Lube-Tech

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Circular fatty acids upcycled from food residues – Caproic acid for sustainable low viscosity polyol esters

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Introduction

Every year, the world generates over 930 million tons of food waste, exacerbating environmental challenges and squandering valuable resources. From production to disposal, food waste significantly contributes to greenhouse gas emissions, water wastage, and lost economic potential. However, a new wave of innovations is turning this problem into an opportunity. ChainCraft's proprietary three-step process using non-GMO, open mixed culture fermentation enables upcycling food residues into valuable chemicals, such as medium-chain fatty acids and fertiliser products.

These fatty acids serve as essential building blocks in industries ranging from specialty chemicals to lubricants, particularly for the production of polyol ester (POE) base oils which are highly versatile lubricants, offering customisable properties by varying the types of fatty acids and polyols used in their formulation, enabling them to meet diverse performance requirements across a wide range of applications.

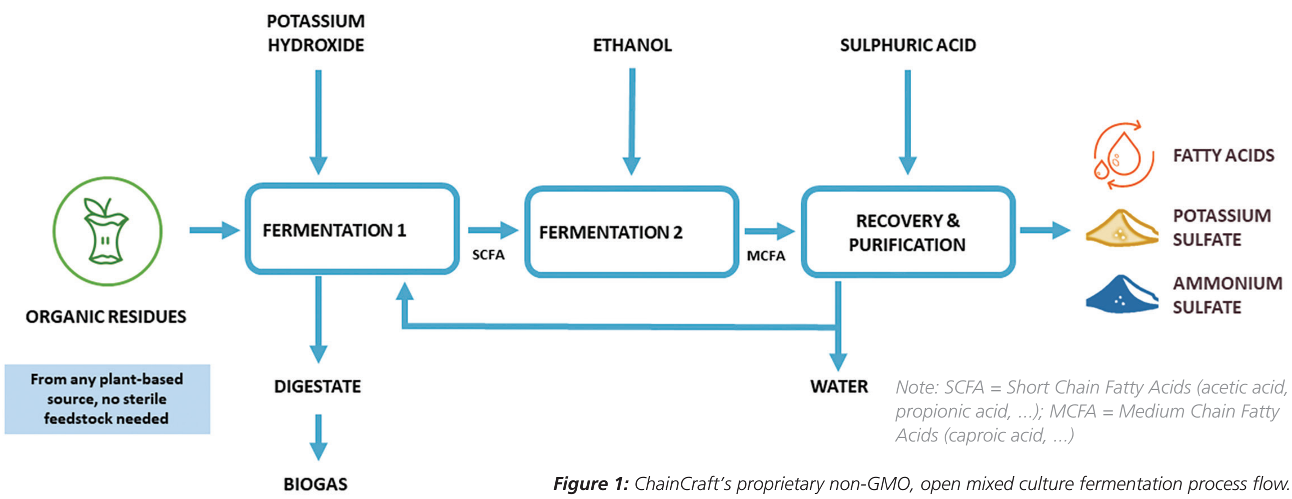

Figure 1: *ChainCraft's proprietary non-GMO, open mixed culture fermentation process flow.*

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C6 to C16 composition in common VO sources

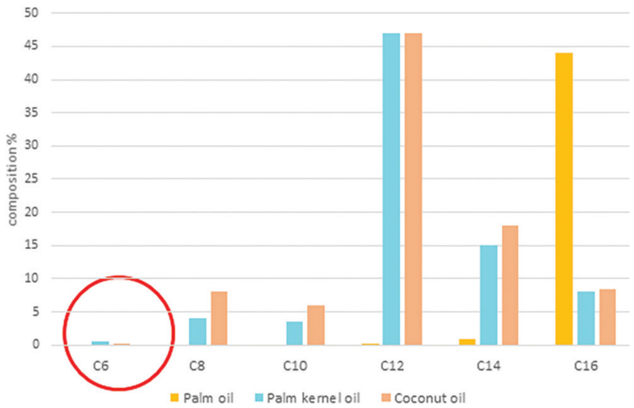

Figure 2: *C6 to C16 composition in common vegetable oil sources as Palm oil, Palm Kernel oil and Coconut oil.*

