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A review on the chemistry, production, and technological potential of bio-based lubricants

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ABSTRACT

The possible scarcity of oil and gas resources in the future (whether in quantity or areas of availability) is a major concern throughout the world. For this reason, governments all over the world are working on reducing their dependence on imported energy resources. Alternative energy resources such as bioethanol, biodiesel and biomass have gained prominence over the years in order to substitute petroleum-derived products. Bio-based lubricants have also gained importance as alternatives to conventional petroleum-based lubricants in various applications, especially the automotive industry. Despite the benefits of bio-based lubricants, these lubricants are still far from being practical substitutes. Since bio-based lubricants are typically produced from raw vegetable oils, these lubricants have poor cold flow properties as well as low thermo-oxidation and hydrolytic stability. However, these shortcomings can be addressed by modifying the vegetable oils chemically or incorporating additives into the oils. This review provides a detailed treatment on bio-based lubricants, the various vegetable oils used as the feedstocks for the production of bio-based lubricants, the physicochemical properties of bio-based lubricants, the processes used for chemical modification of vegetable oils, the lubrication properties of bio-based lubricants, as well as the various additives used to improve the properties of bio-based lubricants. It is believed that this review paper will provide useful insight to researchers and practioners in the field regarding bio-based lubricants.

1. Introduction

Energy plays an essential role in our lives in order to carry out our daily activities as well as to boost the nation's economic growth. In one study conducted by the European Commission [1], the consumption of energy in the world is predicted to reach 22.3 Gtoe (Giga-tonnes of oil equivalent) in 2050 from the current 10 Gtoe. Coal, oil and natural gas provides 5.7, 5.9 and 4.1 Gtoe of energy whereas renewable and nuclear energy contributes 3.4 and 3.2 Gtoe of energy, respectively. Fossil fuels play a major role in fulfilling global energy demands for centuries. However, fossil fuels are depleting over the years due to the increasing energy demands resulting from industrialization and population growth. The ever-increasing consumption of these energy sources is alarming since the depletion of fossil fuels will have a serious impact on people's lives [2]. According to Owen et al. [3], the demand for mineral oils will likely surpass its supply by 2015 – however, this is constrained by strong recession pressures caused by the decrease in demand and thus, the demand for mineral oils is parallel with its supply. The depletion of fossil fuels and the growing concern on the detrimental impact of fossil fuels on the environment has led to the critical need to explore alternative sources of energy.

The use of vegetable oils for lubrication purposes has been in practice for many years. However, this idea was scrapped due to the discovery of petroleum and the availability of low-cost oils. To date, fossil fuel-based crude oils are used as the raw materials to produce fuels and lubricants. However, there is new interest in the use of lubricants from vegetable oils due to growing concern over the environmental impact of fossil fuels. Bio-based lubricants have been produced and marketed by a number of companies [4]. Bio-based lubricants are promising alternatives for mineral oils since they retain the technical specifications of conventional lubricants. Bio-based lubricants are biodegradable lubricants, derived from edible and non-edible vegetable oils and they have high lubricity, viscosity index and flash point [5]. However, bio-based lubricants also have several disadvantages. For instance, these lubricants have poor cold flow properties and oxidation stability, which will lead to polymerization and degradation. This problem can be overcome by chemical modifications of vegetable oils in order to eliminate the β-hydrogen atoms in glycerol. The main factors which influence the tribological properties of vegetable oils are the carbon chain length, the type of fatty acids as well as polarity.

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In order to determine a suitable renewable feedstock for specific lubrication requirement, a comprehensive review is required while focusing on their physicochemical properties, methods to enhance physicochemical properties and variety of additives to improve lubrication. In this regard, recent reviews provide an excellent overview of the bio-based lubricants with applications however lacks significant information on the role of physicochemical properties and additives and the related linkages with lubrication behaviours of such lubricants [6–10].

The main purpose of this review paper is to highlight the key works pertaining to bio-based lubricants. In this regard, the objectives of this review involve the overview of various renewable feed stocks on the basis of their physicochemical properties and the literature survey of chemical modifications and additivation which is being used for improving the lubrication performance of vegetable oils for various applications. This paper is organized as follows. A brief overview of this paper is given in Section 1. A detailed description on lubricants and the functions of lubricants is given in Section 2. The various vegetable oils used to produce bio-based lubricants are presented in Section 3 while the physicochemical properties of vegetable oils are detailed in Section 4. The processes used to modify the vegetable oils chemically (*i.e.* transesterification, hydrogenation, and epoxidation) are described in Section 5. The lubrication characteristics of bio-based lubricants in comparison with conventional lubricants are presented in Section 6. The various types of additives used to enhance the performance of bio-based lubricants (*i.e.* antioxidants, detergents and dispersants, viscosity modifiers, nanoparticles, corrosion inhibitors, pour point depressants and extreme pressure and anti-wear additives) are detailed in Section 7. Lastly, the key findings of this review are summarized in Section 8.

