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The use of alternative feedstocks as renewable and biodegradable lubricants

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Introduction

Bio-based substances have been used as effective lubricants for hundreds of years. Animal and vegetable oils were used in Roman times to lubricate chariot axles, although there is some evidence to support the use of lubricants as early as during the Copper Age. Their adoption and use have become more widespread in the last 50 years due mainly to environmental concerns although in certain applications bio-based components can give a performance benefit over other lubricant chemistry. With increasing drives towards sustainable sourcing and use, the uptake of bio-lubricants continues to rise as does the manufacture of bio-based crude oil equivalent lubricants.

***Figure 1:** Early use of lubricants in chariots*

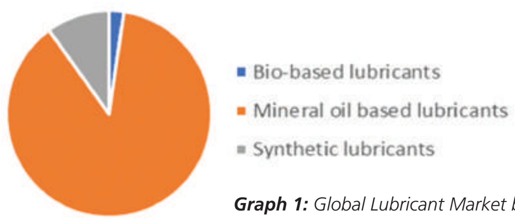
Current bio-lubricant manufacture is derived almost entirely from virgin pressed seed oils or rendered animal fats. Vegetable feedstocks require direct or indirect land use. Whilst still sustainable, the use of land and crops which could otherwise be used for human/animal consumption has been questioned.

Market

The bio-lubricant market continues to grow but is still a fraction of the entire lubricant market. Similarly, mineral oil substitutes/alternatives, are becoming more widely available but still make up a very small proportion of the market.

The global demand for lubricants is shown in Graph 1.

Global Lubricant Uptake



***Graph 1:** Global Lubricant Market by Type*

Graph 1. shows the global lubricant can be divided between mineral oil-based lubricants (87.72%, 32.63 million tonnes), synthetic lubricants (9.95%, 3.70 million tonnes) and bio-based lubricants (2.33%, 870000 tonnes). (1)

Biogenic materials are used in bio-based lubricants and in some synthetic lubricants.

The demand for bio-based lubricants is predicted to rise to 1.06 million tonnes by 2023.

Current Sources of Bio-based Lubricants

Most bio-based lubricants are derived from natural oils, predominantly vegetable oils and vegetable oilseeds such as rapeseed or sunflower. As lubricants they can be used as the naturally occurring esters or triglycerides of vegetable oils, oleochemical esters of fatty acids or complex esters.

The demand for vegetable oils continues to rise. Global annual production of vegetable oils was 55 million tonnes in 1980 which rose to 100 million tonnes by 2000. It is predicted to soon reach 200 million tonnes.

In 2009 21.2% of global fats and oils was used for non-food, industrial purposes. [2]

Alternative Sources of Bio-Based Lubricants

Globally there exists a significant amount of waste fats and oils. These waste oils have found their use in applications such as biofuel production. However, these waste fats and oils contain a significant level of valuable natural fatty acids that could be used in higher value applications such as bio-based lubricants. [3]

Table 1. gives an outline of some of the waste fats and oils types which exist globally along with the potential tonnage currently available.

Waste Type	Origin	Estimated Global Tonnage
Vegetable Waste 1	Virgin Oil Processing	10000s
Vegetable Waste 2	Virgin Oil Processing	10000s
Oil Mill Effluent 1	Seed Processing	100000
Oil Mill Effluent 2	Seed Processing	1200000
Fat Trap	Food Production	100000s
Sewer Grease	Water Industry	100000s (UK)
Animal Waste	Rendering/Slaughter	700000

Table 1: *Types of waste fats and oils*

Analysis of waste fats and oils

To perform effective and accurate analysis of waste fats and oils a combination of using existing analytical test methods, modified test methods and in-house developed test methods is required.

The characterisation of fatty acids contained in waste fats and oils is critical to assess the value and properties of any waste-stream being utilised. Table 2 gives a summary of the fatty acid analysis carried out on waste fats and oils.

Waste Type	< C12s	C14s	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	>C18s
Vegetable Waste 1	N/D	N/D	5.0	N/D	3.0	58.5	23.2	8.2	N/D
Vegetable Waste 2	N/D	N/D	5.0	N/D	4.4	82.7	5.2	N/D	N/D
Oil Mill Effluent 1	N/D	<0.1	13.0	0.8	2.5	73.8	8.2	N/D	1.0
Oil Mill Effluent 2	0.4	1.1	46.3	N/D	4.6	39.7	7.1	<0.1	0.3
Fat Trap	0.8	3.0	21.3	3.1	9.0	31.4	13.2	1.1	7.1
Sewer Grease	0.5	2.8	31.3	N/D	11.8	35.0	12.5	1.2	0.5
Animal Waste	0.3	3.5	22.7	3.4	22.2	33.5	3.8	0.7	1.8

Table 2: *Waste fats and oils fatty acid breakdown*

Several techniques exist for the characterisation of fatty acids and is dependent on several factors. One of the most important is the level of free fatty acids (FFAs) and triglycerides contain in the waste oil. Either the FFAs or triglycerides, are converted into their associated methyl esters and then analysed to give levels of individual fatty acids using gas chromatography.

