Furthermore, the synthetic lubricants life cycle is 3 times longer than that of conventional lubricants, thus compensating for their initial high price and higher manufacturing carbon footprint.[8] Increased engine longevity also offers a more favorable environmental cost with limited oil changes, minimising carbon emissions and oil disposals while exercising fuel conservation. [9]

### Conventional v. synthetic oils: A tribological study by the American Automobile Association

In the past few years, more researchers have been advocating for the transition from conventional lubricants to synthetic lubricants. In 2017, the American Automobile Association (AAA) conducted a study to assess the effectiveness of readily available synthetic oils against conventional oils in gasoline engines. Eight ASTM tests focusing on high-shear viscosity, shear stability, moderate-temperature deposit formation, high-temperature deposit formation, evaporation loss, low temperature pumpability, oxidation stability, and oxidation viscosity were selected to evaluate the individual performances of five branded synthetic oil and conventional oils. [6]

AAA reported using ASTM D4683 to measure minimum HTHS viscosity at 150°C of an oil and ASTM D6278 to assess viscosity loss at 100°C after 30 cycles of shearing through a diesel injector. None of the conventional oils met minimum SAE J300 HTHS viscosity after shear while all but one synthetic oil did. Additionally, conventional oils displayed an average 92% greater viscosity loss than that of synthetic oils.

In the case of deposit formations, ASTM D7097 (TEOST MHT) and ASTM D6335 (TEOST 33C) were conducted to evaluate deposit formations by thermo-oxidation engine oil simulation tests at a moderately high temperature (285°C) and high temperature (485°C), respectively. Despite performing the tests twice on each oil, both tests displayed vastly different results such that a definitive statement could not be proposed. However, from the samples alone, conventional oils formed 41% and 37% more deposits on average when compared to synthetic oils in the two tests, respectively.

In terms of oil volatility, ASTM D5800 was used to determine evaporation loss via heating to 250°C with constant airflow. There were low standard deviations between the two oil groups, but conventional oils showed an average 46% higher volatility.

With regards to low-temperature pumpability, ASTM D5133 was performed to estimate oil viscosity at low shear rates from -5°C to -40°C, a temperature range at which excessive viscosity presence hinders oil pumpability with wax deposition accumulation. At specific temperatures of -28°C, -34°C, and -38°C, conventional oils exhibited an average of 30%, 45%, and 73% lower estimated viscosity than that of synthetic oils, respectively.

In the matter of oxidative stability, ASTM 4742 was carried out to assess the time needed to deplete an oil's antioxidant properties. One synthetic oil brand substantially outperformed the rest of the samples, but there were similar results between conventional and synthetic oils of the same brand.

Overall, AAA noted significant differences between the two oils' performances, with synthetic oils outperforming conventional oils in all tests by 47%, concluding that synthetic oils offer more vehicle protection in extreme environments and less engine wear throughout the lifespan of the vehicle. [6]

### Latest research on synthetic lubrication

Many other researchers are expanding the realm of synthetic lubricants by proposing the fluid synthesis of other organic compounds with tribological performance exceeding that of standard products:

### *1. Waste plastic-derived synthetic lubricants* [10]

In 2021, Hackler et al. attempted to produce synthetic lubricants from upcycled polyolefin waste plastics and compare their tribological characteristics to industrial standard mineral and synthetic oils. According to Hackler et al., more than 410 million metric tons of plastic are produced annually. Nonetheless, around 300 million metric tons of plastic are discarded each year with 58% found in landfills, 24% incinerated for heat and power, and 18% recycled. As shown in Figure 1, most plastics undergo mechanical recycling, a process of converting waste plastic into secondary raw materials for new products, but this method yields unfavorable downcycled products with lower quality than their primary source. On the other hand, chemical recycling proves to be a potentially more cost-effective strategy that upcycles waste plastics into high-value products through plastic polymer conversions to alkanes, alkenes, alkynes, and aromatics. A energy-efficient chemical recycling process known as catalytic hydrogenolysis, a process that severs carbon-carbon bonds by a catalyst and H2 to produce alkanes, has been experimented with a platinum on strontium titanate nano cuboid catalyst (Pt/STO) on high-density polyethylenes (HDPEs). Through this process, HDPEs were successfully transformed into high-quality liquids (HQLs) with potential applications as a base oil component in commercial automobile lubricants. Since total plastic production consists of 29% polyethylene and 17% polypropylene, the two most common polyolefins, hydrogenolysis was performed on various waste plastics with HDPEs, linear low-density polyethylene (LLDPEs), and bubble wrap. The tribological performance of the HQLs created from those polyethylene sources was compared to industrial standard mineral oil (Group III) and synthetic oils (PAO4 and PAO10).

These lubricant base stocks were subjected to an hour-long engine stimulation test with a ball-on-disc tribo-test machine at 100°C to analyse their changes in coefficient of friction (COF), represented graphically as seen in Figure 2. LLDPE-derived HQL displayed the lowest average COF of 0.08, followed closely by HDPE and bubble wrap-derived HQLs, which both had a 0.15. In fact, all HQLs revealed comparable COF

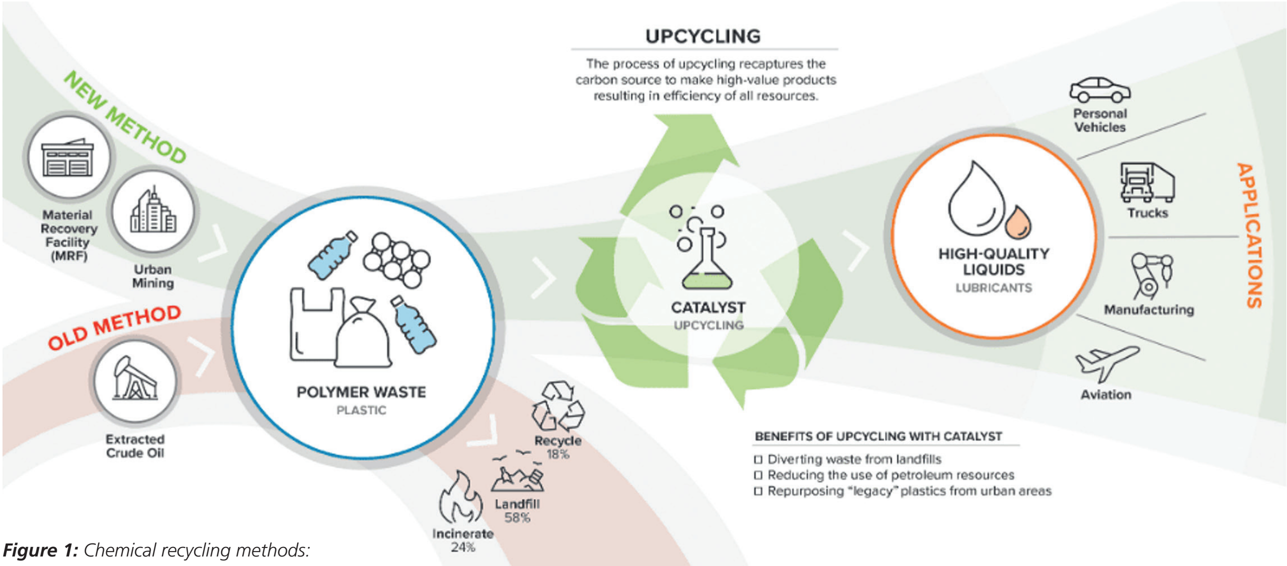

***Figure 1:*** *Chemical recycling methods: downcycling and upcycling [10]*

values to the best synthetic oil, PAO10. Meanwhile, Group III observed the greatest drop in COF over time, but the highest COF range from 0.14 to 0.19 during the first 40 minutes. The increase in COF of Group III is attributed to the abrasive and adhesive interactions between the ball and the significant amount iron oxide debris on the disc, implying Group III's inefficient surface protection.

