

# Chapter 7

## Technologies for Conversion

### Bio-Lubricant Production in Fatty Acids



Yu Cao, Ning Wang, Hongchen Fu, Fei You, and Liangnian He

**Abstract** In response to the increasing environmental pollution concern and depleting petroleum reserves, bio-lubricants have received wide attention in replacement of mineral oil. Vegetable oils can be used as potential source of environmentally friendly bio-lubricants because of their biodegradability, renewability, and excellent lubrication performance. Present chapter introduces properties of several raw oils as well as oil extraction methods. Besides, vegetable oils also have some limitations such as poor oxidative stability and low-temperature fluidity, which can be improved through various modification methods such as direct transesterification or selective hydrogenation. Technology for modification of raw oils has also been described. Additionally, additives have a significant influence on the performance of the lubricating oil. The characteristic and applicability of different commonly used additives in bio-lubricant have been summarized in this chapter. Castor oil has a higher viscosity and a lower viscosity index compared with other vegetable oils. This chapter in particular describes the development of production process for the castor-based biodegradable lubricant.

**Keywords** Bio-based lubricant · Vegetable oil · Chemical modification · Renewable resources · Castor oil

## 7.1 Introduction

With rapid development of machinery industry, the demand and consumption of lubricants rise continuously. Almost all lubricants are composed of base oils and additives. At present, the vast majority of base oil of lubricants is mineral oil. In consideration of the progressive depletion of the world reserves of fossil fuels, it is very necessary to develop alternatives of petroleum-based products. Furthermore,

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lubricants are inevitably discharged into the environment due to transportation, leakage, and natural replacement. Mineral oil-based lubricants which have high ecological toxicity and poor biodegradability may result in pollution to the environment. Such problems have aroused the increasing concern of the government and public. Therefore, the development and utilization of environmentally friendly lubricants is an important issue in the current development of lubricants. In this regard, bio-lubricants may play an important role as substitutes of mineral oil-based lubricants, resulting in significant economic and social sustainable benefits.

## 7.2 Development of Bio-Lubricants

The present consumption of fossil fuels has led to significant levels of environmental pollution and is rapidly diminishing petrochemical and energy reserves. Biomass could be regarded as a promising carbon-based alternative energy source and a sustainable chemical feedstock.

In this context, vegetable oil, which is extracted from the seeds or fruits of plants, is the most commonly used feedstock for developing lubricants. The base oils of bio-lubricants are mainly highly unsaturated or High Oleic Vegetable Oils (HOVOs), including soybean oil, rapeseed oil, olive oil, peanut oil, castor oil, palm oil, etc. Compared with mineral oil-based lubricants, bio-lubricants are environmentally friendly alternatives. Bio-lubricants have a number of advantages over mineral lubricants, such as

1. Renewable ability: very low or almost negligible aquatic toxicity; good lubricating properties.
2. Excellent biodegradability: in general, the biodegradation rate of vegetable oils is between 90 and 98%, whereas in the case of mineral oils this value is around 20% [4].
3. High Viscosity Index (VI): because of the strong intermolecular interactions of the double bonds and the molecule linearity.
4. Low evaporation rates: they have an approximately 20% lower evaporation rate than mineral oil-based fluids [28].

Molecularly, vegetable oil is an unsaturated fatty acid glyceride with an average relative molecular weight of 800–1000. The chain length of the fatty acids is usually in the range of C<sub>12</sub>–C<sub>24</sub>. The saturated fatty acids in vegetable oils mainly contain soft fatty acids (such as palmitic acid), stearic acid, etc. The unsaturated fatty acids mainly include oleic acid, erucic acid, linoleic acid, linolenic acid, and ricinoleic acid. Accordingly, the composition of fatty acids varies between feedstocks, thus determining the properties of vegetable oil.

A low melting point and good oxidative stability are essential to high-performance lubricants. The number of the carbon–carbon double bond and the chain length of fatty acids are two main factors to affect the oil properties. In general, increasing the number of double bonds, i.e., increasing the degree of unsaturation of the oil

usually results in better low-temperature properties. However, high unsaturation in the molecule weight causes poor oxidative stability. A longer chain length results in a higher melting point and viscosity. Monounsaturated fatty acids, such as oleic acid and palmitoleic acid, have low melting point and good oxidative stability. Therefore, plant oil feedstocks which possess high contents of oleic or palmitoleic acid are generally preferred in this purpose.

Among the various crops with oil-bearing seeds, non-edible crops are more desirable than edible crops because they grow on land that is largely unproductive and do not in direct competition with existing edible crops resources. As a non-edible crop, castor is an excellent renewable feedstock for biomass-based energy products, such as biodegradable lubricants, bio-polymers, and biodiesel. It is easy to cultivate under drought, salt, and barren conditions. Besides, castor oil raw material is easy to scale up. At present, among the bio-energy crops, castor produces the highest yield. Castor is a key industrial crop cultivated in tropical and subtropical regions of India, China, and Brazil. Globally, around one million tons of castor seeds are produced every year, with a worldwide market of over \$400 million of castor oil. Currently, US imports about \$41 million worth of castor oil annually.