However, these choices are often constrained by the availability of these building blocks. Linear fatty acids with chain lengths longer than six carbons (e.g., heptanoic – C7, caprylic – C8, capric – C10) are typically sourced from oleochemicals such as palm kernel oil, coconut oil, or castor oil. Since shorter-chain fatty acids are not abundantly present in vegetable oils, these fatty acids such as valeric acid (C5) are usually derived from petrochemicals. Notably, both oleochemical and petrochemical sources contain little to no caproic acid (C6), which limits the possibility of producing larger volumes at a competitive price. Consequently, POE products based on C6 are not widely available in the market. As a versatile building block, caproic acid can unlock novel opportunities for synthetic ester design, paving the way for more sustainable and innovative applications as the demand for eco-friendly materials keep growing.

Since 2019, ChainCraft has been advancing the production of medium-chain fatty acids using its patented non-GMO fermentation technology at its demonstration plant in Amsterdam, which boasts a capacity of 2,000 tons per year. Looking ahead, the company is gearing up to launch its full-scale plant in the North of the Netherlands by 2027, with an impressive annual capacity of 20,000 TPA. At full capacity, approximately 12,000 TPA of this output will be X-Craft® C6 caproic acid, produced with a low carbon footprint and sustainable practices. By repurposing food waste into high-demand compounds like caproic acid (C6), this technology offers a sustainable solution that addresses environmental concerns while opening up new industrial possibilities.

This study investigates the benefits and performance of X-Craft® C6 caproic acid and highlights the potential of this missing molecule to bridge the gap in formulations, enhancing the versatility and performance of POE products. For comparison, fatty acids with similar carbon numbers, valeric acid (C5) and heptanoic acid (C7), were selected as references. Three distinct pentaerythritol-based POEs were synthesised using each fatty acid molecule (C5, C6, and C7). The synthesised POEs were characterised and compared, demonstrating X-Craft® C6's potential to deliver advantageous physical properties, such as low viscosity, reduced volatility, and improved pour point, for specific applications within the lubricants industry.

Evaluating pour point, volatility, and viscosity
The three POE molecules were synthesised through

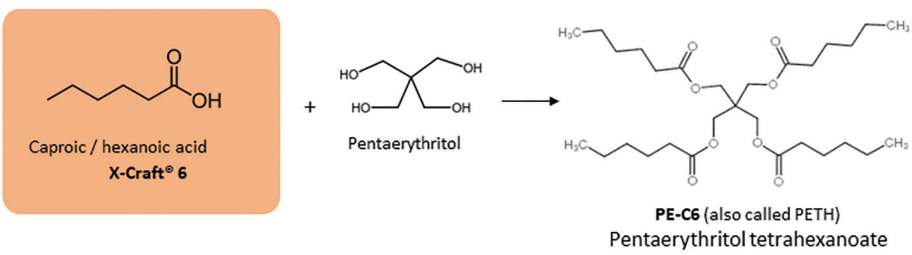

Figure 3: *Esterification of pentaerythritol and caproic acid (C6) to pentaerythritol tetrahexanoate.*

esterification at 170°C, using an ion exchange resin catalyst (Purolite CT269 and CT169) to reach quantitative reaction yields. After synthesis, the esters were distilled and purified.

The purity standard of the lubricant industry for ester base oils is typically higher than 98%. After thorough purification, the sample of PE-C5 could be purified to 98.2% and PE-C6 and PE-C7 reached 97.9% purity, as shown in Table 1. The remaining percentage consists of incomplete pentaerythritol esters (tri-esters instead of the desired tetra-esters). It is also hypothesised that some esters of di- and tri-pentaerythritol are present. Acid values and water content met the requirements reported in the literature and the market standard.