2. Bio-based lubricants

2.1. Historical development of bio-based lubricants

Animal fats and vegetable oils have lubricated every type of machine and moving parts for thousands of years. Ancient Egyptians used greases based on calcium soaps of olive oil as wheel axis lubricants in carriages [11]. By the of the 18th century, the Industrial Revolution began and this pushed the demand for natural oils such as sperm oil, lard oil, olive oil, rapeseed oil and ground-nut oil [12]. More oil was required for lubrication of machinery as the Industrial Revolution started to bloom. Less than 100 years later, in the mid-19th century, the exploitation of petroleum-based lubricants started due its lower price and capabilities and thus, animal and vegetable oils could not compete with petroleum. The beginning of the petroleum industry during this period is important to support the industrial expansion in the 19th and 20th centuries. However, due to a growing awareness regarding the effect of petroleum-based oil on the environment, several companies have been involved in the development of bio-based lubricants in the past few years. For example, Shell and British Petroleum collaborated with French National Railways in the development of biodegradable railway track grease. Mobil Chemicals implemented a clean lubricant production line as part of the Agriculture for Chemicals and Energy (AGRICE) programme [4]. The manufacturers of bio-based lubricants, the trade names of these lubricants and their applications are listed in Table 1 [13].

2.2. Background of lubricants and bio-based lubricants

Lubricants are essential for almost all aspects of modern machinery. As the name implies, lubricants are substances used to lubricate surfaces that are in mutual contact in order to facilitate the movement of components as well as to reduce friction and wear. Lubricants are used for various purposes, as shown in Fig. 1. Choosing the suitable lubricant for the application helps extend the lifespan of machinery and its components as well as increase their efficiency and reliability. Lubricants can be used for open systems and closed systems, as shown in Table 2. In open systems, lubricants such as power saw chain oils and drill fluids are expelled to the environment. In closed systems, the lubricants are not exposed directly to the environment. In practice, lubricants are expelled to the environment through leakages, blown pipes as well as due to human errors. It has been reported that more than 50% of the lubricants used throughout the world are the contributors of environmental pollution due to total-loss lubrication, spillage and evaporation [13]. It has been estimated that 40% (*i.e.* 400,000 t/a) of lubricants is used annually and a significant amount of lubricants is lost to the environment each year [14]. For this reason, it is highly desirable that lubricants are biodegradable and produced from renewable and sustainable sources. In general, a good lubricant should have high viscosity index (VI), high flash point, low pour point, good corrosion resistance and high oxidation stability, as shown in Fig. 2.

In general, bio-based lubricants can be defined as products with low toxicity and excellent biodegradability. Bio-based lubricants are not necessarily derived from vegetable based oils but they are usually derived from these oils. Thus, it can be classed as renewable because plants can be regrown. Bio-based lubricants may also be synthetic esters, which are partially derived from various natural sources such as solid fats, waste materials and tallow. The Unites States Secretary of Agriculture defined the term 'bio-based product' as 'a commercial or industrial product (other than food or feed) that is composed, in whole or in significant part, of biological products or renewable domestic agricultural materials (including plant and animal) or forestry materials' [15]. Bio-based lubricants can be categorized as sustainable because it is derived from renewable raw materials. As mentioned by Andreas Willing [14], the sustainability of the application of raw materials can be classified into two aspects; the origin of the resources and the pollution caused by it. In the case of bio-based products (oleochemicals), it is discharged *via* several pathways at the end of their lifespan and the organic chemicals are disintegrated into carbon dioxide and water. The carbon cycle of oleochemicals is closed because the amount of carbon dioxide released equals to the carbon dioxide that was originally taken up by the plants from the atmosphere. Therefore, it has zero effect with regard to the carbon dioxide balance of the atmosphere. On the other hand, the mineral oil-based products increase the atmospheric carbon dioxide and therefore lead to global warming, which can be referred to as indirect environment pollution. The life cycle of lubricants derived from renewable sources is shown in Fig. 3.

The main component of vegetable oils is triacylglycerols (98%) as well as a variety of fatty acid molecules attached to a single glycerol structure. The minor components of vegetable oils are diglycerols (0.5%), free fatty acids (0.1%), sterols (0.3%), and tocopherols (0.1%) [13]. The triglyceride structure consists of three hydroxyl groups esterified with carboxyl groups of fatty acids, as shown in Fig. 4. The triglyceride structure gives these esters a high viscosity (and thus, high viscosity index) because of their high molecular weight. The triglyceride structure is also responsible for the structural stability of the esters over a reasonable operating temperature range [16–19]. The carbon chain of a fully saturated fatty acid is almost straight. The carbon atoms share a double instead of a single bond when the hydrogen atoms are missing from the adjacent carbon atoms. This type of fatty acid is known as unsaturated fatty acid. In contrast, the fatty acid is known as polyunsaturated fatty acid if the double bonds occur at multiple sites. In general, fatty acids can be classified as saturated, mono-, di- and tri-unsaturated fatty acids. Excessive amounts of long-chain saturated long chain fatty acids lead to poor low-temperature behaviour whereas excessive amounts of certain polyunsaturated fatty acids lead to unfavourable oxidation behaviour as well as resignation at high temperatures [17,19–21]. The flash point of the lubricant is also higher due to the very low vapour pressure and volatility. This reduces potential fire hazards of the lubricant during use [22–24]. It should be noted that even monounsaturated fatty acids with long chains will deteriorate the low-temperature behaviour of the lubricant. Even though bio-based lubricants have poor oxidation stability compared to