In recent years, the development and utilization of castor oil has gained wide attention. Castor is one of the top ten oil crops with high oil content, which is 45–60% [25]. And it is unique because main of its fatty acid content is ricinoleic acid, a monounsaturated, 18-carbon fatty acid with a hydroxyl function at 12-position. It is the only major commercial source of hydroxy fatty acid. Due to the unique molecular structure and facilely processing of castor oil, it can be considered as a great alternative to petroleum to produce a wide range of products including lubricants, coatings, surfactants, plasticizers, cosmetics, pharmaceuticals, polymers, cosmetics, soaps, inks, fungicides, and others.

With the development of castor technology and industry, green high-performance lubricants have been developed. Castor-based biodegradable lubricate is a kind of promising product with high viscosity and nice performance characteristics at low temperature. Castor oil is the only one which has high content of hydroxy fatty acid among vegetable oils. Its viscosity at ambient temperature is five times more than that of most vegetable oils and it also has a high viscosity index. The advantages of castor oil as lubricant base oil covers (1) renewable, non-food biomass; (2) biodegradable, eco-compatible; (3) outstanding anti-oxidation, anti-wear properties, low-temperature fluidity, and long life-time; (4) the properties controlled by easily modifying their structures.

Bio-lubricants are potential alternative lubricants. This chapter gives an overview of a bio-lubricant based on vegetable oil, especially castor oil. In Sect. 7.2.1, the source as well as oil extraction methods of the bio-lubricant are discussed. Section 7.2.2 introduces the main modification methods of raw oil, including biological modification and chemical modification. Additives have a significant influence on the performance of the lubricating oil. Section 7.2.3 describes the commonly used additives in bio-lubricants.

## 7.2.1 Raw Oil for Bio-Lubricants Production

Lubricants consist of base oil and additives. Base oil can be divided into mineral oil, synthetic oil, and bio-lubricant base oil. Unlike mineral oil and synthetic oil, bio-oil is generally obtained from the modification of plant raw oil. For the bio-lubricants, the raw oil is the oil extracted from seeds via a series of procedures. Therefore the properties of raw oil are of great importance to bio-lubricant. In this section we will introduce production methods of raw oil.

As vegetable oils are being engaged for industrial lubricants usage, the competition between using oil as food or as industrial lubricants have prompted the search for non-edible oils as suitable raw material. Castor oil, a non-edible vegetable oil produced from the seeds of castor plant, is one of the largest investigated oils for industrial and automotive lubrication [3]. Relative to other vegetable oils, it has a good shelf life and does not deteriorate unless subjected to excessive heat [27]. The castor oil is characterized by high viscosity although this is unusual for a natural vegetable oil. This behavior is largely due to hydrogen bond of its hydroxyl groups. With these advantages, castor is mainly produced as a promising resource for bio-lubricants, and the industrial production technology is developed. So we choose castor oil as an example to illustrate the process of oil manufacture.

The extraction of oil from castor seed is by one or a combination of mechanical pressing and solvent extraction. In mechanical pressing, the seeds are crushed and then adjusted to low moisture content by warming in a steam-jacketed vessel. Thereafter, the crushed seeds are loaded into hydraulic presses and they are pressed by mechanical means to extract oil. The oil from mechanical pressing has light color and low content of free fatty acids. However, mechanical pressing will only remove about 45% of the oil while the remaining oil in the cake can be recovered only by solvent extraction. In the solvent extraction method, the crushed seeds are extracted with a solvent in a Soxhlet extractor or commercial extractor. Solvents used for extraction include heptane, hexane, and petroleum ethers [27]. The seeds can be extracted after pretreatment. Conventional pretreatment may include dehulling, size reduction, breaking, grinding, and thermal treatment (cooking) with the purpose of debilitating the cell coats and preparing the material for optimal oil extraction.

### 7.2.1.1 Transportation

Castor seeds have a thin and crisp crust which makes seeds easy to break. Meanwhile, the nutlet of castor is soft. Once the crust is broken, the nutlet will cohere with the dust and it is difficult to separate them. Taking these into consideration, the seeds should be transported into the factory after cleaning. To avoid the breaking of seeds and tedious procedure, cleaning process is operated with the combination of hull beater and double-layer aspirated plansifter. The aspirated plansifter provides both high cleaning efficiency and low damage percentage. The size of castor seeds is generally around 13, 8.5, and 6 mm, so the holes' diameter of first layer should be

around 15 mm. For second layer, the holes' diameter should be 5–6 mm, less than the minimum size of seeds. This kind of design can simplify the cleaning process. After cleaning, the seeds are transported into factory by chain-type bucket elevator, which will not skid and block. Additionally, using chain-type bucket elevator as transport implement can keep the system steady with the help of frequency control and e-metrics.