	PE-C5	PE-C6	PE-C7
Purity (w/w%)	98.2	97.9	97.9
Acid value (mg KOH/g)	0.05	0.01	0.37
Water content (w/w%)	0.01	0.01	0.02

Table 1: *Purity, acid value and water content of the three synthesised POEs.*

All three batches of POEs had a light odour and were clear with a slight yellow colour. Due to the possibility of slight degradation of the catalyst during the synthesis, the final products were tested for residual sulphur; all samples were below 500 parts per million. This catalyst residue might have affected the base oil properties; however, adjustments in the synthesis process can easily avoid this issue.

To evaluate the potential of PE-C6 as a base oil, its general physicochemical properties were analysed and compared with those of PE-C5 and PE-C7.

The kinematic viscosities of PE-C6 at 100°C and 40°C fall between those of PE-C5 and PE-C7 (Figure 4). The same is observed for the viscosity index (VI) (Figure 5). As expected, the viscosities and VIs increase with the length of the fatty acid chains.

Kinematic Viscosity (ISO 3104)

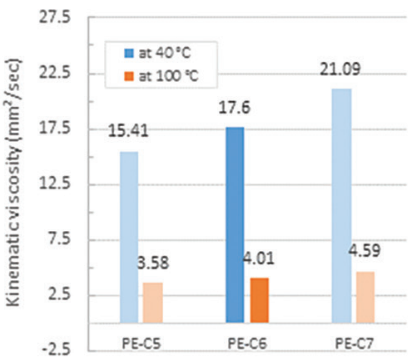

Figure 4: *Kinematic viscosity of PE-C5, PE-C6 and PE-C7*

Viscosity index (ISO 2909) (ISO 3104)

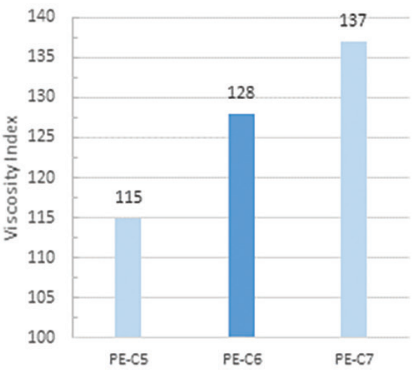

Figure 5: *Viscosity index of PE-C5, PE-C6 and PE-C7*

Base oils used in internal combustion engine (ICE) oils, electric vehicle (EV) fluids, and aviation lubricants can benefit from lower viscosities, achievable through the use of low molecular weight POEs. These applications also benefit from low volatility for safety and durability reasons. The volatility of all three molecules was found to be lower than 1.5% weight loss at 150°C for 22 hours, as shown in Figure 6.

Compared to PE-C5, PE-C6 has a lower volatility, offering a better compromise between viscosity and volatility for many applications. Volatility is influenced by factors such as purity and molecular weight, with the general trend being a decrease in volatility as the fatty acid chain length increases. However, the results showed a deviation: PE-C7 exhibited higher volatility than PE-C6, which could likely be due to the lower purity of the PE-C7 batch, that had a slightly higher acid value and water content. It could also be further analysed by including PE-C8 in the testing to investigate the variation of even/odd chain molecules.

Volatility (ASTM D 972)

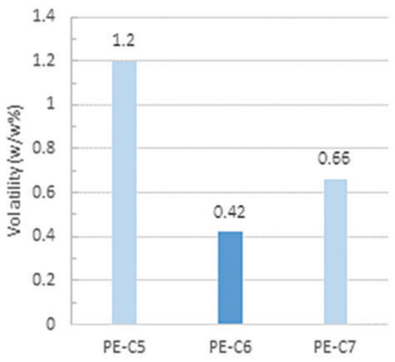

Figure 6: *Volatility of PE-C5, PE-C6 and PE-C7*

Pour point (ISO 3016) and Flash point (ISO 2719/A)

