

# Green lubricants. Environmental benefits and impacts of lubrication

Steve Boyde

Uniqema Lubricants, Wilton, UK. E-mail: stephen.boyde@uniqema.com

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This paper is a review of the environmental impact of lubricants and lubrication, from a chemical perspective. It is intended to give an overview of our current understanding and to provide some specific examples of how optimising lubricant chemistry can contribute to reducing the environmental impact of human activities. Lubricants affect this impact in many ways, but they have a particularly important contribution to make in relation to energy conservation, minimisation of waste and development of durable products. Truly green lubricants are those that optimise energy efficiency and minimise wear in the machinery which they lubricate and which have maximised service lifetimes in order to reduce the amount of lubricant required. Increasing importance of these criteria in lubricant selection and design is expected to lead to more widespread use of high performance synthetic basefluids and effect additives.

## 1 Introduction. What is a lubricant?

This section outlines the functions and performance requirements of a lubricant and describes the chemical components of a modern lubricating oil formulation, in order to provide a brief introduction for those unfamiliar with this area of technology.

### 1.1 The role, functions and requirements of a lubricant

A lubricant is a material used to facilitate relative motion of solid bodies by minimising friction and wear between interacting surfaces. Most, although not all, lubricants are non-aqueous liquids. This paper concentrates on such lubricating oils, which are used in a very wide range of equipment, on scales ranging from industrial metal rolling mills, through car engines and gear boxes to computer disk drives. The paper also considers related functional fluids used in applications where their primary purpose is not friction and wear reduction, although some degree of lubricity may be required. Examples of such applications include hydraulic fluids, electrical transformer fluids, heat transfer fluids and metal working coolants.<sup>1,2</sup>

In addition to the primary purposes of reducing friction and wear, lubricating oils are also required to carry out a range of other functions, including removal of heat, corrosion prevention, transfer of power, providing a liquid seal at moving contacts and suspension and removal of wear particles.<sup>3,4</sup> In order to perform these roles, lubricating oils must have specific physical and chemical characteristics.

Perhaps the fundamental requirement is that a lubricating oil should be liquid over a broad temperature range. In practice the usable liquid range will be limited by the pour point at low temperatures and the flash point at high temperatures. The pour point should be low to ensure that the lubricant is pumpable when equipment is started from extremely low temperatures. The flash point should be high to allow safe operation, with minimum volatilisation, at the maximum operating temperature. For the most demanding applications, such as aviation jet engine lubricants, an effective liquid range of over 300 °C may be required.

The efficiency of a lubricating oil in reducing friction and wear is greatly influenced by its viscosity. The relationship of

the coefficient of friction in a lubricated system to the lubricant viscosity is shown schematically in Fig. 1.<sup>3,4</sup> At high speed, high viscosity or low load, sufficient hydrodynamic pressure is generated that the solid surfaces are fully separated by a thin film of lubricant. This condition is known as hydrodynamic lubrication. At lower speeds and viscosities, or higher loads, the hydrodynamic pressure generated is insufficient to fully separate the surfaces and asperities on the opposing surfaces come into contact. This condition is known as boundary lubrication. To minimise friction and wear, equipment is designed for hydrodynamic lubrication where possible. For any given lubricated system, the optimum lubricant viscosity depends on the relative velocities of the surfaces, and on the

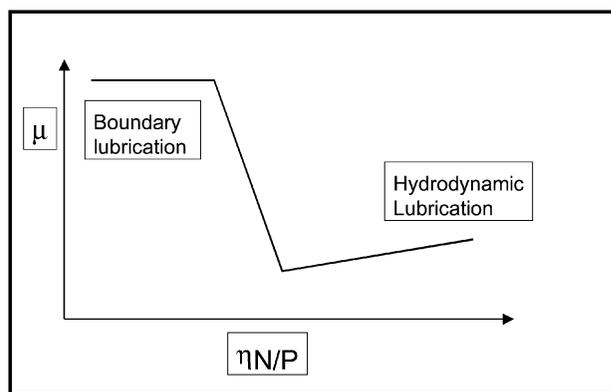


Fig. 1 The Stribeck curve. Schematic dependence of coefficient of friction,  $\mu$ , on lubricant viscosity,  $\eta$ , relative velocity  $N$ , and load,  $P$ . (ref. 4, p. 227).

## Green Context

Lubricants are ubiquitous, but are often overlooked in terms of environmental impact compared to *e.g.* fuels, which are continually under the spotlight. This overview places lubrication in context, in terms of its function currently, environmental impact and future trends, in particular from a green perspective.

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load to be supported. Since velocities and loads vary enormously between different types of machine, and even between different locations in the same machine, a correspondingly wide range of lubricant viscosities are required. Industrial lubricants are normally classified according to their ISO grade, the approximate viscosity in cSt at 40 °C.<sup>5</sup> Lubricants in current commercial use span a range of ISO grades from <10 to >1000. (Car engine oils are usually classified according to the SAE grade system, which gives greater discrimination over the viscosity range of interest in the application<sup>6</sup>).

For a given load and velocity, too high a viscosity means that the hydrodynamic lubricant film is thicker than necessary and energy is wasted in shearing the thick lubricant film. The excess energy is converted to heat, which increases both the local temperature and the bulk lubricant temperature. This accelerates lubricant decomposition reactions and mechanical failure of the surfaces, leading to reduced lifetime for the lubricant and for the equipment.<sup>3,4</sup>

Too low a viscosity means that the system will operate in the boundary lubrication regime. Friction coefficients are much higher in boundary than in hydrodynamic lubrication, because energy is required for surface deformation and to overcome adhesion.<sup>7</sup> Energy is wasted in overcoming the higher frictional forces. Wear of the metal components also occurs, again leading to reduced equipment lifetime.

Viscosity of a fluid is a function of temperature, pressure, and in some cases, shear rate. It is generally desirable that the viscosity of a lubricating oil should change as little as possible over the temperature range of operation. The temperature dependence of viscosity of lubricants varies significantly, and is normally expressed in terms of an empirical parameter known as Viscosity Index (VI), where a higher VI implies a lower rate of change of viscosity with temperature.<sup>8</sup>

The pressure-dependence of viscosity is also a critical parameter in lubricant selection. The true hydrodynamic pressure in some lubricated contacts can exceed 1 GPa. Under these pressures, fluid viscosities may be orders of magnitude higher than their ambient pressure values.<sup>9,10</sup> Some fluids effectively solidify under these high pressures. For many applications, this increase in viscosity with pressure is essential to maintain a liquid film in the contact and prevent failure of components. In other applications a low viscosity increase is preferable to minimise friction and energy consumption.

The lubricant must maintain its physical properties throughout a long operating lifetime, during which time it is exposed to high temperatures in the presence of atmospheric oxygen. Thermal degradation and autoxidation affect fluid physical properties, so a lubricant must have extremely good thermal and oxidative stability in order to maintain performance.<sup>11</sup> It must also be inert to any other potential chemical reactants to which it may be exposed, *e.g.* water, fuels and process gases. A lubricant must also be stable under the extremely high shear rates characteristic of lubricated contacts, which are capable of mechanically fragmenting large molecules.

In addition to having the correct viscometrics and stability, a lubricant must deliver many other application effects. One of the most important of these is antiwear activity. This is a function of the lubricant chemistry under the extreme conditions occurring where asperities on the surfaces of opposing mechanical elements come into contact. Asperity contact gives rise to very high local flash temperatures and causes emission of electrons as the metal is deformed. The passivating metal oxide layer may be removed, exposing virgin metal surfaces. Any lubricant in proximity to an asperity collision is therefore subjected to extreme thermal and electrochemical excitation, while in contact with a potentially catalytic metal surface.<sup>12,13</sup> The lubricant must react under these conditions, for example by formation of an adherent, viscoplastic layer, which can be deformed sacrificially to relieve stress on the underlying metal surfaces and prevent wear.

The interfacial physical and chemical characteristics under milder conditions are equally important. The lubricant must contribute to minimising friction between contacting surfaces and prevent corrosion of metals. Wear and soot particles must be maintained in dispersed suspension to avoid formation of sludge and surface deposits. At the liquid air interface, low foaming and rapid air release are required.<sup>1-4</sup>

With such a range of physical and chemical parameters to consider, as well as economic, safety and environmental constraints, it is clear that lubricant design and formulation inevitably involves compromises between the different performance requirements of any given application. There is no single ideal lubricant, only more or less appropriate lubricants for any particular purpose.

Lubricants are best viewed as liquid materials. Their study and development requires a broad, interdisciplinary, materials science approach. However, lubricants are *molecular* materials, and their chemistry underlies the delivery of all of their physical and chemical properties, as well as being fundamental to their manufacturing processes and fate at end of life. Lubricant chemistry is therefore the key to understanding, quantifying and minimising the environmental impact of lubricants and lubricated systems.

## 1.2 The chemical composition of lubricants

Until the mid 19th century, essentially all lubricating oils were based on natural oils, *i.e.* animal fats, vegetable oils and marine oils, which are triglycerides of mixed C<sub>8</sub>–C<sub>22</sub> linear fatty acids.<sup>14</sup> Natural oils have some good lubricant properties, including high viscosity indices, high flash points and low boundary friction coefficients. However, natural oils have a limited viscosity range because of their limited range of structures. They also suffer from poor low temperature fluidity, and very poor thermal and oxidative stability, which leads to rapid degradation, thickening and deposit formation in use.<sup>15</sup>

Industrial development during the 19th century, mainly based on coal-fired, steam-powered equipment, increased the demand for lubricants, but the industry was completely transformed at the end of that century by the widespread adoption of the gasoline-powered internal combustion engine. This created a new demand for lubricants which rapidly exceeded the supply of natural oils. However, the increased exploitation of petroleum as a fuel source also provided a new raw material, mineral oil, which was co-produced when crude oil was refined for gasoline production.