### **7.2.1.2 Crushing**

The nuts of castor are easy to adhere with each other, so rolled compact procedure is necessary for the production of oil. To simplify the steam-roasted process, the seeds should be crashed as small as possible. The thickness of the castor seeds should be rolled between 2.2 and 2.5 mm. Furthermore, the seeds of castor are large and have a smooth shell, which makes it difficult to get into the machine, so there should be a wide gap between two rollers

### **7.2.1.3 Steam-Roasted**

During steam-roasted process the seeds produced from crushing are humidified, heated, and dehydrated, to make it fit for pressing. The time of steam-roasted should be no longer than 1 h. The temperature and moisture should between 115–120 °C and 4–5%, respectively. Additionally, the cooker should be designed with a shallower bottom, a higher rotate speed, a larger entrance, and a stronger draft fan. Thirdly, the drive device should have a large power.

### **7.2.1.4 Oil Manufacture**

The castor seeds are soft and contain plenty of oil, so the seeds can be squeezed with shell. Compared with the ordinary seeds, the oil press for castor needs stronger power, higher rate of feeding, and narrower gap between the cage bar and pressed cake. The time for squeeze should also be prolonged. The residual oil ratio of the castor cake, which is produced by the oil press device, should be no more than 13% constantly. Only in this way can provide a prerequisite for the low residual oil ratio for the castor flake.

### **7.2.1.5 Filtration**

The crude oil should be filtered at high temperature, generally between 80 and 85 °C, as a result of the presence of high viscosity and adhesive impurities in the unrefined rough oil. Among several types of filtration equipments, the leaf filter with stainless wire net is the most effective, as it has a less adhesive force for the rough oil and

residue than the filter cloth. Before the filtration, there is no need to remove the dregs thoroughly from the oil, as appropriate amount of big-diameter residues can prevent the filtration equipment from being bunged up. After the filtration, the filtrate can go on next process without further refined filtration. Dregs are beneficial to the separation during the alkali refining process.

#### **7.2.1.6 Extraction**

There are two difficulties in the extraction process. The first one is that compared with other oils, the castor oil is more difficult to lixiviate when using ordinary conditions, as the existence of hydroxyl group in the molecule results in high polarity and viscosity. The other one is that castor cake has a strong tackiness and poor permeability, which lead to the difficulties in the solvent leaching and desolventizing. The key to solve these two problems is increasing extraction temperature and unchoking the blockings. To ensure the temperature of the cake is above 60 °C, the delivery system should be equipped with a heat insulation layer. The solvent preheater should pre-heat to 55 °C. The pipelines that transport miscella should be equipped with heating jacket, ensuring the extraction temperature is 57–60 °C at which the castor oil has a good solubility and low viscosity. Meanwhile, countermeasures should be taken to prevent the blocking of the extractor and desolventizer. Combining these measures with other technical means, such as prolonging time of extraction and reducing the height of the castor cake, the residual oil ratio of castor could be controlled under 1%.

#### **7.2.1.7 Desolvation**

To assure the airflow channel unobstructed, there should be a pre-desolvation in desolventizer toaster and the thickness of the bed material should be decreased. It is of great importance for desolvation to intensify internal heat transfer, as this can avoid the oilseed meal absorbing water and clotting with each other.

#### **7.2.1.8 Refinement**

During vegetable oils' production, it is usual to refine the crude oil obtained from either mechanical pressing or solvent extraction. The main aim of refining is to remove impurities (e.g., colloidal matter, free fatty acid, and coloring matter) and other undesirable constituents, thus making the oil more resistant to deterioration during storage. Refining includes (a) removing solid and colloidal matter by settling and filtration, (b) neutralizing the free fatty acid by alkali, (c) removing colored matter by bleaching, and (d) deodorizing by treatment with steam at high temperature and low pressure. The general method of refining used for edible oils is applicable to castor oil [27]. But the condition for the refinement is harsher than other oils as a

result of the high viscosity of castor oil. The ricinoleic acid is gadoleic acid with a hydroxy group, so it has a strong polarity and strong affinity to water, which means ricinoleic acid is easy to emulsify and difficult to demulsify. Although castor oil is stable at the room temperature, the acid value will decrease after a long time storage, normally below 10 mg KOH/g. Castor oil is easy to dehydrate and be oxidized under high temperature, deepening the color, reducing the transparency, increasing the viscosity as well as reducing oil quality. According to these features of the castor oil, semi-continuous refining technics, the combination of batch caustic refining and continuous desiccation, decoloration and deodorization (desolvation), is the best choice, as it can prevent the emulsification and simplify the separation steps. What's more, semi-continuous can also keep the system stable, preventing the production line breaking off.

The proportion of phospholipids in castor oil is no more than 0.3%, so the castor oil can undergo caustic refining process directly. The temperature for alkali refining is normally 60 °C. To avoid the formation of loose nigre during this process, it is necessary to use lye with high concentration. Meanwhile, adding hot water during alkali refining process can prevent the emulsification. Oil refining caldron should have enough space to add a large amount of water as well as demulsifier. After washing, alkali process is completed.