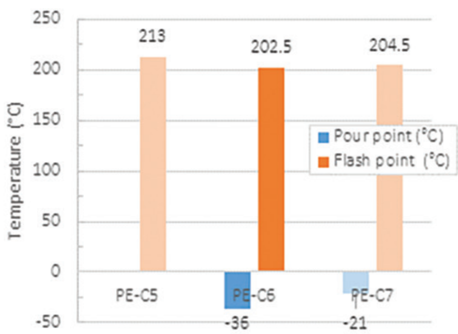

Figure 7: *Pour point and Flash point of PE-C5, PE-C6 and PE-C7*

Flash point is another important parameter for applications where temperatures reach elevated levels and fire safety is important, such as transformer oils and hydraulic fluids. All three molecules achieved a flash point above 200°C, as shown in Table 2 and Figure 7. While an increase in flash points with longer fatty acid chains was anticipated, PE-C5 showed a slightly higher flash point than both PE-C6 and PE-C7. It is hypothesised that this is due to the higher purity of PE-C5 compared to the other batches.

The performance of the base oil at low temperatures plays a crucial role in applications such as aviation and industrial lubricants. POEs usually perform well in such conditions, and PE-C6 reached a pour point of -36°C, as shown in Table 2 and . In order to further reduce the pour point, using pour point depressants or incorporating shorter or branched fatty acids into the molecular structure could be considered. Unfortunately, in this study, the pour point of PE-C5 could not be assessed with certainty.

Property	Method	Unit	PE-C5	PE-C6	PE-C7
Kinematic Viscosity @40 °C	ISO 3104	cSt	15.41	17.60	21.09
Kinematic Viscosity @100 °C	ISO 3104	cSt	3.584	4.010	4.591
Viscosity Index (VI)	ISO 2909		115	128	137
Pour Point	ISO 3016	°C	–	-36	-21
Flash Point	ISO 2719/A	°C	213.0	202.5	204.5
Volatility	ASTM D 972	% (w/w)	1.20	0.42	0.66
Specific Gravity	EN ISO 12185	kg/m³	1022.5	999.5	982.5

Table 2: *Physicochemical properties of PE-C5, PE-C6 and PE-C7.*

After evaluating the general properties of the synthesised POEs, we further explored some indicative application-specific properties such as thermal and dielectric properties of the three molecules.

Permittivity (C EI 60247)

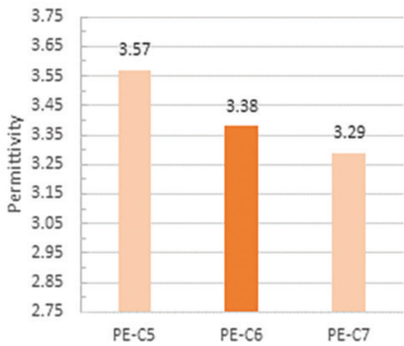

Figure 8: *Permittivity of PE-C5, PE-C6 and PE-C7*

Thermal conductivity (internal method)

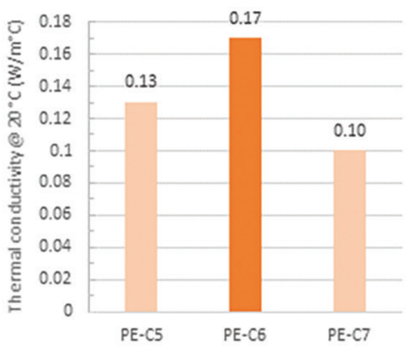

Figure 9: *Thermal conductivity of PE-C5, PE-C6 and PE-C7*

The three POEs showed good permittivity which decreased linearly with the increase in change length of the fatty acid chain (Figure 8). These permittivity results are higher than the permittivity of mineral oil, which is commonly used as dielectric fluid, but still in a very reasonable range, which allows the employment of PE-C6 as a dielectric fluid.

The thermal conductivity of the three molecules also resulted in being in a good range with PE-C6 having a significantly higher thermal conductivity compared to the other two esters (Figure 9). Thermal conductivity is a relevant parameter for refrigerant fluids, and these results indicate that PE-C6 would perform well.