Furthermore, each base stock's wear scar volumes from the ball-on-disc tribo-test were also examined with HQLs exhibiting a 43% reduction in wear compared to Group III. Both Group III and PAO4 were unable to protect their surfaces and produced large wear scars, which were results of high degrees of carbon branching that limited intermolecular forces within alkane chains and incapability of forming a protective layer with small molecules, respectively. However, PAO10 and all HQLs exhibited the lowest wear scars due to their extremely low carbon branching that encouraged methylene interactions in between alkane chains to maintain a protective film. The COF and wear scar volume results highlight HQLs' comparable tribological property of surface protection to that of industrial grade synthetic oils and both their superior performance over standard mineral oil.

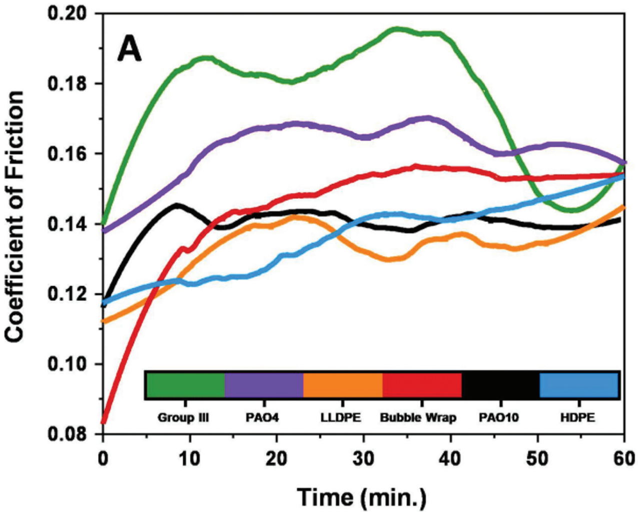

***Figure 2:*** *COF Changes at 300°C for Group III, PAO4, LLDPE, Bubble Wrap, PAO10, and HDPE [10]*

Figure 2. COF Changes at 300°C for Group III, PAO4, LLDPE, Bubble Wrap, PAO10, and HDPE[10]

Since HDPEs and PAO10 performed exceptionally well with similar COF results, synergistic interactions between the two were examined. 0, 10, 20, 30, 50, 70, 90, and 100 percent weight of HDPE-derived HQL was added to PAO10 before undergoing friction and wear tests at 25˚C and 100°C. Before the synergy, virgin HQL presented lower wear scar volume due to its high viscosity and increasing COF from the formation of an iron oxide tribolayer on the test disc at 25°C (Figures 3 and 4). However, virgin HQL obtained much lower COF with increased fluidity and wettability that prevented iron oxide accumulation at 100°C (Figure 5). After the various trials, an optimal 20-30% HQL in PAO10 at 25°C and 100°C demonstrated the most decrease in friction and wear of around 9% and 30%, respectively. The COF and wear scar volume results are even lower than that achieved by virgin PAO10 due to the addition of linear polymer chains in HQL enhancing the fluidity and polydispersity of bulky PAO10 molecules, creating a finer friction reduction.