The castor oil produced from alkali refined process is deep in color as a result of the oxidation at high temperature. Therefore attapulgate, sometimes combined with a small amount activated carbon, is always used to decolor castor oil. To meet the demand of the national standard, castor oil is stirred with atlapulgate at 95 °C for 1 h. After separating castor oil and atlapulgate, decolored castor oil is produced.

To increase the efficiency of the deodorization, the vacuum degree of equipment should achieve 667 Pa. The temperature and time should also be controlled precisely for the purpose of preventing the intermolecular dehydration of the castor oil. The temperature should between 130 and 140 °C and the time should be no more than 30 min. After decreasing the temperature to 90 °C and removing vacuum, castor oil can be obtained with high quality.

### 7.2.1.9 Mixed Oil Refining

Although the refining process introduced before has been used widely, there are some drawbacks for this method as a result of the unique properties of castor oil. Firstly, castor oil has a high polarity and strong affinity to water, which results in the emulsification during the alkali refining process and difficulties in separation. Adding sodium chloride solution is an efficient way to demulsify, but this will cause the waste of the castor oil and the increase in cost. Additionally, the density of castor oil and water is close, so they are difficult to separate from each other after the washing process. During the desiccation, ricinoleic acid is easy to dehydrate under high temperature, yielding unsaturated diolefinic acid, which will decrease the transparency and quality of the oil. The temperature of desolvation and deodorization should be controlled strictly as castor oil is liable to be oxidized [34].

Mixed oil refining technique means that the mixed oil produced from extraction is directly refined without desolvation [8]. In mixed oil, there are lots of solvent molecules around the glyceride molecule. These solvent molecules can prevent alkali contacting with the glyceride, so the oil molecule will not be saponified. However, the free fatty acid can react with alkali as a result of a smaller steric hindrance. The purified castor oil will be produced after a combination of alkali refining process, decoloration, evaporation, and desolvation.

Compared with the first refining method, mixed oil refining process has several advantages [34]. Firstly, the viscosity and density of mixed oil are much smaller than castor oil. These features make the alkali refining process, separation and filtration simplified. Secondly, the temperature is low during the whole process, thus the pigments will not be oxidized and is easy to be adsorbed by atlapulgite. Thirdly, the impurities have been removed before evaporation, so the quality of oil and efficiency of the equipment are improved.

The production of raw oil needs a series of complicated procedures, and the quality of raw oil is influenced by the parameters of these processes. Although refined raw oil has much better properties, it cannot be used as lubricants directly. The modification and additives are needed to further improve the properties of raw oil.

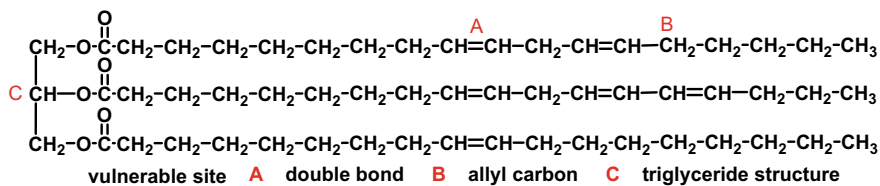
## ***7.2.2 Preparation of Bio-Lubricant Base Oil***

Plant oils are produced by photosynthesis with the characteristics of cleanness, richness, and renewability. Due to the mature cultivation, refining and processing technology, there are a wide range of sources and relatively low-cost plant oils. The structure of plant oil is very different from that of mineral oil. The main component is ester, whose the molecular weight is large, and it contains unsaturated Triacylglycerol (TAG). The differences among various plant oils lie mainly on the content and species of fatty acids. According to the differences of fatty acids, it can be divided into saturated fatty acids, monounsaturated fatty acids, and polyunsaturated fatty acids. Most oilseed crops produce TAG containing a mixture of fatty acids with a chain length of 18 carbons and 1–3 double bonds. The structures and species of fatty acids play a decisive role in various properties [14].

### **7.2.2.1 Principles of Preparation of Bio-Lubricant Base Oil**

Because of the good biodegradability and excellent lubrication performances of plant oils, they can be applied to the production of lubricants. Due to the limitation of the structure and performance of plant oil, it is difficult to apply the raw oil to the field of lubrication directly. The most important performances such as high-temperature oxidation stability and low-temperature fluidity of plant oil must be improved. Because the molecular structure of plant oil determines that it is vulnerable to be attacked by oxygen, resulting in oxidation and thermal decomposition. The





**Fig. 7.1** Triacylglycerol (TAG) and the vulnerable sites

vulnerable parts of plant oil molecular, including double bond (A), allyl carbon (B), and triglyceride structure (C) (Fig. 7.1).

Saturated fatty acid glycerides are usually solid under normal temperature conditions and cannot directly be applied to lubricant base oil. The fluidity of plant oil at low temperature is closely related to the degree of unsaturation and the structure of triglyceride. TAG is easy to accumulate and form larger crystals at low temperature, which leads to poor low-temperature performance of plant oil. Different triglycerides in plant oils eventually lead to different melting points (or freezing points). In general, the longer the carbon chain and the higher unsaturation degree of fatty acids, the lower the triglyceride melting point (or freezing point) will be.