Resistivity (C EI 60247)

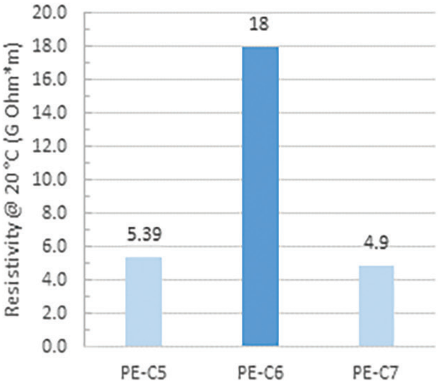

Figure 10: *Resistivity of PE-C5, PE-C6 and PE-C7*

Dielectric dissipation factor (C EI 60247)

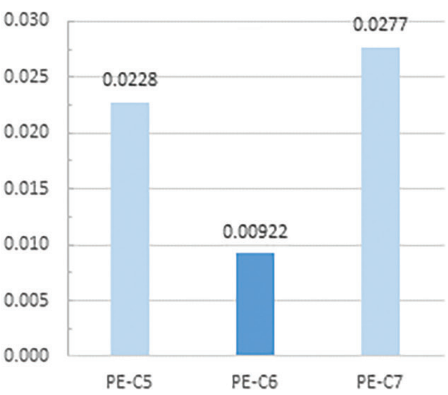

Figure 11: *Dielectric dissipation factor of PE-C5, PE-C6 and PE-C7*

Positive results were achieved also in terms of electrical resistivity, with PE-C6 demonstrating a significantly higher resistivity compared to the other two esters (Figure 10). Another positive note is the fact that the dielectric dissipation factor of PE-C6 was significantly lower than the one of the other two esters (Figure 11).

By evaluating the performance of PE-C6 as a dielectric fluid we can suggest that this molecule would perform quite well as a dielectric and coolant. However, other parameters should be investigated to be able to conclude this, namely the breakdown voltage (also referred to as dielectric strength) and the heat capacity.

Thermal and oxidative stability results of the esters are also important for this study, as these are critical parameters affecting the performance of a base oil at high temperatures. The results of the thermal stability assessment are shown in Table 3 and Figure 12. All three esters performed well in this test both in terms of total sludge formation, which was significantly below the 25 mg /100 ml threshold, and in terms of visual evaluations. However, PE-C5 resulted in having a significantly higher total sludge weight compared to PE-C6 and PE-C7, which both produced less than 2 mg/100 ml.

Thermal stability (ASTM D 2070)	Unit	PE-C5	PE-C6	PE-C7
Acidity change	mg KOH/g	1.05	1.25	1.26
Weight loss of the copper rod	mg	2.1	-0.4	1.2
Weight loss of the steel rod	mg	-0.5	-0.2	-0.4
Visual evaluation of the copper rod		4	2	2
Visual evaluation of the steel rod		2	2	2
Total sludge weight	mg/100ml	6.3	1.9	1.8

Table 3: *Thermal stability results of PE-C5, PE-C6, and PE-C7 characterisation.*

It is worth noticing how the visual evaluation of the steel and copper rods for PE-C6 is very good as both rods of PE-C6 show almost no sludge residue.

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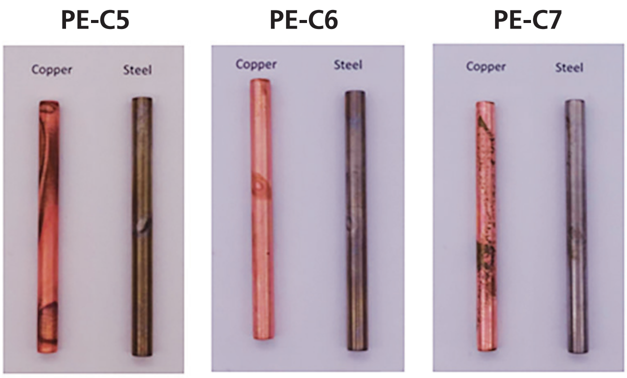

Figure 12: *Dielectric dissipation factor of PE-C5, PE-C6 and PE-C7.*

POEs derived from pentaerythritol and linear, saturated fatty acids are typically expected to exhibit excellent oxidation stability due to the complete saturation of the side carbon chains and the lack of beta hydrogens on the molecular structure.