Mineral oils are extremely complex mixtures of C<sub>20</sub>–C<sub>50</sub> hydrocarbons containing a range of linear alkanes (waxes), branched alkanes (paraffinics), alicyclic (naphthenic), olefinic and aromatic species. They also contain significant concentrations of heteroatoms, mainly sulfur.<sup>1,4</sup>

Mineral oils were found to be more stable than natural oils. However, although also cheaper and more readily available in a wider range of viscosities, early mineral oils did not immediately replace natural oils. One problem was that mineral oils from different oil fields had different characteristics. Another was that straight mineral oils gave inferior performance in several other key respects. For example, mineral oils have broader molecular weight distributions than natural oils. Volatilisation of low molecular weight components leads to a tendency to thicken in use. The low molecular weight components also reduce the flash point of mineral oils relative to natural oils of the same viscosity. Mineral oils also typically have low viscosity indices and high boundary friction coefficients compared to natural oils.

During the 20th century, the rapid growth in the number of vehicles led to a volume of demand for lubricants which could only be met by mineral oils and technical developments have overcome many of their performance deficiencies. Improve-

ments in refinery technology have given refiners better control over the composition and characteristics of the mineral oil basefluid. At the same time, the developments of the science of chemistry and of the petrochemical industry have made available a diverse range of chemical products for use as performance additives.<sup>1,16</sup>

Hindered phenols and aromatic amines are used as anti-oxidants which retard the rate of autoxidation of lubricant basefluids and extend their useful lifetime. Long chain fatty acids and diacids are used as rust and corrosion inhibitors. They adsorb to ferrous metal surfaces, displacing water and preventing corrosion. Benzotriazole and other heterocyclics act as metal passivators which bond strongly to non-ferrous metals such as copper and its alloys, modifying the surface properties so as to prevent chemical attack and electrochemical processes at junctions between dissimilar metals.

Zinc dialkyldithiophosphates (ZDDPs) and other S- or P-containing compounds such as dithiocarbamates and trialkyl phosphates are used as antiwear agents which react under tribochemical conditions to form a protective film on the metal surfaces. ZDDPs are also powerful antioxidants.

High molecular weight polymers such as poly(acrylates) and styrene-butadiene copolymers are used as viscosity index improvers. The polymer molecules are more strongly solvated by the basefluid, and therefore thicken the fluid more effectively, at higher temperatures. This effect counteracts the decrease in viscosity with increasing temperature and increases the viscosity index.

Amphiphilic molecules with a polar ionic headgroup, *e.g.* a sulfonate, phenate or salicylate, attached to an oil-soluble hydrocarbon tail, act as detergents which adsorb to wear and soot particles to keep them in colloidal suspension in the basefluid. In over-based detergents, the amphiphilic molecules stabilise a colloidal suspension of a basic oxide or carbonate, *e.g.* CaCO<sub>3</sub>, which neutralises acidic combustion gases to limit corrosivity. Non-ionic amphiphiles such as alkyl succinimides are used as dispersants which associate with the polar molecules formed by oxidative and tribochemical reactions in the lubricant to prevent formation of sludge and deposits.

However, even with all of the additive chemistries now available, there are still some applications where performance requirements cannot be met by mineral oil formulations, and it is necessary to chemically synthesize a lubricant basefluid having the required properties. A variety of such synthetic lubricant basefluids have been developed.<sup>17,18</sup>

Poly( $\alpha$ -olefins) (PAOs) are synthetic hydrocarbons manufactured by cationic oligomerisation of C<sub>8</sub>–C<sub>12</sub> olefins, followed by hydrogenation and fractionation. They have characteristics similar to very highly refined paraffinic mineral oils, with the additional feature of a more narrowly defined molecular weight distribution. This gives particularly good low temperature fluidity and high temperature volatility characteristics. PAOs have been widely used as the main basefluid component of synthetic car engine oils.

Alkylbenzenes are synthetic hydrocarbons manufactured by Friedel–Crafts type alkylation of benzene. Monoalkylbenzenes are manufactured in large volumes for use in surfactant applications. Lubricant alkylbenzenes are typically derived from the dialkylbenzenes and diphenylalkanes which are formed as byproducts. Although the surfactant industry now uses almost exclusively linear alkylbenzenes, branched alkylbenzenes have better low temperature fluidity and are generally preferred in lubricant applications.

A very wide range of synthetic organic esters are used as lubricant basefluids. Examples include esters of C<sub>8</sub>–C<sub>13</sub> monoalcohols with diacids such as adipic acid (diesters) and esters of C<sub>5</sub>–C<sub>18</sub> monoacids with neopentyl polyols such as pentaerythritol (polyol esters). The presence of the ester group confers good low temperature fluidity and reduces volatility at high temperature, as well as providing some affinity for metal

surfaces. Esters were originally developed for lubrication of aircraft jet engines, but have subsequently found more widespread use, particularly in applications where biodegradability is required.

Poly(alkylene glycols) (PAGs) are polymers of ethylene and/or propylene oxide. Control of molecular architecture gives access to a very wide range of viscosities. The polarity of PAGs can be varied to give materials which are soluble in water, mineral oils or neither. PAGs have exceptionally high viscosity indices and give very low friction when used as gear lubricants.

Phosphate esters are triesters of orthophosphoric acid with alkyl or aryl alcohols. They have particularly good fire retarding properties, and are used where this is an essential performance requirement, *e.g.* in aircraft hydraulic systems.

For applications where chemical stability is an overriding requirement, non-hydrocarbyl basefluids such as poly(dimethyl siloxanes) and perfluoroalkyl ethers may be used. However, the use of these non-hydrocarbyl lubricants is restricted both by their relatively high cost and by their incompatibility with other lubricants and standard additives.

All of the synthetic lubricant basefluids are normally used as formulations containing the same types of functional additives as are used in mineral oils. They are frequently blended with mineral oil or other synthetics in order to provide desired combinations of properties.

As a result of these technical developments, the chemical composition of lubricants has evolved over the last century from straight natural oils to today's complex formulations, containing one or more basefluids and a package of effect additives, tailored to meet the specific performance requirements of the intended application.

## 2 Environmental impact of lubricants and lubrication

This section considers various ways in which lubricants can impact the environment, in relation to the concepts of Green Chemistry and Life Cycle Analysis.

### 2.1 Assessing the scale

The annual global production of lubricants and related functional fluids (*e.g.* hydraulic fluids, transformer oils, heat transfer fluids and metal working coolants) is approximately 38 Mtes, of which lubricant additives account for 1.5–2 Mtes pa., while synthetic lubricant basefluids represent approximately 0.7 Mtes pa.<sup>19</sup> By comparison, annual global production of chemicals in total is estimated at 400 Mtes.<sup>20</sup> The latter figure includes additives and synthetic basefluids, but not mineral oils. If mineral oils are regarded as chemical products, the lubricants industry is responsible for approximately 8.5% of the total global chemical production by weight.

Manufacture and eventual disposal of this very large volume of material obviously represents an environmental burden. It is therefore not surprising that environmental aspects of lubricants and lubrication have been to the fore throughout the lifetime of the industry, and continue to be an active area of investigation.<sup>21–23</sup>

### 2.2 Life Cycle Assessment

A robust quantification of the overall environmental impact of lubricants would entail a detailed Life Cycle Assessment (LCA),<sup>24</sup> with a scope covering manufacturing, use and fate at end of life, and with system boundaries encompassing petroleum, petrochemical, oleochemical and engineering industry

activities. This would be a dauntingly complex process, due to the very broad scope required, and also to some particular issues which are characteristic of the industry and the applications.

One complication is that lubricants are typically manufactured as coproducts in integrated product networks, based on petroleum refining, oleochemical refining or chemical processing. Consequently, allocation of resource requirements and environmental impacts to the lubricant elements of these networks is necessarily somewhat arbitrary.

Secondly, since different lubricant types differ greatly in their performance and in the amount required for a particular purpose, a detailed knowledge of application performance is required in order to define an appropriate functional unit for comparison. LCA comparisons are made on the basis of equivalent outputs so a simple comparison of different lubricant types, based only on their resource requirements per kg or per litre, would therefore give misleading results.

Thirdly, because lubricants are used so widely in many different products and applications, tracing fate at end of life is very difficult. End of life treatment of industrial lubricants used at a single manufacturing site can be controlled and monitored, but following the fate of used car engine oils is a more challenging problem. The eventual fate of a large proportion of overall lubricant production is not accurately known.

Finally, even where data are in principle available, they may be regarded as confidential to the product manufacturers or users, and not openly published. Publishable LCAs generally require coordination by an independent body to facilitate pooling of commercially sensitive information.

Practical illustrations of the magnitude of the task are provided by studies from related sectors of the chemicals industry. These include the 1995 European Life Cycle Inventory for detergent surfactants production<sup>25</sup> and the Eco Profiles of the European plastics industry.<sup>26</sup> This scope of the former study was an inventory of energy and resource requirements for production of seven major surfactant types, with no consideration of impact assessment. Even with these restrictions, the study required two years to prepare, involving 17 technical professionals from 13 companies. A key conclusion was that no technical basis existed to support a general environmental superiority claim either for an individual product type, or for the various options for sourcing raw materials from petrochemical, agricultural or oleochemical feedstocks.