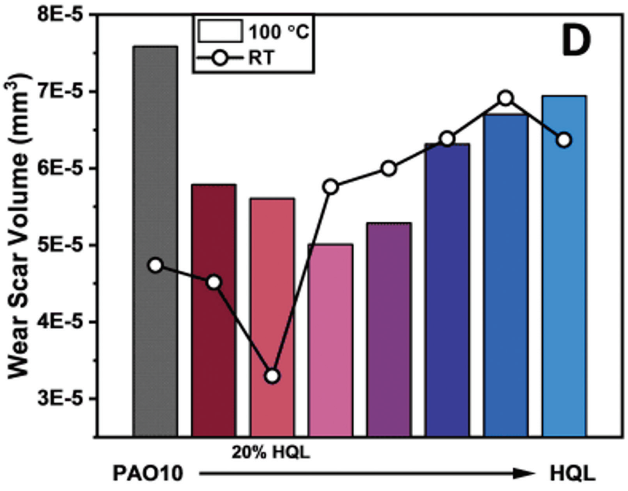

***Figure 3:*** *Wear Scar Volumes of PAO10 and HQL Concentrations [10]*

In the end, the performance of HQLs supersedes that of mineral oil and is on par with synthetic oil standards. The upcycling of mixed waste plastics as base oils for lubricants and additives for commercial lubricants proves itself a worthwhile, environmentally friendly investment towards lubrication technology that could reinforce our carbon economy. [10]

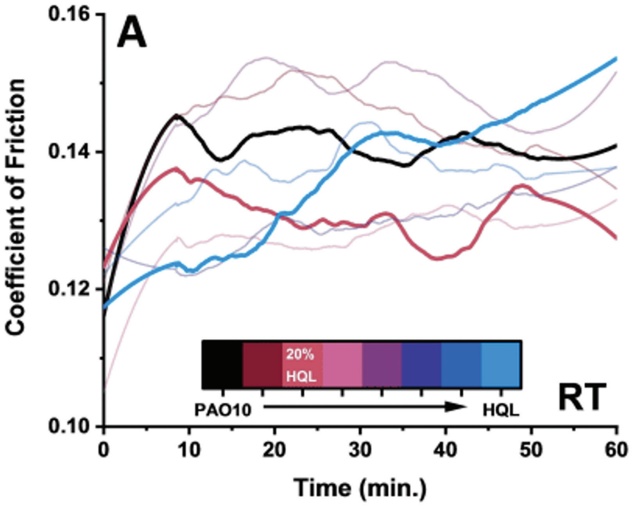

***Figure 4:*** *COF of PAO10 and HQL Concentrations at 25°C [10]*

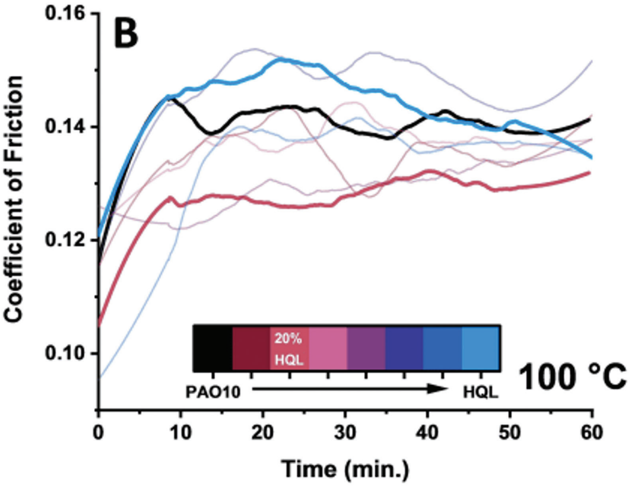

***Figure 5:*** *COF of PAO10 and HQL Concentrations at 100°C [10]*

## *2. A New Class of Synthetic Lubricants: "Triangle Ester"* [11]

In 2023, Sharma et al., explored a new class of cyclic esters that could have potential in lubrication applications. They have synthesised unprecedented three-membered heterocyclic rings known as "triangle esters" (LCEE and LCTE) derived from fatty acids and compared their properties on various substrates with esters synthesised from linear and alicyclic alcohols, LCLE and LCCE, respectively. Figure 6 displays the unique chemical structures of these esters. According to Sharma et al., effective lubrication is contingent upon the wettability of the lubricant or the affinity of a lubricant towards the substrate. The wettability of a lubricant can be evaluated by its spreading parameter (SP) or spreading-wetting tendency, a trait dependent on chemical structure, surface tension, and polarity. Here, the surface tension and polarity of synthesised esters, the building blocks of lubricant oils, will be measured to calculate spreading parameters that reflect their overall lubrication potential.