Oxidation stability (ISO 4263-3 - dry TOST)

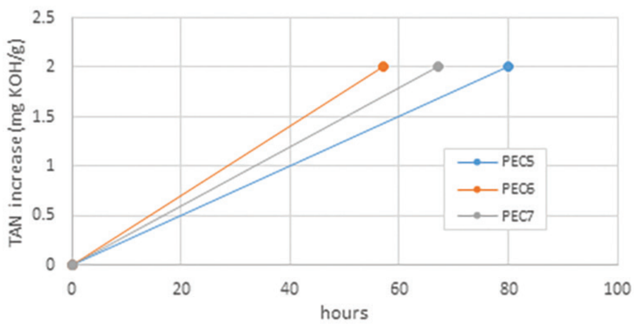

Figure 13: *Oxidation stability of PE-C5, PE-C6, and PE-C7.*

As per the results shown in Figure 13, unfortunately, all three esters showed relatively poor oxidation stability, reaching an increase of 2 mg KOH/g in TAN (total acid number) after 57 - 80 hours. This unexpected result indicates that due to the limitations of small-scale lab synthesis, the presence of residual moisture in the samples and possibly some residues of the catalyst employed for the synthesis might have affected the performance results. However, the correlation between the results in the chart still gives a good indication that with better purification of samples, the performance of PE-C6 should be expected to be between PE-C5 and PE-C7.

High-purity fatty acids are employed (>98%) for the synthesis of POEs at an industrial scale. Although fermentation is a novel way of deriving fatty acids for the lubricants industry, this production method does not have any negative effect on the quality of the product, and the highest purities can certainly be achieved.

X-Craft® C6 that ChainCraft offers for industrial applications has a purity of over 98%. The remaining fraction is comprised of other fatty acids with chain lengths ranging from C4 to C8 due to the nature of the fermentation process.

Fatty Acid Composition	% by GC Analysis
C6	>98%
C4, C5, C7, C8	<2%

Table 4: *Composition of X-Craft® 6 with >98% C6 purity for industrial applications.*

Lower your CO_2 Footprint

In addition to the unique characteristics of X-Craft® C6, using food waste-derived fatty acids for ester base oils has a significant environmental benefit.

Global warming impact including biogenic uptake

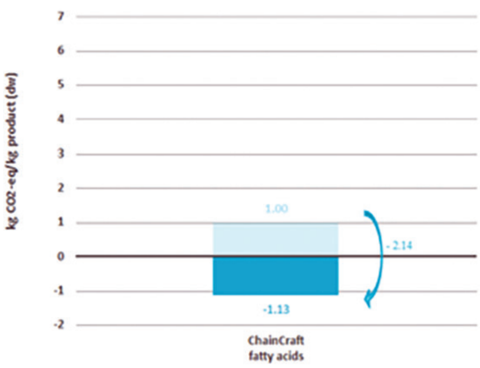

Figure 14: *Global warming impact of ChainCraft fatty acids excluding and including biogenic content.*

Figure 14 shows the carbon footprint assessment of ChainCraft fatty acids produced from potato residues through fermentation. This cradle-to-gate life cycle assessment (LCA) shows ChainCraft's fatty acids have a negative Carbon footprint with a value of -1.13 kg CO_2-eq/kg product including biogenic intake.

Global warming impact excluding biogenic uptake

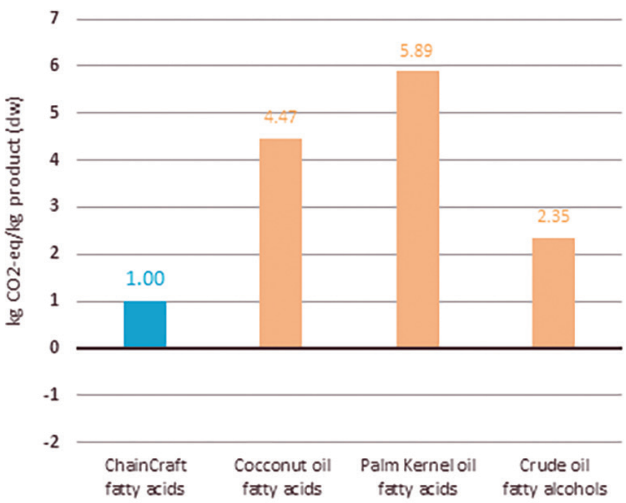

Figure 15: *Global warming impact of ChainCraft fatty acids compared to fatty acids from common sources, including biogenic content*