For these reasons, no such comprehensive lubricant Life Cycle Assessment has yet been attempted, although lubricating oils and related fluids have been considered as elements of LCA studies focussing on particular application areas such as hydraulic equipment for forestry applications and municipal cleaning,<sup>27</sup> and domestic refrigerators.<sup>28</sup> Furthermore, most companies involved in the industry carry out more or less detailed analyses of environmental impact in order to guide their strategy and internal decision making. However, the results of these analyses are not generally made available externally, although some limited studies have been published,<sup>29–31</sup>. Single company studies are limited by the access to data of the company involved, and may also raise concerns as to the independence of any conclusions from the commercial interests of that company.

### 2.3 Green Chemistry metrics

Although a full cradle to grave LCA study would be the ideal, its absence does not imply that no information is available. As Anastas has shown, the concepts of Green Chemistry<sup>32</sup> reinforce and complement those of Life Cycle Assessment.<sup>33</sup> This section will summarise some relevant available information and review its implications, in terms of the principles of Green Chemistry, in order to arrive at some general qualitative conclusions.

**2.3.1 Lubricant manufacturing—mass efficiency and process energy requirements.** The overall manufacturing process for a typical lubricant product involves a number of distinct steps, which can be broadly divided into basefluid manufacture, additive manufacture and formulation. The environmental impact of these processes can be assessed in terms of their reaction mass efficiencies<sup>34</sup> and process energy requirements.

By far the highest volume lubricant basefluid is mineral oil derived from petroleum processing. The typical energy requirement for mineral oil basefluid production has been estimated at 9 MJ kg<sup>-1</sup>, or approximately 20% of the Energy of Material Resource (EMR) of the product (*ca.* 42 MJ kg<sup>-1</sup>).<sup>30</sup> The required process energy in an integrated refinery is derived from combustion of a portion of the feedstock. Because a refinery produces a slate of different product types from LPG to asphalt, essentially all of the incoming raw material is either converted to products, or is used for energy production. Therefore, following the convention that raw materials used for energy production are not included in the overall mass balance, the mass efficiency of mineral oil basefluid production is essentially 100%.

A smaller proportion of lubricants are based on natural oils. Lubricants represent a minor application for natural oils as a whole and the range of sources of natural oils is very broad. Allocation of agricultural resource requirements to lubricant basefluids is therefore arbitrary and highly sensitive to assumptions about the raw material mix, geographical origin and the extent to which mechanised equipment and fertilisers are used. Data presented in the Surfactants LCI report<sup>25</sup> suggest a typical overall energy requirement of approximately 3 MJ kg<sup>-1</sup> for vegetable oil production.

It is difficult to generalise about manufacturing metrics for lubricant additives and synthetic basefluids due to the wide variety of chemistries involved. Also, since both mass efficiencies and process energy requirements significantly affect variable costs of manufacture, this information is normally maintained as confidential by manufacturers.

From published information, lubricant additives are frequently manufactured in single vessel reactions with little subsequent processing of the reaction mixture, using as solvent a mineral oil which is included in the product as sold.<sup>1,3,16</sup> For products of this type, reaction mass efficiencies are generally in the range 95–98%, with losses due only to process inefficiencies such as reactor washouts and filtration losses. Although there is little published information on process energy specifically relating to lubricant additives, by reference to data for closely related materials in surfactant and polymer applications, it is estimated that overall process energy requirements for the entire manufacturing chain typically approximate the EMR of the products, *i.e.* 35–40 MJ kg<sup>-1</sup>, to within a factor of 2.<sup>25,26</sup>

Similar arguments can be applied to the manufacture of synthetic basefluids. From process details disclosed in ref. 17, mass efficiency values for production of most synthetic basefluids may be estimated to be >85%. Higher values will apply to products such as PAOs and PAGs which are produced by addition polymerisation, and lower values to products such as phosphate esters or silicones where the manufacturing route involves substitution reactions of a chlorinated raw material (POCl<sub>3</sub> or SiCl<sub>4</sub>), with coproduction of HCl. Process energy requirements for the entire manufacturing chain for synthetic fluids are similar to those for lubricant additives, although the energy requirement for the final processing step involved in basefluid manufacture may be significantly lower than for mineral oil, particularly where distillation is not required.<sup>29</sup>

Lubricant formulation is typically a liquid blending operation, with a nominal 100% mass efficiency. Energy required for heating and agitation during the blending process is estimated at 3.6 MJ kg<sup>-1</sup>.<sup>29</sup>

Overall then, the manufacturing of lubricants is characterised by high mass efficiencies, and relatively low process energy

requirements, as would be expected for such high production volume materials.

**2.3.2 Renewable raw materials.** The natural fats and oils which were the first lubricants still provide a source of renewable raw materials. They are used in modern lubricants either directly, in formulations containing vegetable oils such as rapeseed and soybean oils, or after chemical processing as raw materials for the manufacture of synthetic basefluids and effect additives. The former approach has lower process energy requirements but gives a very restricted range of products, whose usefulness is restricted by their relatively poor stability and low temperature properties.<sup>35,36</sup> Also, the range of natural materials which can be used directly as fluids is obviously limited to those which are liquid over an appropriate temperature range.

Greater flexibility of utilisation is achieved through hydrolysis of natural fats and oils to produce the constituent fatty acids as raw materials for further chemical synthesis. A wide variety of natural sources, including solid fats and low grade or waste materials such as tallow from rendering of animal carcasses or tall oil from wood pulp processing, can be converted through controlled chemical processing into pure fatty acids of consistent quality.<sup>37</sup> Fatty acids of appropriate chain lengths and degree of unsaturation can then be used in the manufacture of synthetic basefluids or effect additives having precisely controlled structures which can be tailored for optimum application performance.

The major fatty acids derived from natural oils are linear, with an even number of carbon atoms, in the range C<sub>8</sub>–C<sub>22</sub>. For carbon numbers up to C<sub>16</sub>, the natural fatty acids are typically fully saturated, with unsaturation or polyunsaturation becoming more common for higher carbon numbers.<sup>14,37</sup> Commercially, these C-even fatty acids and their derivatives are always derived from renewable resources. Because of their ready availability from natural oils, petrochemical routes to these materials have never been developed to a significant extent.

The saturated short chain acids, octanoic and decanoic, can be reacted with neopentyl polyols, such as trimethylolpropane, to give thermally stable esters that are used as components of high performance synthetic car engine oils and as textile lubricants. Saturated acids with higher carbon numbers and their ester derivatives are solids at room temperature and not generally suitable in synthesis of lubricant basefluids. However, esters of longer chain *cis*-unsaturated acids such as oleic (*cis* 9-octadecenoic) acid have lower melting points and can be used. In particular, the trioleate ester of trimethylolpropane is widely used as a basefluid in applications such as biodegradable hydraulic fluids and cutting fluids, where oxidative stability is less critical.<sup>38</sup>

Both saturated and unsaturated longer chain fatty acids, and their derivatives such as amides and glycerol monoesters, are used as surface active lubricant additives. Sulfurised unsaturated fatty acids and derivatives are used as antiwear agents under extreme pressure conditions.

An important atypical natural fatty acid is the hydroxy acid ricinoleic (12-hydroxyhexadecenoic) acid, which is obtained from castor oil. Castor oil consists mainly of glycerol triricinoleate. It is more viscous than typical vegetable oils, due to hydrogen bonding, and has relatively good oxidative stability and low temperature fluidity. It has been widely used as a lubricating oil in its own right. Ricinoleate esters and amides are used as lubricant additives, and ricinoleic acid can be hydrogenated to give 12-hydroxystearic acid, which is extensively used as a gellant in lubricating greases in the form of its alkali metal salts.<sup>1</sup>

Although they have good low temperature fluidity, polyunsaturated acids are not preferred for use in lubricant applications because of their poor oxidative stability. However, with oleic acid, they can be converted by acid catalysed oligomerisation

and isomerisation, followed by hydrogenation, to give branched C<sub>18</sub> monoacid (isostearyl), C<sub>36</sub> diacid (dimer acid) and C<sub>54</sub> triacid (trimer acid), which are useful raw materials for the synthesis of high viscosity ester fluids.<sup>37–39</sup>

The double bond in the unsaturated acids offers many obvious possibilities for chemical derivatisation, some of which are already commercially exploited. For example, the linear diacids azelaic acid (C<sub>9</sub>) and sebacic acid (C<sub>10</sub>) are manufactured industrially by oxidation of oleic acid and alkali fusion of ricinoleic acid, respectively.<sup>40</sup> These diacids are raw materials for synthetic ester basefluids such as the respective diesters of 2-ethylhexanol.<sup>38</sup> The production of azelaic acid gives the C-odd monoacid nonanoic acid as coproduct. Another C-odd monoacid, heptanoic acid, is derived from ricinoleic acid by pyrolysis, as a coproduct in the manufacture of undecenoic acid. Nonanoic and heptanoic acids are used in the same way as their C-even homologues in manufacture of neopentyl polyol esters, where the C-odd chain lengths confers some low temperature fluidity benefits.<sup>41</sup> Manufacture of these C-odd monoacids from renewable resources is economically competitive with petrochemical routes, although the supply from the renewable route is limited by the demand for the more valuable co-product, in each case.