The presence of double bonds improves low-temperature fluidity, but the more the double bonds in the plant oil, and the worse the oxidation stability of the oil [14]. The oxidation mechanism of plant oil is mainly characterized by active allyl radical reaction, which is the main reason for its poor oxidation stability. The oleic acid molecule contains only one double bond, which has good thermal oxidation stability and low-temperature performance. In contrast, the oxidation stability of the polyunsaturated compounds such as linoleic acid and linolenic acid is very poor.

Currently, the main modification methods include biological modification and chemical modification:

- (1) Plants with high oleic acid content are cultivated by modern biotechnology (mainly genetic engineering technology); the key to biological modification of bio-lubricant lies in increasing the content of oleic acid in plant oils.
- (2) Chemical modification of plant oil aims to reduce the content of double bond or adjust the triglyceride structure to achieve the purpose of improving lubricating performance. Through chemical modification, the content of unstable location points (double bond and allyl carbon) in plant oil can be reduced, thereby enhancing the oxidation stability of plant oils.

### 7.2.2.2 Biological Modification of Bio-Lubricant Base Oil

Improvement of plant oils by genetic modification to obtain high oleic oils has led to better acceptance of these oils as lubricants [14]. By genetic analysis of sunflower seeds with high oleic acid content, it is confirmed that the presence of dominant gene in the sunflower crop dominates oleic acid content. Besides, the characteristics of high

oleic acid are controlled by three dominant complementary genes. A study combines the standard intrinsic genome sequences of high oleic acid characteristics and obtains self-flowering high oleic acid plants from several generations of backcross breeding programs [11]. Oil crops with high oleic acid content have been highly valued. The content of oleic acid in common sunflower seed oil is about 30%, but that in high oleic acid plant oils, which are cultivated by modern biotechnology, oleic acid content is more than 90% [24]. Genetic engineering is an effective approach to further improve the lubricity performances of high oleate plant oils. By expressing a fatty acid hydroxylase gene from castor in canola, oil containing up to 16% hydroxy fatty acid can be produced in a high oleate background. Results show that the introduction of hydroxy fatty acids significantly increases the viscosity and oxidation stability of plant oils [14].

However, the biological modification of plant oil will inevitably meet the problems of biological genetic stability and long research cycle. Industrial manufacture requires a stable and effective means to modify plant oil in order to achieve the purpose of applying to the field of lubrication.

### 7.2.2.3 Chemical Modification of Bio-Lubricant Base Oil

Although biological modification can increase the content of oleic acid and therefore improve the overall oxidation stability and low-temperature fluidity, it has the problems of genetic stability. The chemical modification method has higher biological safety, better industrial processing basis and product performances. The vulnerable parts of plant oil molecules include double bond, allyl carbon, etc. Chemical modification is mainly directed against these vulnerable parts [24].

At present, the research on chemical modification of plant oil is mainly focused on improving its degree of saturation and branching. The main ideas of chemical modification are hydrogenization, polymerization, transesterification, esterification, and isomerization. The selective hydrogenation, oligomerization, and cyclization of plant oil can reduce the unsaturated components in plant oil, that is, to improve the service life of the oil, and have no obvious effects on its low-temperature performance [13].

#### Selective Hydrogenation

Selective hydrogenation has great application prospects in the synthesis of lubricating oil. In the process of hydrogenation, if the unsaturated fatty acids are completely converted to saturated fatty acids, which are solid under normal conditions, the oxidation stability can be improved, while the low-temperature fluidity becomes worse. It is generally believed that the unsaturated fatty acid triglyceride containing one double bond has good oxidation stability and low-temperature fluidity. Therefore, selective catalytic hydrogenation, to a certain extent, reduces the unsaturation, and is

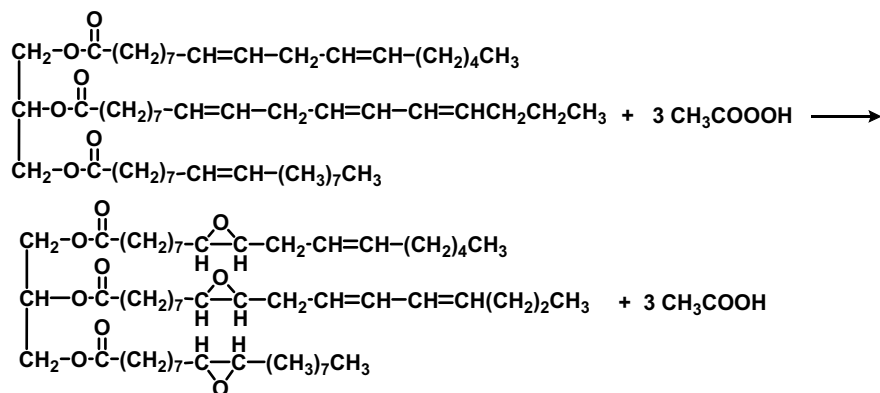


Fig. 7.2 The epoxidation reaction

one of the key points for the preparation of lubricating base oil by chemical modification. The selective hydrogenation can transform polyunsaturated fatty acids, such as linolenic acid and linoleic acid, into monounsaturated fatty acids, which will improve the oxidation stability of plant oil without affecting the low-temperature performance.