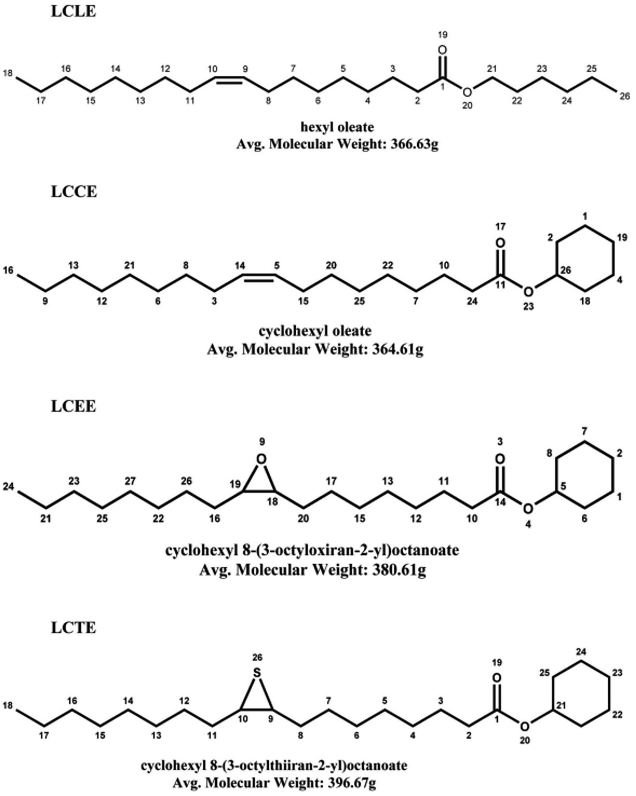

***Figure 6:*** *Chemical Structures of Synthesised Esters [11]*

The surface tension of LCEE, LCTE, LCLE, and LCCE on various substrates, including aluminum (AL), phosphor bronze (PB), brass (BRS), stainless steel (SS), and gun metal (GM), were measured via a pendant drop method at 25°C. The average surface tension values on these substrates, alongside the general physicochemical properties of the esters, are summarised in Figure 7. The average surface tension values in descending order were LCTE > LCEE > LCCE > LCLE; the greater surface tension values found in LCTE and LCEE imply the greater intermolecular forces and degree of polarity within these esters with three-membered rings.

| Lubricants | LCLE | LCCE | LCEE | LCTE |
|---|---|---|---|---|
| Total surface tension at 25 °C | 17.86 | 19.51 | 20.57 | 21.68 |
| $\gamma$(p) at 25 °C | 7.40 | 7.10 | 9.01 | 9.78 |
| $\gamma$(d) at 25 °C | 10.46 | 11.41 | 11.56 | 11.90 |
| PF | 0.420 | 0.364 | 0.438 | 0.446 |
| Kinematic viscosity (mm$^2$/s) 40 °C | 15.671 | 10.886 | 13.424 | 16.642 |
| 100 °C | 3.986 | 3.086 | 3.385 | 3.764 |
| Viscosity index | 160.542 | 152.579 | 128.772 | 115.641 |
| Density (g/cm$^3$) | 0.896 | 0.854 | 0.889 | 0.914 |
| Total acid number (mg KOH/g oil) | 0.24 | 0.33 | 0.29 | 0.37 |

***Figure 7:*** *Physicochemical Properties of LCLE, LCCE, LCEE, LCTE Synthesised Esters [11]*

Based on the surface tension values and contact angles of the esters across all substrates, the SP of the esters in ascending order was LCEE < LCTE < LCLE < LCCE. The less polar lubricants, LCCE and LCLE, exhibit high SP values that suggest their weak Van der Waals interactions with polar substrates and inability to protect the substrate from wear. Meanwhile, polar lubricants like LCEE and LCTE offer lower SP values that exemplify their strong interaction with substrates and wettability to protect surfaces. Moreover, SP models are useful in predicting the coefficient of friction (COF) trend between lubricants and substrates with higher SP values implying higher COF values. The direct correlation between SP and COF is verified with a ball-on-disc friction test to precisely measure the COF of each lubricant on different substrates, which in descending order was LCCE > LCLE > LCEE > LCTE. The values of SP and COF of each lubricant with its respective substrate are listed in Figure 8.