C<sub>19</sub> diacid based on carbonylation of oleic acid, and C<sub>21</sub> diacid from Diels–Alder addition of acrylic acid to conjugated dienic acids have also been developed and proposed for use as lubricant raw materials, although they have not found significant commercial application.<sup>40</sup> Many other fatty acid derivatives have been proposed for lubricant applications, including products of olefinic aralkylation, sulfonation, phosphorylation or halogenation,<sup>42</sup> epoxidation/addition products<sup>43</sup> and oligomeric estolides produced from oleic acid by 1,2 addition of the acid head group to the double bond.<sup>44</sup>

Currently, the vast majority of lubricant components are derived from fossil carbon sources, but because of the size of the overall market, even the relatively small proportion currently derived from renewable resources represents a large volume of material. It is estimated that lubricants derived from renewable raw materials account for approximately 2% of the European market, or 100 ktes pa.<sup>45</sup>

**2.3.3 Fate at end of life. Reuse and recycling.** Obtaining meaningful data on fate at end of life is challenging because of the enormous range of end use applications for lubricant products. The most comprehensive data are available for Europe, where studies have been carried out both by industry<sup>46,47</sup> and government,<sup>48,49</sup> typically focussing on automotive lubricants, hydraulic fluids and metal working fluids. All studies have reported a high degree of uncertainty, with a large proportion of material unaccounted for. According to the most recent survey,<sup>42</sup> annual lubricant demand in the EU is approx. 5.1 Mtes of which 2.65 Mtes (52%) is consumed in use. This leaves 2.45 Mtes (48%) generated as waste oils, of which 0.6 Mtes (25%) is unaccounted for and presumed to be burned illegally or dumped into the environment. The remaining 75% is collected, of which 36% is rerefined into lubricating oils and 64% burned as fuel. These data are summarised in Fig. 2.

Waste oil disposal in the EU is regulated according to Directive 75/439/EEC. This directive specifies a hierarchy of waste oils management which gives preference to regeneration or refining, but accepts burning under environmentally acceptable conditions. It was originally anticipated that the proportion of lubricant being refined would progressively increase from levels then estimated at around 30% in Germany and 5% in the UK. However, in practice, levels have not increased as expected<sup>50</sup> and are believed to be currently declining in favour of use as fuels. There has been much debate over whether it is environmentally preferable for used oils to be regenerated for reuse as lubricants or used as fuel. Inevitably, because of the

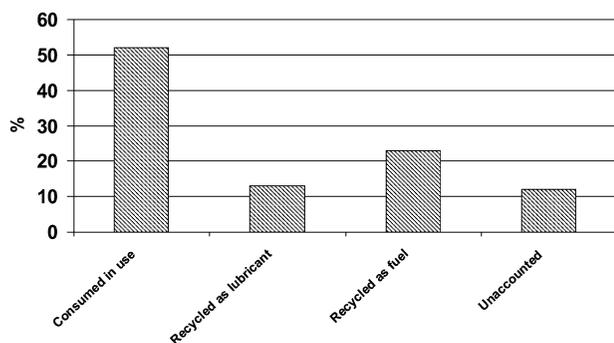


Fig. 2 Fate of waste oil in the EU (ref. 48).

wide range of product types and applications, there is no universally correct answer, and it is necessary to consider the details of each specific case.

The difficulty of re-refining used lubricating oils depends on the severity of the application, and the degree of control which can be applied to the recovery and collection process. For some industrial oils such as hydraulic fluids and transformer fluids, which are subject to regular condition monitoring, it has long been common practice to periodically 'launder' the oils by filtration, ion exchange and additive replenishment as required in order to restore them to a standard specification.<sup>51</sup> Material processed in this way is not recorded as used oil, so this type of re-use is not captured in the EU figures cited above.

Used car engine oils present much more of a challenge, both in terms of the degree of refining required and the difficulty of controlling the collection process in order to prevent contamination. However, collection and recycling processes are well established. Approximately 0.5 Mte pa of used engine oils are currently recycled in Europe,<sup>46</sup> and the capacity exists for a throughput of approximately 0.8 Mte pa.<sup>52</sup> A range of different refining processes have been commercialised, including acid/clay treatment, solvent extraction, distillation/clay treatment and distillation/hydrotreatment. All involve generation of process effluents such as acid sludge, solvent wastes, spent clays and catalysts. All also require significant process energy inputs, in some cases comparable to that required for original manufacture. Recovered base oil yields range from 60–95% depending on the technology and the quality of the input oil.<sup>30,53</sup>

In general, lubricant additives are not recyclable due to degradation in use.<sup>46</sup> They are therefore removed as sludge during lubricant re-refining and contribute to waste generation. However, most are combustible because they contain long chain hydrocarbon substituents in order to render them oil soluble. It is therefore not necessary to remove lubricant additives prior to combustion under suitable conditions. When used oils are used as fuel for cement and asphalt manufacture, any ash arising *e.g.* from presence of metal-containing additives may be sequestered in the product.

The case for recycling synthetic lubricant basefluids is stronger than that for mineral oils, due to the relatively higher process energy requirements in original manufacture of the synthetics. Additionally, oxygen-containing basefluids such as esters and polyalkylene glycols have significantly lower calorific value and therefore lower value as fuels than hydrocarbons. Where synthetic oils can readily be segregated and handled in large volume, reprocessing of specific high grade oils can be a realistic option, *e.g.* for the polyol esters used for aviation jet engine lubricants.<sup>54</sup>

Recycling technology continues to be an active area of research, with recent developments including separation of unoxidised baseoil components using supercritical fluid extraction,<sup>55</sup> separation of additives,<sup>56</sup> and separation of mineral oils from higher value synthetic basefluids.<sup>57</sup>

**2.3.4 Fate in the environment.** A very large proportion of overall lubricant production is dispersed into the environment on first use, either in the form of spills or leaks of virgin oils, spills and leaks of used oils, or emission of partially combusted oil derivatives in automotive exhausts. Lubricating oils are generally mobile liquids which are insoluble and less dense than water. They therefore tend to spread over surface waters in the form of highly visible oil slicks. These may have a damaging effect on aquatic life and are visually polluting. Consequently, considerable attention has been given to lubricant biodegradability and persistence in the environment.<sup>58</sup>

For complex substances, biodegradation is a multi-step process, and different measurements can be applied to the rate or extent of biodegradation, depending on the intended purpose of the measurement. The biodegradability of lubricants has generally been assessed according to two different types of test protocol, primary biodegradability and ultimate biodegradability.

As oils begin to biodegrade, they are first transformed into carboxylated or hydroxylated intermediates having higher water solubility, leading to disappearance of any visible oil slick. The rate of these first steps of the overall biodegradation pathway is described as primary biodegradability. It is normally determined by the CEC-L-33-A-93 test,<sup>59</sup> which measures the extent of disappearance of C–H stretching vibrations from the IR spectrum in a perhalogenated solvent extract of the test medium, over 21 days.

Disappearance of a visible slick does not imply that degradation is complete. In order to assess persistence in the environment, it is necessary to determine ultimate biodegradability. This is a measure of how readily the biodegradation process is completed and the test substance is fully mineralised, *i.e.* converted to carbon dioxide and water. Ultimate biodegradability of lubricating oils has generally been assessed according to the OECD 301 test protocols,<sup>60</sup> in particular OECD 301B which measures the amount of carbon dioxide evolved from a flask containing the test substance over 28 days and compares to the theoretical value based on the total organic carbon content of the sample. In general, biodegradability values of 100% are not obtained in the OECD 301B test because a portion of the substrate is converted into biomass rather than being fully oxidised to CO<sub>2</sub>. A substance is considered readily biodegradable if the final test value after 28 days is >60%, and if 50% biodegradation occurs within a 10 day period.

Typical values for biodegradability of a range of basefluids by OECD 301B and CEC-L-33-A-93 are listed in Table 1.<sup>61</sup> As expected, primary biodegradability values are generally significantly higher than ready biodegradability. From the viewpoint of assessing persistence in the environment, the OECD test protocols represent an extremely stringent test in relation to true environmental exposure, where microbes have the opportunity to acclimate to the substrate. A modified version has recently been proposed, involving preacclimation of the microbial inoculum and a longer test duration, in order to give a more practically useful indication of the likely extent of

Table 1 Primary and ready biodegradability of lubricant basefluids (ref. 54)

Lubricant type	Primary biodegradability CEC-L-33-A-94 21 days	Ready biodegradability OECD 301B 28 days
Mineral oil	10–45	10–40
PAO	20–80	5–60
Alkylbenzene	5–20	0–20
Diester (aliphatic)	75–100	50–95
Polyol ester	0–100	0–85
Vegetable oil	90–100	75–95

biodegradation in the environment. This measurement has been defined as inherent biodegradability and a draft protocol submitted for consideration by OECD.<sup>62,63</sup>

The results illustrate that biodegradability of mineral oils is generally much lower than that of vegetable oils, reflecting the adaptation of the microbial enzymic chemistry set to metabolism of naturally occurring substrates. In particular, microbes are equipped with enzymes for ester hydrolysis and oxidation of linear alkyl and alkenyl groups. Branched alkyl groups, particularly those containing quaternary branching, are more resistant to biodegradation.<sup>64</sup> These principles can be used to design and select synthetic basefluids having desired biodegradation characteristics.

Among synthetic basefluids, esters can have ready biodegradabilities essentially equivalent to those of natural oils. Poly( $\alpha$ -olefins) show higher biodegradability than mineral oils of equivalent viscosity because of their higher degree of linearity. Alkylbenzenes having a high degree of branching are generally of low biodegradability. The specialised non-hydrocarbon synthetic basefluid types such as silicones and perfluoroalkyl ethers are essentially non-biodegradable.

**2.3.5 Hazards and toxicity.** Lubricant basefluids and additives are generally low hazard materials. Because of the performance requirements, lubricating oils are viscous liquids with low vapour pressure, which are not highly flammable, have low VOC content and are not easily inhaled or ingested. Acute toxicity of lubricant basefluids and additives is also typically very low with  $LD_{50} > 2\text{ g kg}^{-1}$  for most major additive types.<sup>65–68</sup>

Some materials used historically as lubricant additives have been found to present potential hazards. Use of these materials, such as lead naphthenates, chlorinated naphthalenes and tris(*o*-cresyl)phosphate, has generally been discontinued.<sup>68</sup> Some unrefined and lightly refined mineral oils have been shown to induce skin cancers, due to presence of polynuclear aromatic hydrocarbons (PAHs). Refined mineral oils with low PAH content are now specified for most applications.<sup>68</sup>

Current health issues with lubricants primarily relate to inhalation of mists and to skin contact. Prolonged skin contact with oils can lead to defatting of the skin, which can cause dermatitis, while some additives are classified as irritant or sensitising.<sup>65</sup> Avoidance of skin contact, through good working practices and appropriate protective clothing, is recommended for all lubricant products.