#### Dimerization/Oligomerization

Dimerization and oligomerization are also approaches to modify double bonds. Two or more fatty acid molecules are involved in this process, which contain a carbon chain of 18 carbons with one or more double bonds, to form dimer or trimer-aliphatic product [38]. Polymerized modified plant oil has better viscosity and temperature performances. Polymerization can eliminate the double bonds in lube base oil and obtain base oils with different viscosity. If the polymerization reaction produces too many branched chains, the biodegradability and acidity of the products will be increased.

#### Epoxidation

The double bonds easily react with peracid. Therefore, the epoxidation is one of the main reactions to reduce the number of double bonds in fatty acids (Fig. 7.2). But the epoxidation oil is not stable. The reason is the epoxy group is a three-membered ring with high tension. It is a highly reactive chemical and tends to react with other substances containing active hydrogen in the presence of acid or alkali [37].

The thermal oxidation stability and tribological behavior of Epoxy Soybean Oil (ESBO), soybean oil, and high oleic acid soybean oil are compared, and it is found that ESBO which has better thermal oxidation stability is a potential lubricant base

oil. In boundary lubrication, ESBO shows the most excellent wear resistance [1]. After epoxidation, it is found that the oxidation stability of rapeseed oil is also improved [37]. And biodegradation tests show that epoxidation does not affect its biodegradability [33].

Both selective hydrogenation and epoxidation can improve the oxidation stability of plant oils, but they cannot improve the low-temperature performance. So there is a good idea to change the low-temperature performance and oxidation resistance at the same time by improving the branching degree of plant oils.

## Branching

Branched-chain fatty acid esters have good physical properties such as excellent low-temperature performance and stronger hydrolysis stability due to the increase of steric hindrance chain. Low pour point, good fluidity, high stability, and high flash point make them widely used in the fields of lubricating oil, cosmetics, plastics, and so on.

There are some effective methods of branching modification of plant oil. (1) Esterification of hydroxy plant oil. By esterification of castor oil with C1 ~ C3 linear chain or branched chain anhydride, a mixture of monohydric, dihydroxy, and trihydroxy castor oil ester will be produced with good lubricating performances. The pour point can be reduced to - 40 °C, and the viscosity index is more than 135 [32]. (2) The direct branching modification of unsaturated fatty acid bonds in plant oil. Unsaturated double bonds can be removed by using cyclopentadiene and methylcyclopentadiene on the fatty acid chain, and hydrogen reacts with the double bonds on the alkyl ring after addition reaction, the oxidation stability and low-temperature fluidity of the products will be improved [19].

## Transesterification or Esterification

The glyceryl group in plant oil has a strong tendency of hydrolysis and thermal degradation. The structure of triglycerides can be replaced by transesterification to yield polyol esters which have good oxidation stability and low-temperature performances [29]. There are two main ways to prepare polyol esters from plant oil: one is to produce fatty acids from oil and then esterified with polyols [21]; another one is to convert oil into methyl ester and then conduct transesterification with polyols [9, 10]. The corresponding polyol esters are prepared by transesterification of plant oil with Trimethylol Propane (TMP), pentaerythritol, and 2,2-dimethyl-1,3-propanediol. The transesterification products have good low-temperature fluidity, oxidation stability, viscosity temperature, and lubricity [20].

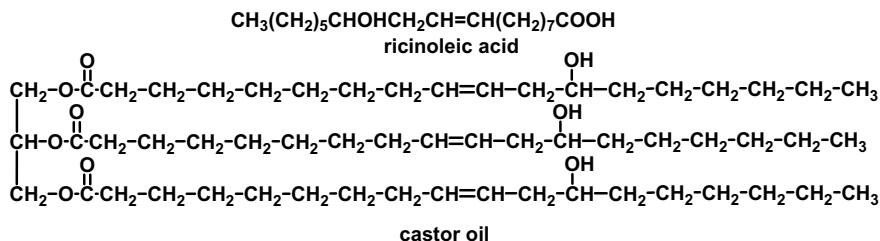


Fig. 7.3 The structure of ricinoleic acid and castor oil

#### 7.2.2.4 Modification of Castor Base Oil

##### Structure and Composition of Castor Oil

Castor oil, one of the most commonly used vegetables oils, contains a hydroxyl group in addition to an olefinic linkage in its predominating fatty acid. Ricinoleic acid (or 12-hydroxy oleic) accounts for about 80% of the total fatty acid content produced upon hydrolysis of castor oil (Fig. 7.3).