| Substrate | Lubricant | SP | COF |
|---|---|---|---|
| AL | LCLE | 14.52 | 0.148 |
| BRS | LCLE | 13.26 | 0.141 |
| PB | LCLE | 9.77 | 0.131 |
| SS | LCLE | 8.64 | 0.127 |
| AL | LCCE | 15.72 | 0.16 |
| BRS | LCCE | 14.49 | 0.147 |
| PB | LCCE | 11.03 | 0.132 |
| SS | LCCE | 9.95 | 0.129 |
| AL | LCEE | 13.50 | 0.122 |
| BRS | LCEE | 12.30 | 0.117 |
| PB | LCEE | 9.05 | 0.095 |
| SS | LCEE | 7.90 | 0.072 |
| AL | LCTE | 12.29 | 0.109 |
| BRS | LCTE | 10.95 | 0.105 |
| PB | LCTE | 7.23 | 0.078 |
| SS | LCTE | 6.01 | 0.060 |

***Figure 8:*** *SP and COF of LCLE, LCCE, LCEE, LCTE Synthesised Esters on Substrates [11]*

The exceptional wetting behavior of LCEE and LCTE highlights the potential future applications of novel "triangle esters" for synthetic lubricants over traditional linear and acyclic esters lubricants, like LCLE and LCCE. Nonetheless, this study limits its results to the substrates chosen and specified lubricants of the same carbon chain length, requiring further studies with other types of lubricants and higher-pressure environments. From a holistic view, this innovative research has expanded the field of synthetic lubricants by introducing a preliminary, improved classification of synthetic esters that may widen future industrial and consumer options. [11]

## Conclusion

Looking into the 21st century, synthetic lubricants are gradually becoming the new frontier of tribology as researchers recognise the limited understanding of mineral oil in conventional lubricants. Cross examinations between conventional and synthetic lubricants prove the latter can be more energy-efficient, and possibly provide a long-term solution to global friction and wear prevention. As this field of study continuously expands with the creative synthesis of unconventional organic sources, like waste plastic and triangle esters, it is feasible that these new, green synthetic methods and variety could eventually substitute more conventional lubricants on a commercial and industrial scale. However, before then, future analysis into methods and feasibility in executing these research projects on a commercially viable scale would need to be another step to assist in the transition to synthetic lubricants.

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## About the Authors

***Dr. Raj Shah*** is a Director at Koehler Instrument Company in New York, where he has worked for the last 30 years. He is an elected Fellow by his peers at IChemE, CMI, STLE, AIC, AOCS, 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 2nd Edition Now Available" (https://bit.ly/3u2e6GY). He earned his doctorate in Chemical Engineering from Pennsylvania State University and is a Fellow of 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. 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 the State University of New York, Farmingdale (Mechanical Technology and Engineering Management); Auburn University (Tribology); and the State University of New York, Stony Brook (Chemical Engineering/Materials Science and Engineering). An Adjunct Professor at Stony Brook University, in the Department of Materials Science and Chemical Engineering, Raj also has over 675 publications and has been active in the energy industry for over 3 decades. More information on Raj can be found at https://bit.ly/3QvfaLX.

Contact: rshah@koehlerinstrument.com

***Ms. Rachel Ly*** is part of a thriving internship program at Koehler Instrument Company in Holtsville and is a student of Chemical Engineering at Stony Brook University, Long Island, NY, where Dr. Shah is the current chair of the external advisory board of directors.