Used oils present a more complex toxicological picture. Their hazards are harder to quantify since used oils may have a wide range of compositions, reflecting the potential range of service conditions and possibilities of contamination. It is known that PAH concentration increases in used oils, particularly in petrol engine crankcase oils, but also for diesel engine oils and hydraulic fluids. It is believed that the greater part of the PAH content is derived from fuel combustion by-products, and a minor part from tribochemical or thermochemical decomposition of the lubricant. Because of PAH formation in service, used engine oil is recognised as a potential carcinogen.<sup>65,69,70</sup> One implication is that careful monitoring of re-refining processes is required in order to control the level of PAH in recycled oils, particularly as increasing lubricant drain intervals may offer more opportunity for accumulation of PAH during the service lifetime of a given lubricant charge.

**2.3.6 Performance in use.** The previous sections have illustrated that lubricants generally rate well against Green Chemistry metrics associated with manufacture and fate at end of life. Mass efficiencies in manufacture are high, the materials are generally low hazard, and routes for recycling or re-use are established.

However, the principles of Green Chemistry also include consideration of product use, and in particular the impact of the product on energy consumption and waste generation in the intended application.<sup>32,33</sup> It is in this area that there is the greatest scope for further optimisation.

The fundamental purpose of lubricants is to reduce friction in machinery. Reducing friction implies reduced energy consumption for equivalent output of useful work, so optimising friction performance offers the possibility of reducing overall consumption of energy and associated emissions to the environment. The potential for improvement is enormous.

As noted above, global annual lubricant production is approximately 38 Mtes. However, this is only approximately 1% of total refinery throughput of crude oil. The major petrochemical raw materials collectively represent approximately 3%, and other nonfuel uses (solvents, asphalt, waxes) another 1%.<sup>71</sup> The remaining 95% or approximately 3.6 Gtes pa are burned as fuel.

Crude oil in turn accounts for only approximately 40% of global annual energy consumption, with large contributions also arising from combustion of other fossil fuels including coal and natural gas. In total, this energy production is responsible for emission of approximately 6 Gtes of  $CO_2$  expressed as elemental carbon (GtC)<sup>72</sup> and is the greatest source of atmospheric pollution by other acidic gases such as oxides of sulfur and nitrogen and by particulates.

Although a large amount of this energy is used in direct heat generation in buildings and industrial processes, the majority is used to power machines, primarily as transport fuel and in electricity generation. Most of these machines use some form of lubricant to reduce frictional losses and ensure efficient conversion of energy input into useful work. As will be shown in the next section, correct lubricant selection can lead to improvements in energy efficiency of up to 10%. The efficiency of utilisation of the enormous flow of energy through our industrial economy is therefore significantly dependent on lubricant performance.

A further purpose of lubricants is to reduce wear. Minimising wear by efficient lubrication prolongs the useful life of machines, thereby minimising the consumption of non-renewable resources such as fossil energy and metal ores required for manufacture and disposal of the machinery itself. Wear of mechanical elements can also cause machinery to operate less efficiently, so wear reduction has a secondary benefit in terms of overall reduced energy consumption throughout the operating lifetime of the equipment.

A third key performance measure of lubricants affecting the environmental impact is the stability or lifetime of the lubricant itself. For applications where lubricant is regularly replaced, there is an inverse relationship between lubricant stability and consumption. If a lubricant can be made to last twice as long, only half as much lubricant will be required, with corresponding reductions in the energy and material requirements for lubricant manufacture, and in the environmental impact of lubricant disposal. Increased sophistication of lubricant technology is already leading to an overall reduction in volume of demand for lubricants globally, for example, through use of high stability automotive engine lubricants offering extended drain intervals. Fig. 3 shows how lubricant demand during the period 1989–99 decreased by approximately 5%, despite an increase in world GNP of 48.5% over the same period.<sup>73</sup> Fig. 4 shows lubricant consumption per unit of GNP in 1990 and 1997 for the major economic regions. All regions show a significant decrease over the period. Lubricant consumption per unit GNP is significantly lower in the most developed economies such as Europe, which lead in their adoption of high performance lubricant technologies, such as synthetic basefluids (Fig. 5).<sup>71</sup>

Therefore, in summary, optimisation of three lubricant performance parameters; friction reduction, wear reduction and lubricant stability, will lead to a positive environmental impact

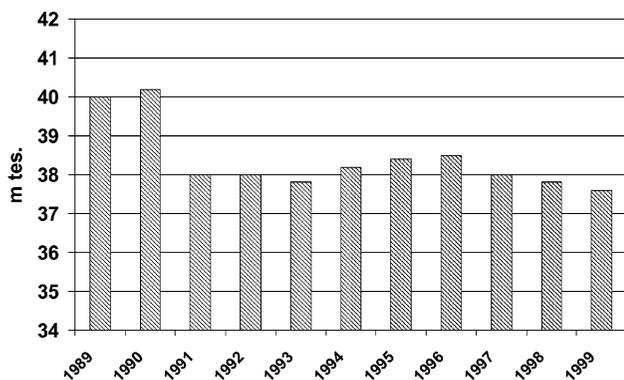


Fig. 3 Global lubricants demand (mtes) 1989–99 (ref. 73).

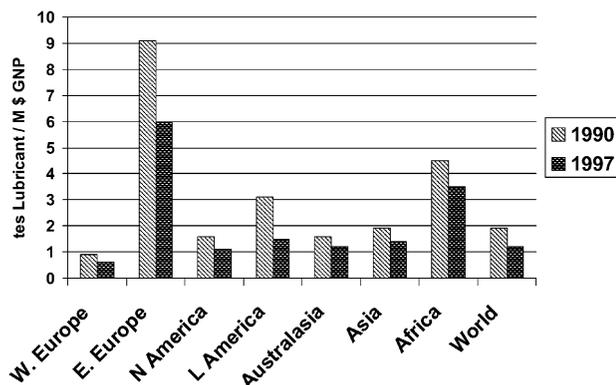


Fig. 4 Lubricant demand per unit of GNP (ref. 73).

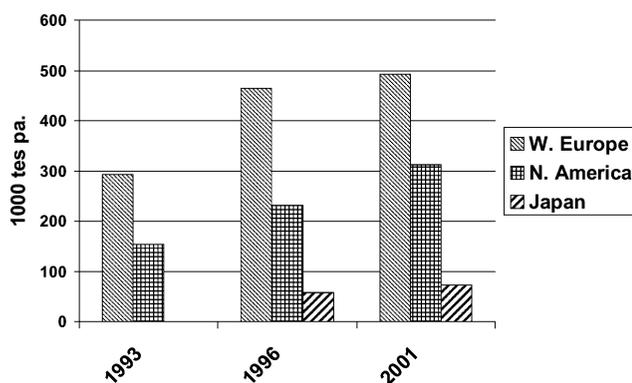


Fig. 5 Consumption of synthetic lubricants (ref. 71).

in use. The next section presents practical examples of how innovative product development is being used to improve lubricant performance in these key areas.

### 3 Practical examples

This section provides some examples of current technical developments which are leading to reduction of the environmental burden of lubricants and lubrication technology.

#### 3.1 Refrigeration compressor lubricants. Reducing electrical energy consumption through lubricant basefluid design

5–10% of the UK's domestic electricity consumption is used to power refrigerators and freezers. Industrial and commercial refrigeration and air conditioning represents a similar proportion of non-domestic power consumption. With the growing

recognition of the importance of energy conservation, refrigeration engineers are exploring all options for increased efficiency, including optimisation of lubricant performance.<sup>74</sup>

A domestic refrigerator or freezer contains a small reciprocating or rotary compressor directly coupled to an electric motor. Both the compressor and the motor bearings require lubrication, and the system imposes some very specific performance requirements on the lubricant. Since the motor and compressor are hermetically sealed inside the refrigeration circuit, the lubricant cannot be changed, and must be stable for the lifetime of the appliance, typically 10–20 years. Since the lubricant is not exposed to atmospheric oxygen and water, oxidative and hydrolytic stability are of less importance than thermal stability. Because of the contact with the electric motor, refrigeration lubricants must have very good electrical insulation properties and must be stable to electrically induced decomposition. They must also have very good low temperature fluidity characteristics, with no tendency to deposition of waxes.<sup>75</sup>

Most importantly, a refrigeration lubricant must be miscible with the refrigerant gas so that any lubricant transported into the refrigeration circuit is returned to the sump and does not foul heat exchanger surfaces or restrict pipework, which would lead to reduced energy efficiency. Hydrofluorocarbon (HFC) gases are currently the most widely used non-flammable, zero ozone depletion potential refrigerants. HFCs are relatively polar and are not miscible with mineral oils. Polyol esters (POEs), which are esters of monoacids with neopentyl polyol alcohols, have become the lubricant of choice for use with HFC gases for reasons of miscibility and also because of their inherently good lubricity<sup>75</sup>

Esters also represent a very versatile chemistry for assembly of synthetic basefluids because a wide range of organic acid and alcohol raw materials are available, derived both from oleochemical and petrochemical sources. By appropriate selection of raw materials so as to control molecular properties such as molecular weight, polarity, linearity and structural diversity, ester fluids having a very wide range of physical and chemical properties can be produced.<sup>33,36</sup> Some of the relevant structure–property relationships are illustrated in Fig. 6.