Fugure15 shows the global warming impact of X-Craft® fatty acids is three to six times lower compared to fatty acids derived from currently common sources such as palm kernel oil, coconut oil and crude oil. Furthermore, upcycling residual food streams into fatty acids does not take up any farmland or compete with food production.

Switching to raw materials with a lower carbon footprint allows companies to reduce their Scope 3 emissions. Furthermore, these fermentation-derived acids allow for POEs with a 100% bio-based carbon content, facilitating EU ecolabel "bio-based" and "bio-lubricant" claims.

Additionally, POEs derived from linear and unsaturated fatty acids excel for their biodegradability. Specifically referring to POEs derived from MCFA are expected to qualify as readily biodegradable - according to the OECD testing series —and to have quite low ecotoxicity. This makes them suitable for EALs (environmentally acceptable lubricants), which are used in applications where there is a risk of the lubricant coming into contact with the environment (e.g., total loss, partial loss, or accidental loss scenarios). Examples include marine lubricants and lubricants used in outdoor machinery for agriculture and forestry. POE base oils can also be suitable for food-grade lubrication (NSF H1).

The ease of registration processes of caproic acid enhances the development of innovations

An innovation often raises concerns about the need to overcome the hurdle of lengthy registration processes. Fortunately, PE-C6 is included in existing POE REACH registrations. However, the technical innovation that C6 offers doesn't need to stop there; C6 serves as an innovative building block that can be used in the production of POEs, not just based on pentaerythritol, but also other polyols. Moreover, it can be used in the synthesis of complex esters and polymeric molecules to produce, such as bio-based greases.

Outcome: unlocking the middle ground between PE-C5 and PE-C7

A comprehensive assessment of the test results shows that X-Craft® C6 caproic acid has great potential for various base oil formulations. The synthesised POE based on C6 has a viscosity that falls between that of PE-C5 and PE-C7 and the volatility of PE-C6 is lower compared to PE-C5. The low pour point of PE-C6, combined with the balance of low viscosity and low volatility could allow its use in low-temperature applications where the higher volatility of PE-C5 poses a safety risk.

Additionally, the expected environmental safety and biodegradability of PE-C6 can also offer advantages over existing materials in the market. Other properties of the PE-C6 prove its potential use in a wide variety of applications, such as dielectric properties for use in immersion cooling, chemical compatibility for use in refrigerant fluids, and thermo-oxidative stability for use in the automotive industry.

These results are only an introduction to the unique benefits that can be achieved by using C6 in ester based lubricants —and this is just the starting point. Ester chemistry is incredibly versatile, with a multitude of polyols available to synthesise new molecules with unique characteristics. C6 can also be combined with other fatty acids of higher chain lengths or molecules with different functional groups for creating tailor-made formulations.

Upcycling food waste to an abundant supply of caproic acid opens up opportunities to produce sustainable synthetic esters for use in various lubricant applications.

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Authors:

Maddalena Cesaro *is driven by a passion for sustainability, both within and beyond the chemistry industry. As an Application Scientist with a background in Material science, she contributes to ChainCraft's mission of promoting innovative and circular solutions, by exploring new applications for its product line.*

Dilek Ersu *holds a Bachelor's degree in Chemical Engineering and a Master's in Polymer Science and Technology. In her role at ChainCraft, she leverages her extensive experience to drive industrial business development and forge strategic partnerships. Passionate about sustainability, Dilek focuses on advancing bio-based solutions that promote circularity within the chemical industry. She collaborates with major chemical companies to develop ChainCraft's innovative bio-based molecules, which serve as sustainable building blocks for various applications, including synthetic esters used in novel lubricants.*