The handling of waste fats and oils is inherently challenging as waste materials are discarded substances or substances of little value to the original user. Table 3 gives an approximate summary of some of the impurities found in waste fats and oils along with their indicative levels.

Impurity	Range of Levels
	(%)
Solids	0-80
Metals	0-5
Water	0-70
Unsaponifiables	0-4

Table 3: *Levels of impurities within waste fats and oils*

A range of analytical techniques and methods are used for assessing the quality of waste oils and fats which in turn informs the level of pre-treatment required for their resultant use.

Table 4 gives a non-exhaustive list of some of the techniques used when assessing waste fats and oils.

Parameter	Test Method	Analytical Technique
Free Fatty Acids and Acid Value	ISO 660 ASTM D664	Titration
Moisture	ISO 12937, ISO 8534, ISO 662	Karl Fisher, Oven
Unsaponifiables	ISO 3596	Titration
Sulphur	ISO 20846	UV Flourescence
Ash	ISO 6245	Furnace
Metals	ISO 21033	ICP-OES, XRF
Fatty acid profile	ISO 12966 + Bespoke developed	Gas Chromatography
Oxidative stability	ISO 6886	Rancimat
Oil:Water:Solids	Developed	Centrifugation
Iodine Value	ISO 3961	Titration
Soaps	ISO 685	Titration
Viscosity	ASTM D445	U-Tube
Flash Point	ISO 15267	Closed cup
Insoluble Impurities	ISO 663	Solvent Filtration

Table 4: *Analytical methods used in assessing waste fats and oils*

Treatment of waste oils and fats

There are a variety of process techniques and methods available to ensure the quality of waste fats and oils is met for them to be used in different applications.

Most waste oils will have a certain level of water contained within them. Sometimes this can be removed by storage over time as the oil and water will eventually split gravimetrically. However, other techniques like centrifugation and sonication can also encourage separation. Certain metallic impurities can help create emulsions and mono and di-glycerides are also natural emulsifiers which can lead to persisting emulsions when waste oils are delivered. These emulsions can be broken by using acids, heat or even specific demulsifiers.

Metallic impurities can be removed by using a variety of filter agents. Bleaching earths are commonly used and depending on the amount of removal required chelating agents can be used also. Other commercially available techniques like ion-exchange and electrodialysis can be used as well. Removing metallic impurities will improve the oxidative stability of oils and fats.

Plastic impurities can be seen in waste fats and oils, depending on their original source. Cellulosic filters can be used to removed them.

Solids can be removed by tri-cantering. This technique separates oil-water-solids.

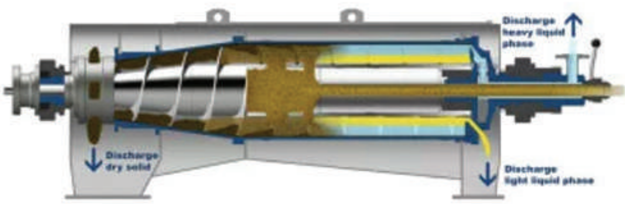


Figure 2: *Tri-canter used for water-oil-solids separation*

Waste fats and oils are nearly always degraded comprising mono, di and tri-glycerides and free fatty acids. Depending on the application required the glycerol component can be removed. This can be carried out by a physico-chemical route or enzymatically by using lipases. [4] [5]

Once glycerol has been removed, we are left with fatty acids which can be separated further into constituent fatty acids or used as mixed fatty acids for a breadth of applications.

Critical in the handling of waste fats and oils is the use of the waste-from-waste. High Chemical Oxygen Demand (COD) water can be used to produce biogas, as can some waste solids (sludges). Used filter media can be recycled using solvent extraction or can be used as a fuel source for biomass boilers for steam and energy production. [6]

Future Considerations

It has been shown that there are significant amounts of waste fats and oils available which could be used as feedstocks for bio-lubricants with the correct amount of pre-treatment. There are also many transformational techniques available which can use these highly renewable and sustainable feedstocks to create other types of lubricant.