As described in Section 1, for any given lubricated system, the coefficient of friction depends on the lubricant viscosity, the relative velocities of the surfaces and on the load to be supported.<sup>3,4</sup> Lowest friction, and greatest energy efficiency, is obtained by operation at the minimum of the curve shown in Fig. 1. Small appliance refrigeration compressors are designed to operate under conditions of hydrodynamic lubrication, where metal to metal contact is avoided by ensuring that a full fluid film separates the surfaces. The energy required for shearing the entrained hydrodynamic film increases with the viscosity of the lubricant. Therefore, the energy requirement of an appliance compressor can be reduced by reducing the lubricant viscosity.

However, if the lubricant viscosity is reduced too far, it is no longer high enough to ensure that a full fluid film is entrained, and the system will move into the boundary lubrication regime.

Property	Molecular Weight	No. of ester groups	Branches	Longest linear chain	Structural diversity
Viscosity	+	+	+	+	
VI	+		-	+	
Flash point	+	+	-	+	-
Low temp fluidity	-	+	+	-	+
Solvency	-	+	-	-	+
Biodegradability	-	+	-		

Fig. 6 Structure–property relationships for ester basefluids. + indicates positive correlation, – indicates negative correlation (ref. 38).

Here, metal to metal contact occurs, so some wear is unavoidable. Wear reduces efficiency of operation, and eventually limits the lifetime of the appliance. Also, friction coefficients in mixed and boundary lubrication are much higher than in the hydrodynamic regime, leading to increased frictional losses. Friction converts mechanical energy to thermal energy, so higher friction also leads to overheating of the fluid and the contacting surfaces, which further reduces the expected lifetime of the appliance.

Loss of full fluid film lubrication will also occur if the load increases, or if the relative velocity decreases, in particular at startup and shutdown conditions. Therefore, in order to exploit the energy efficiency benefits of operation at the minimum friction point, the lubricant must be designed to have not only the correct viscosity under operating conditions, but also good inherent antiwear capabilities to prevent wear occurring during excursions to non hydrodynamic lubrication regimes.

Structure–property relationships such as those shown in Fig. 6 have been used to develop a range of POEs optimised for energy efficiency in refrigeration lubrication applications. These optimised POEs have permitted a progressive reduction in the industry standard lubricant viscosity, from 18 cSt at 40 °C when polyol ester lubricants were first introduced, to a typical value of 10 cSt today. This has delivered real benefits in energy efficiency, as shown in Fig. 7, which illustrates the dependence of energy consumption on lubricant viscosity for a standard domestic refrigerator. Reductions of energy consumption of approximately 10% as compared to the 18 cSt benchmark are achievable.<sup>74</sup>

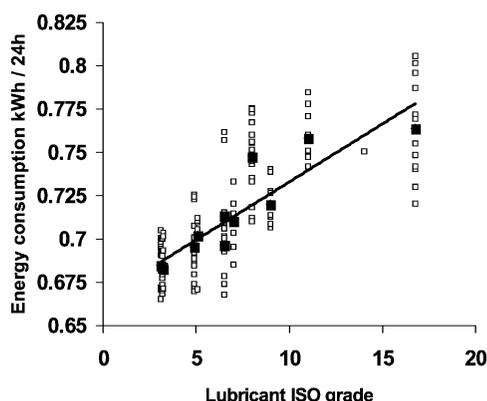


Fig. 7 Dependence of refrigerator energy consumption on lubricant viscosity, ref. 74.

The annual energy saving for a single appliance attributable to the viscosity reduction from 18 to 10 cSt is approximately 60 MJ. This is significantly higher than the process energy requirement for manufacture of the lubricant. Since the lifetime

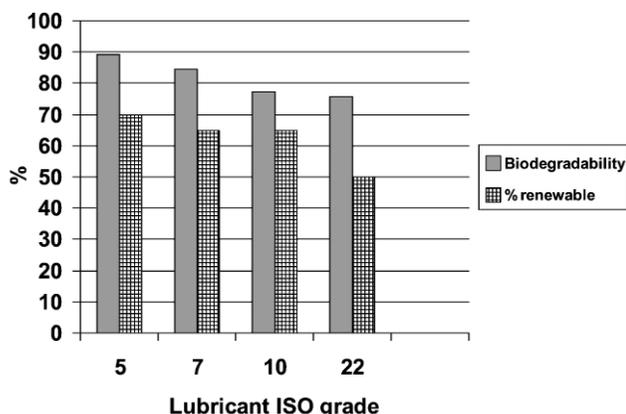


Fig. 8 Biodegradability by OECD 301B and percentage of renewable raw materials for a range of polyol ester refrigeration lubricant basefluids.

of a typical refrigerator is approximately 10 years, it is apparent that the lifetime energy saving greatly outweighs the total energy requirement for lubricant manufacture. A secondary benefit has been that the new generation optimised POE lubricants have been designed to be readily biodegradable and to use a significant proportion of raw materials derived, or potentially derivable, from renewable resources (Fig. 8).

### 3.2 Hydraulic fluids. Reducing resource consumption through extended lubricant lifetime

Hydraulic fluids are used to transmit power. Typically, the fluid is pumped in a circuit from a central pumping unit *via* pipework to remote motors or actuators where the fluid energy is converted back to mechanical motion. Although lubrication is not their primary purpose, hydraulic fluids are regarded as a class of industrial lubricant because they must provide adequate lubrication to prevent wear of the pump and actuators, which would impair efficiency. For efficient power transmission, without high viscous losses or internal leakage, the viscosity of hydraulic fluids should normally be in the range 22–46 cSt at 40 °C. High thermal and oxidative stability, so as to maintain viscosity and prevent formation of sludge and varnish, is therefore a critical performance requirement.

Hydraulics are a very flexible, lightweight and efficient method for power transmission, and their use is particularly widespread in mobile equipment used in transportation, construction and agriculture. In such mobile hydraulic equipment, the pressurised hydraulic fluid is contained in flexible hoses, which are vulnerable to puncture or rupture. Any failure of containment leads to accidental discharge of hydraulic fluid to the environment. Consequently, where hydraulic equipment is used in environmentally sensitive applications such as water-course maintenance and forestry, the fluids are increasingly required to be biodegradable.<sup>27,76</sup>

In some applications, the requirement for biodegradable hydraulic fluids can be met by use of natural oils. However, the applicability of natural oils is limited by their relatively low thermo-oxidative stability which restricts their useful lifetime. Also, their poor low temperature fluidity makes them unsuitable for use in low ambient temperature. Consequently, there is a developing requirement for high performance fluids, with thermo-oxidative stability equivalent or superior to that of mineral oil-based fluids, good low temperature fluidity and acceptable biodegradability characteristics. Synthetic esters are well suited to meet this requirement.

Consideration of the mechanisms of chemical decomposition of natural oils can be used to guide the molecular design of synthetic esters having improved stability. The structure of a typical vegetable oil is shown schematically in Fig. 9. Under high temperature oxidation conditions there are two distinct modes of reaction leading to decomposition, namely thermolysis and autoxidation.

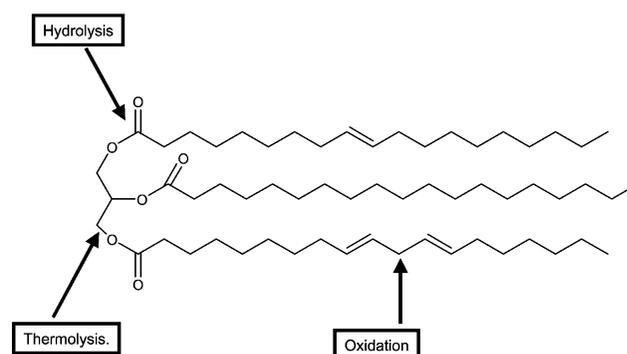


Fig. 9 Schematic structure of triglyceride natural oil, showing positions vulnerable to chemical degradation.

Thermolysis occurs by  $\beta$ -elimination at the ester group. The thermolysis pathway can therefore be prevented by transesterification to substitute the glycerol moiety in the original vegetable oil by a neopentyl polyol such as trimethylolpropane. The resulting ester contains no beta hydrogen atoms and therefore cannot undergo thermal decomposition by  $\beta$ -elimination.

Autoxidation is initiated by hydrogen abstraction from the carbon atoms vicinal to the olefinic bonds in the fatty acid residues. The rate of autoxidation is greatly reduced in compounds containing no olefinic unsaturation. Olefinic unsaturation can be removed by hydrogenation. However, hydrogenated vegetable oils are typically solid at ambient temperature and therefore not suitable for lubricant applications. Fatty acid isomerisation to introduce branching prior to hydrogenation gives good low temperature fluidity, but increases viscosity too much for the application. To substantially improve oxidative stability it is necessary to look to alternative basic structures, such as diesters or polyol esters of short chain saturated fatty acids. The structure–property relationships illustrated in Fig. 6 can be used to design materials having the appropriate properties for the application.

These principles have been used to develop high performance biodegradable hydraulic fluids based on synthetic esters. Biodegradability was assessed according to the OECD 301B protocol.<sup>60</sup> Thermo-oxidative stability was measured by determination of the oxidation induction time using high pressure differential scanning calorimetry (HP-DSC).<sup>77</sup> The HP-DSC induction time correlates with the expected oxidation-limited service lifetime for the lubricant.