The introduction of this hydroxyl group into the fatty acid chain gives castor oil unique physical and chemical properties. One important physical property is viscosity, of which castor oil is considerably higher than other fatty oils. Since viscosity is a measure of the ease with which the molecules are able to slide past one another, it seems likely that the hydroxyl groups may protrude from the fatty chains in such a way as to impede their free flow. Another quite different physical property is solubility in various types of solvents. Castor oil tends to dissolve in oxygenated solvents like alcohols and not to dissolve in hydrocarbon-type solvents, while the other fatty oil is opposite. This peculiarity is also attributable to the presence of the hydroxyl group [12]. The other typical performance of castor oil is oxidation stability, which is better than other plant oils. It is mainly due to the low content of polyunsaturated acid, such as linoleic acid and linolenic acid.

Most of the plant oils have low viscosity, and castor oil is a nice choice when preparing high viscosity environmentally friendly lubricants, such as gear oil and grease. It has found that castor oil is a promising biodegradable lubricant based on the viscosity, oxidation stability, deposition tendency, volatility, lubricity, and compatibility with additives [2].

##### Modification and Application of Castor Base Oil

The castor is further modified to produce a series of lubricating oils with better performance. The biological modification of castor is mostly used to increase the oil yield and environmental suitability of the castor oil plant. In 1984, the first species of *ricinus parthenogenetic* was discovered, and the female inbred line of castor plant was

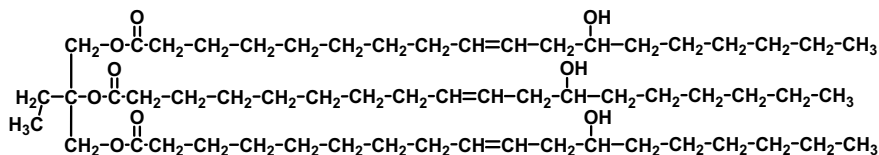


Fig. 7.4 Trimethylolpropane ester

bred by Agronomy Measures. In 1996, the first castor hybrid in China was approved, which improved the oil yield and environmental adaptability of castor [31].

Besides, similar to the chemical modification methods of common plant oils, hydrogenation, branching, and esterification/transesterification can be applied to modification of castor oil as well.

Hydrogenated Castor Oil (HCO), the main component is 12-hydroxy stearic acid triglyceride prepared by catalytic hydrogenation of castor oil, is a powder or flake substance with a melting point of 86 °C. It can be used in cosmetics, hair beauty, and ointments, as paraffin substitute and brightener, and it can also be used in the preparation of hydrogenated stearic acid and its derivatives. The high-pressure lithium-based lubricant prepared through HCO has been used in automotive and military fields because of its gel action, which greatly improves the lubrication performance, with high drop points and excellent water resistance [26].

By isomerization modification of natural castor oil, the length of the molecular side chain is increased, which is able to improve its viscosity index and decrease its pour point.

Ethyl/methyl ricinoleate, produced from the transesterification reaction between castor oil and ethanol/methanol, is the main component of castor biodiesel. A transesterification reaction between this ricinoleate and the superior alcohol TMP results in polyolester (Fig. 7.4). Because of the saturation level and the presence of branching, the product is a synthetic base stock with good oxidative stability and low-temperature properties. After isomerization modification, the rheological properties have been greatly improved, and its anti-wear and antifriction properties are better than those of the same viscosity mineral oil, equivalent to pentaerythritol ester or dioctyl sebacate [30].

The shorter chain derivatives of castor oil are also excellent lubricating base oils. In the modification process, sebacic acid or other medium or short-chain fatty acids are often obtained from cracking castor oil, and then esterification occurs with 2-octanol to produce the lubricating oil with excellent performance. But sebacic acid production would employ phenol or cresol as a thinning agent in current process, thus causing environmental pollution [6, 23]. He's group has developed a novel clear process without phenol for producing sebacic acid from castor oil at high temperature [16] (Fig. 7.5). Firstly, by mixing alkali solution, thinning agent, and castor oil at sufficient temperature, sodium ricinate can be generated by saponification. Volatiles such as 2-octanol can be distilled off. After dehydrogenation and isomerization, pyrolysis reaction happened and formed disodium sebacate. After acidified, sebacic