Simple esters can be created through esterification with alcohols. Methyl, ethyl, propyl and butyl esters can all be easily transesterified from waste fats and oils.

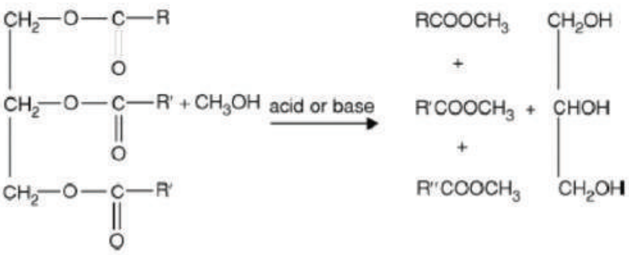


Figure 3: *Transesterification of a mixed fatty acid triglyceride to simple ester and glycerol*

Some waste oils are almost or completely degraded and so would transesterify and produce water rather than glycerol.

Higher quality esters can be made from separated fatty acids and reaction with polyols. Alcohols such as neopentyl glycol, pentaerythritol, 2-ethyl hexanoic and trimethylpropane are already used with veg-sourced oleic acid and other fatty acids to yield high performance esters.

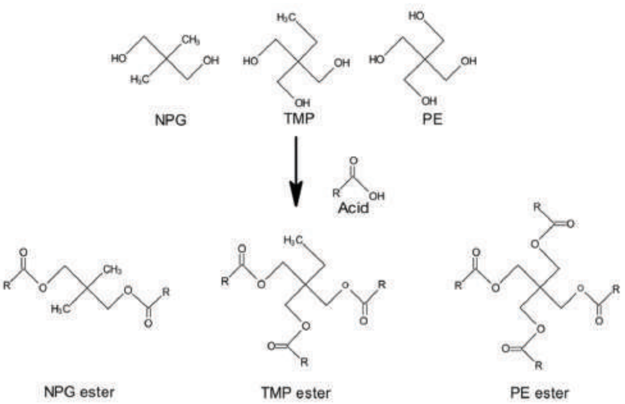


Figure 4: *Catalytic esterification of acid and polyol to polyol ester*

A waste-based source of these acids would create a highly-sustainable alternative compared to the existing supply of sources which could otherwise be used as a source of food. Furthermore, fatty acids can be transformed catalytically to create a range of products which can replace existing mineral oils. [7][8]

Another potential transformation of waste fats and oils is to create epoxidised vegetable oil/fatty derivatives. From this platform a variety of further transformations can be achieved to produce lubricant base fluids or additives. Waste oils can be transformed using peracids and varying certain reaction parameters such as, reactant molar ratio, temperature, nature of the solvent, presence or absence of a catalyst (this is usually a mineral acid or an ion exchange resin), stirring speed, type of peroxyacid (peracetic, performic, m-chloroperbenzoic acid), mode and rate of the addition of peroxide/acetic or formic acid, the reaction period and contacting pattern (batch/semi-batch mode/ azeotropic distillation). Due to their biogenic origin the resultant products have been shown to have a better solubility for synthetic esters along with an improved performance over mineral oil alternatives. These epoxidised products have been shown to possess impressive anti-corrosive, anti-wear, lubricity, thermo-oxidative and pour point suppressing qualities. Waste soya-bean oil, with its inherent unsaturation is an ideal candidate as a precursor for these lubricants. [9]

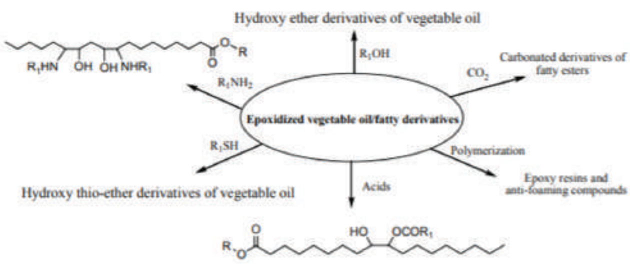


Figure 5: *Epoxidised vegetable oil/fatty derivatives as a starting material to prepare different biolubricants/ additives for lubricants*

Waste oils and fats are incentivised in a variety of countries for use in biofuel production. The biofuel market is increasing due to higher levels of incentives and mandates for their use by national governments. As a result, demand for waste fats and oils for use in the transport sector is increasing. The challenge for other markets to be able to use waste fats and oils will be chiefly extracting appropriate value and securing a supply of feedstock. However, given the emphasis on economies becoming more circular and needing to de-carbonise the use of waste fats and oils as an exceedingly sustainable feedstock will be more attractive for a variety of applications going forward. [10]

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