Fig. 10 compares HP-DSC induction time for a series of oils including commercial formulated hydraulic oils based on vegetable and mineral oil basefluids, a formulation based on a trimethylolpropane ester of natural fatty acids, and a petrochemically derived fully saturated diester. At 150 °C, the induction time for the trimethylolpropane ester is higher than that for the vegetable oil formulation. The induction time for the saturated diester is shown to be equivalent to that of the mineral oil formulation, and approximately 10 times longer than that of the vegetable oil formulation. This illustrates that the autoxidation pathway is more significant than the thermolysis pathway under these conditions.

However, the thermolysis pathway still makes a significant contribution to overall decomposition, and thermo-oxidative stability can be further improved by combining the two approaches and designing synthetic esters based on neopentyl polyols with fully saturated acid groups. In saturated polyol esters of this type, both oxidative stability and biodegradability can be additionally improved by increasing the average number of ester groups per molecule and reducing the amount of tertiary

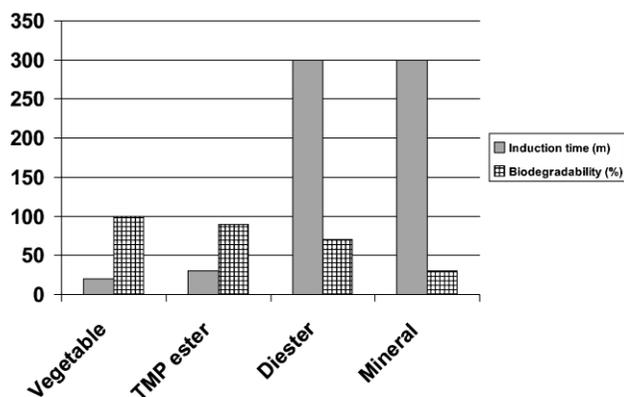


Fig. 10 Comparative HP-DSC induction time at 150 °C and biodegradabilities for formulated hydraulic fluids based on vegetable oil, trimethylolpropane ester of natural fatty acids, petrochemical diester and mineral oil.

branching. Operating within these constraints increases the manufacturing cost of the products, but can give significantly enhanced performance.

Fig. 11 shows HP-DSC induction time under higher severity conditions for an optimised example of this type of saturated polyol ester, compared with the diester and mineral oil based formulations. At this higher test temperature, the diester can be seen to have significantly higher induction time than the mineral oil, but the optimised saturated polyol ester shows an induction time approximately five times greater than that of the mineral oil formulation, while retaining biodegradability equivalent to that of the vegetable-based formulation.

Products based on both types of synthetic ester have already been commercialised as basefluids for biodegradable hydraulic fluid formulations. Field experience has confirmed that the products deliver the predicted high stability and extended lifetime in practice.

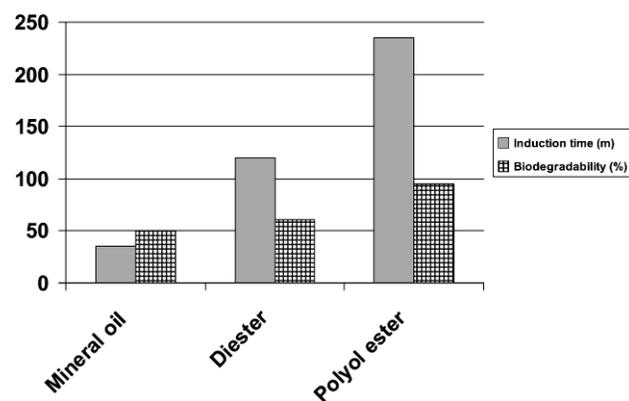


Fig. 11 Comparative HP-DSC induction time at 200 °C and biodegradabilities for formulated hydraulic fluids based on mineral oil, petrochemical diester and saturated short chain polyol ester.

### 3.3 Automotive lubricants. Improving fuel efficiency through additive technology

A very large proportion of overall fossil fuel consumption is used as transport fuel in internal combustion engines. Improving the fuel efficiency of these engines has long been a key objective of the automotive industry and it is generally recognised that the crankcase and transmission lubricants can contribute to improving energy efficiency in many ways.<sup>78</sup>

In a typical car engine, only around 20–35% of the chemical energy of combustion is converted to useful mechanical work. The remainder is lost as heat through the exhaust and through the engine cooling system, or as frictional or pumping losses in the engine and transmission.<sup>79</sup> Potentially the greatest gains in fuel efficiency would come by reducing the amount of energy lost as heat. Exploitation of this in so-called low heat rejection engines, coupled with other trends, such as cooling on demand, suggests that in future, lubricants will be required to operate at higher sump temperatures than at present.<sup>78</sup> This will obviously increase the thermo-oxidative stress and favour use of synthetic fluids having inherently good oxidative stability, as illustrated above for hydraulic fluids.

A further contribution to energy efficiency will come from the more widespread use of lower viscosity fluids. Ford Motor Company have recently announced a change from 5W-30 to lower viscosity 5W-20 lubricants for factory-fill for the majority of their vehicles. This is expected to deliver a net average 0.6% fuel economy saving across the product range. Ford believes the switch to lower viscosity oils in the USA alone will reduce carbon dioxide emissions by 190,000 metric tons a year and reduce fuel consumption by over 21 million US gallons a year.

The continuation of this trend will also lead to greater application of synthetic fluids. Lower viscosity generally implies lower molecular weight and consequently higher volatility. The combination of higher sump temperatures with lower viscosity fluids will be a major driver towards more widespread use of polar fluids such as esters, which have lower volatility than hydrocarbons of the same viscosity. High stability synthetics can also reduce the viscosity increase associated with oxidative degradation. This will give better retention of energy efficiency through the lifetime of the lubricant charge, and allow extension of drain intervals, which will reduce overall consumption of lubricant.

Thus, the same lubricant design considerations as outlined above in the hydraulic fluid and refrigeration lubricant examples will also contribute to energy conservation in internal combustion engines. However, for the internal combustion engine there is an further contribution to be made by friction modifier additives.

Unlike a domestic refrigeration compressor, a significant contribution to overall frictional losses in an internal combustion engine arises from contacts which operate under boundary lubrication conditions.<sup>80,81</sup> Under boundary conditions, the friction coefficient is essentially independent of lubricant viscosity, and becomes dependent on the nature of the contacting metal surfaces. Surface-acting additives can be used to modify the surface chemistry and reduce friction.

Inorganic friction modifiers based on molybdenum dithiocarbamate complexes act by chemical reaction to give *in situ* deposition of MoS<sub>2</sub>, which is an effective solid lubricant because it has a lamellar structure with low interatomic forces between the planes.<sup>82</sup> Since this reaction is irreversible, soluble Mo concentration decreases over time and activity decreases with fluid ageing.<sup>83</sup> Furthermore, the molybdenum dithiocarbamates contribute to emissions of heavy metals and sulfur compounds. There is therefore growing interest in organic friction modifiers based on derivatives of natural long chain fatty acids. These are believed to act by reversible formation of mono- or multilayer surface films having low surface energy, which reduce friction through minimising adhesive forces between the opposing surfaces.<sup>84</sup>

Boundary friction coefficients can be measured using a pin on disk tribometer, which measures the friction force between metal test pieces under controlled load, relative velocity and temperature. Fig. 12 shows the variation of friction coefficient with sliding velocity at constant load and temperature for lubricants formulated with and without organic friction modifier. At high speeds the system is in the hydrodynamic lubrication regime and the test pieces are separated by a lubricant film. The friction force measured is due only to the viscosity of the bulk fluid and the additive has no effect. At low speeds the system is in the boundary lubrication regime, there is metal-metal contact and the presence of the additive reduces the friction coefficient by approximately 20%.

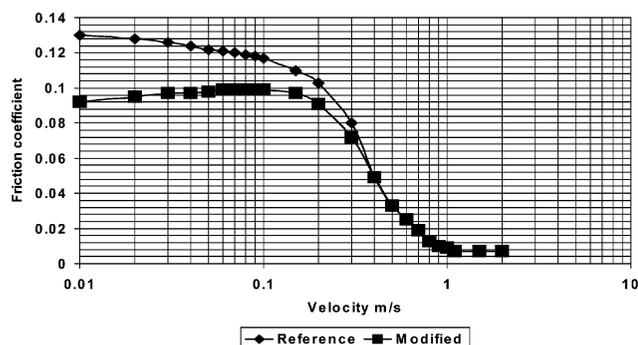


Fig. 12 Effect on boundary friction coefficient of friction modifier additive in reference lubricant, using a pin on disk tribometer.

Approximately 5% of the overall fuel energy in a typical internal combustion is dissipated in overcoming boundary friction,<sup>79,80</sup> so this translates in practice to a potential for approximately 1% reduction in fuel consumption. At present, both inorganic and organic friction modifier additives systems lose activity during the lifetime of a lubricant charge, due to oxidative instability. Development of improved additive systems offering higher activity and improved oxidative stability is an active area of research.

## 4 Discussion. What makes a lubricant 'green'?

This final section offers provisional conclusions as to how the principles of Green Chemistry should be applied to support future development of more sustainable lubricant technologies.

### 4.1 The importance of performance in use

The previous sections have developed the theme that lubricants have a unique capability to deliver environmental benefits in use, mainly through their role in reducing friction in machinery, which improves energy efficiency, thereby conserving fuel resources and reducing emissions of CO<sub>2</sub> and acid gases.

For car engine oils, the difference in fuel consumption between an optimised low friction oil and a standard oil can be as much as 5%.<sup>85</sup> In mobile hydraulics, fuel consumption savings of up to 3% may be obtainable through optimising the hydraulic fluid properties.<sup>29</sup> Even greater reductions in power consumption of domestic refrigerators have been demonstrated<sup>74</sup> and the same principles may be exploited to reduce power losses in hydro-electricity generation.<sup>86</sup>

These energy efficiencies potentially accessible through lubricant optimisation are significantly greater than the energy requirements for lubricant manufacture.<sup>27,31</sup>

The other key role of lubricants is reducing wear. This obviously serves to extend the useful life of machinery and thus also contributes to resource conservation. At the same time, consumption of the lubricants themselves, and of the resources involved in their manufacture, can be minimised by optimisation of the stability of the lubricant basefluids. Therefore, the most important issues to consider in assessing the environmental impact of lubricants are the performance parameters; friction reduction, wear reduction and lubricant stability.

Although these broad principles are applicable to lubricant optimisation in general, their implementation across many widely different lubricant applications, each having very different performance criteria, will require a very wide range of optimised lubricant solutions. To continue to develop this range of increasingly specialised products, lubricant developers will need to draw on the full range of available raw materials, and will make increasing use of synthetic basefluids and functional additives which permit optimisation of application performance through chemical design at the molecular level.

These conclusions are important in the context of the growing recognition of the necessity to make a transition to more sustainable technologies. Governments, industry and pressure groups are seeking to accelerate this transition by use of economic incentives to promote more sustainable technologies and by harnessing the power of consumer choice through ecolabelling schemes. It is essential that these measures are correctly targeted, or their effects will be counter-productive.

### 4.2 The role of renewable raw materials

The current focus on sustainable development has led to increasing interest in lubricants derived from renewable

resources. In particular, the use of vegetable oils in lubricant and hydraulic fluid applications is being promoted.<sup>87–90</sup> Vegetable oils are renewable, biodegradable, have relatively low manufacturing process energy requirements and show some good lubricant properties. However they also have performance deficiencies which mean that their use is not necessarily an environmentally preferable option. The poor thermo-oxidative stability of vegetable oils reduces operational lifetime and increases the amount of lubricant required to be manufactured and disposed of.<sup>27,36</sup> Also, in applications where a closely specified viscosity is required for optimum energy efficiency, the narrow range of viscosities available from natural oils may not be optimal, with consequent energy inefficiencies.

Because of their particular combination of properties, natural oils are a good option for total loss, once-through applications like chainsaw lubricants and railroad greases, where stability is not an issue and ready biodegradability is a requirement. Vegetable oils such as rapeseed, canola and soybean oils are already widely used in such applications.

Considerable effort is being applied to modifying the properties of vegetable oils in order to make them more suitable for use in other applications. Conventional plant breeding and genetic modification of oil producing crops has been undertaken in order to alter the composition of the oils that they produce, for example by controlling polyunsaturation in order to improve oxidative stability,<sup>91</sup> and introducing branching to improve low temperature flow properties or increase viscosity.<sup>92</sup> However, the performance improvements achieved so far are marginal when compared to mineral oil or synthetic lubricant formulations.

The issue of operational lifetime is particularly significant in this context, in view of the very large volumes of lubricants currently consumed. Agricultural yields of vegetable oils from oilseed crops such as rape are typically in the range 1–2 t ha<sup>-1</sup>,<sup>93</sup> so to produce enough vegetable oil to meet current European demand for around 5 Mtes pa of lubricants would require approximately 5 Mha (or around twice the area of Wales) to be cultivated for the purpose. However, because the lifetime of the vegetable oil derived products is shorter than that of the mineral oil formulations they would to replace, as in the hydraulic fluid example shown in Fig. 10, then a greater volume of vegetable oil would be required, and the land requirement would increase further.

Clearly, if renewable resources are to make a significant contribution, it must be in the form of raw materials for high performance synthetic lubricants and effect additives that will have extended lifetimes and therefore reduced material requirements, as compared to mineral oil based formulations. As described in Section 2.3.2 above, natural fatty acids and their derivatives are already used in the manufacture of high performance synthetic ester lubricants, and this use can be expected to increase. However, at present, synthetic lubricants having optimised performance cannot be manufactured from renewable resources alone. Petrochemically derived materials, such as the neopentyl polyols, are also essential components. Although these components could in principle be derived from biomass it is presently not economic to do so. Therefore, in the medium term there will continue to be an essential role for petrochemically derived components in lubricants.

The simplistic assumption that renewable resources are necessarily sustainable must also be questioned. True sustainability requires economic and social, as well as environmental sustainability. The exploitation of renewable resources is not necessarily sustainable in this broader sense. For example, the debate around the environmental impact and land use requirements for production of biodiesel (methyl esters of vegetable fatty acids)<sup>93</sup> has highlighted the fact that contemporary Western agriculture requires very high inputs of energy in the form of fertilisers and fuel for agricultural machinery and crop processing. The sustainability of these agricultural practices has

been widely questioned, and the social implications in terms of land and labour requirements to deliver the same outputs without use of fossil fuel inputs have yet to be addressed.

In summary, exclusive use of renewable resources is not a sufficient condition for a sustainable technology, and may not be the most appropriate first step on the way. At present, legislation or economic incentives to restrict options for lubricant raw materials to those currently derived from renewables would lead to use of inappropriate or inferior products and would have a net detrimental effect on overall environmental burden. In a fossil-fuel powered society, where 95% of crude oil is consumed as fuel, it is both rational and responsible to divert some of that material for use as raw materials for lubricants, in order to ensure that our utilisation of the remainder is as efficient as possible.

### 4.3 Recycling or re-use as fuel

Another area where there is potential for legislative or economic incentivisation to have counterproductive effects arises at end of life, in the debate over whether it is preferable to recycle used lubricants by re-refining, or to re-use them for fuel value by combustion.

The European Waste Oil Directive is currently under review. The European Commission favours increased incentivisation of recycling and has considered a mandatory requirement for incorporation of a minimum percentage of recycled fluids into all new lubricant products. This prospect is of obvious concern to lubricant users and their suppliers, since it would constrain the development of products tailored to the requirements of particular applications, such as the examples given in Section 3. The composition of basefluids from recycling processes as currently practised is similar to that of lightly processed mineral oils, which have low biodegradability and relatively low thermal and oxidative stability. Incorporation of significant levels of this material would preclude development of biodegradable lubricants for use in environmentally sensitive areas, or high stability fluids with extended service lifetimes. Consequently, the lubricant industry, and most national governments generally regard fuel use as a more practical and equally acceptable option.

This debate over the extent to which recycling into the same application should be incentivised by legislation is common to many other product groups where recycling is becoming significant *e.g.* polymers and paper products. Recycling processes are greatly facilitated by standardisation, and reduction of the number of different materials used. However, enforced standardisation of materials, or requiring a minimum recycled component, can lead to inappropriate use of materials which may compromise economic or environmental performance and even safety. Well-intended legislation to require a pre-determined arbitrary level of recycling can be a blunt instrument having unintended adverse consequences.

A recent article outlined the arguments for and against the recycling and combustion options, concluding that highest priority should be given to encouraging collection of used oil for disposal by whichever route.<sup>85</sup> It can also be argued that the issue would be best addressed by promoting the use of lubricants having improved stability and extended drain intervals, in order to reduce at source the amount of waste oil requiring disposal.

### 4.4 Ecolabelling schemes

In addition to legislative requirements, labelling schemes are increasingly being developed in order to promote the use of

more environmentally acceptable materials. Recent articles have reviewed the current status of labelling schemes and environmental legislation for lubricants.<sup>21,94,95</sup> Particularly influential developments in Europe have included the German Blue Angel labelling scheme for hydraulic fluids, saw lubricants and metal working fluids,<sup>96</sup> and the voluntary section on environmental properties included in the Swedish Standard for hydraulic fluids.<sup>97</sup> These initiatives set criteria for all components of a lubricant formulation and have prompted considerable effort in the industry to develop products meeting the requirements.

Ecolabels have played a valuable role in aiding decision making and influencing market activities. However it must be understood that they represent an attempt to compress all of the potential environmental impacts of a product or process into a single criterion for decision making. This necessarily involves judgements about the relative importance of the various potential impacts, which will reflect the needs of a particular application and the values of the organisation responsible. Thus, whereas LCA or Eco-profiles provide objective and quantitative information, ecolabels represent subjective interpretation. Ecolabels should therefore only be used in the context for which they were originally developed and are potentially misleading if conclusions are taken out of context.<sup>98</sup> In particular, existing ecolabelling schemes have focussed on toxicity, ecotoxicity and biodegradability and do not recognise the potential environmental benefits of optimised performance in use.

A further criticism of current labelling schemes is that they are based on the properties of unused lubricants and do not take account of the significant changes in toxicology or ecotoxicity which may result from ageing of oils in use.<sup>99,100</sup> However, given the range of potential operating conditions there is currently no consensus on what would constitute a meaningful standardised oil ageing protocol in order to generate reproducible and representative samples of aged oils.

## 5 Conclusions. Towards sustainability

A recent OECD workshop considered the contribution of chemistry to sustainable development, and concluded that 'We should strive to maximise resource efficiency through activities such as energy and non-renewable resource conservation, risk minimisation, pollution prevention, minimisation of waste at all stages of a product life cycle and the development of products that are durable and can be re-used and recycled'.<sup>101</sup>

There is scope for development of lubricant technology in all of these areas, but lubricants have a particularly important contribution to make in relation to energy conservation, minimisation of waste and development of durable products. While material recycling and use of renewable raw materials are undoubtedly requirements of a future sustainable technology, they are not necessarily the first issues to address. Truly green lubricants are those that optimise energy efficiency and minimise wear in the machinery which they lubricate, and which have maximised service lifetimes in order to reduce the amount of lubricant required. These principles are expected to lead to increasing use of high performance synthetic basefluids and effect additives. Green Chemists will have an important role to play in the design and manufacture of the novel materials which will be required.

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