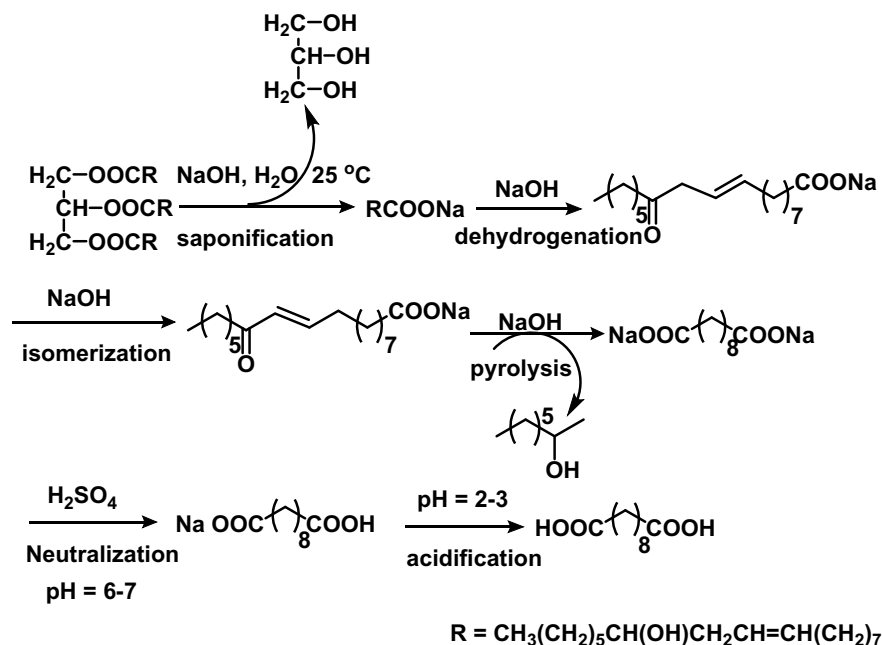
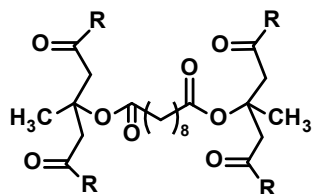


Fig. 7.5 Sebacic acid production starting from castor oil

Fig. 7.6 Synthetic lubricant from castor oil



acid and thinning agent can be effectively recovered from reaction mixture. The multi-component thinning agent used in this process is relatively inexpensive, non-foaming, non-volatile, and resistant to decomposition under the reaction conditions.

In order to improve its lubricating and anti-wear performances as well as environmental friendliness, a novel lubricant—ester derivative of sebacic acid has been developed (Fig. 7.6). The lubricant does not include any of the contaminating components used to manufacture traditional industrial lubricants [17].

Sebacic acid is produced in laboratory. After success at laboratory level, production plant in Tianjin (Fig. 7.7) has been set up for manufacturing castor-based lubricate with annual capacity of 5000 tons. This technology was given as a golden award for patents in Tianjin, and recognized nationwide supported by Department of Agriculture, China [17]. The method has obvious advantages over traditional method. Products operate smoothly in extremely cold conditions and can reduce the use of



**Fig. 7.7** Bench scale facility for sebacic acid preparation (left) and Pilot plant for production of environmentally friendly castor-based lubricate with annual capacity of 5000 tons (right)

fuel by 8% without the decrease of lubrication performance. Besides, the sulfur and nitrogen content in our products is negligible thus leading to a low sulfur and nitrogen emission. With these advantages, they have been certified as bio-based labeled product by United States Department of Agriculture (USDA), which is the authority certification of the biomass industry. Engine oil Energy-saving Bench is the lubrication industry certification authority, which proves that the product can save fuel. This product passed the certification of Sinopec in 2016 and is the first of its kind.

Poor oxidative stability and low-temperature performance are the bottlenecks that affects the application of plant oil. The main purpose for modification is to reduce the double bond content of plant oil. Biological modification can be used to increase the content of oleic acid in plant oils to improve oxidative stability. Furthermore, it is feasible to improve its oxidation stability by chemical modifications, such as hydrogenation, transesterification, isomerization, and esterification. By modifying the plant oil, the oxidation stability and low-temperature fluidity are improved, which makes the plant oil exhibit better lubrication performance. The bio-lubricant products are then prepared by blending additives.

### **7.2.3 Bio-Lubricant Blending Technology**

The plant-based oil obtained after the modification cannot be directly used, and it is also necessary to add additives for blending. Lubricating oils can be prepared by mixing base oils and additives in intermittent or continuous blending process. Additives have a significant influence on the performance of the lubricating oil. Different uses of additives make lubricants differ in their physical and chemical properties.



### 7.2.3.1 Bio-Lubricant Additives

Plant oils used as base oils need to be selected from the following aspects: good dispersion and dissolution of additives, excellent low-temperature properties, fine lubricating properties, and high flash point. The inadequacies of plant oils such as substandard oxidation stability, poor hydrolytic stability, deficient low-temperature fluidity, blistering compared to mineral oil, and poor filterability can be improved by adding appropriate additives [35].

Additives are chemical compounds that give the lubricants some special properties. Some additives make lubricants have new beneficial properties, for example, cleanliness and dispersion, abrasion resistance, corrosion resistance, and emulsifying ability. Other additives can improve the existing performance of lubricants, such as viscosity, viscosity index, pour point, antirust properties, and anti-oxidation properties. Firstly, when additives are added to the lubricants, the real contact area increases, the contact stress decreases, and non-smooth friction surface can be filled and repaired. Secondly, because most additives are polar substances, they can react with metal surfaces to form a chemisorbed film which has extreme pressure protection. Finally, when the friction surface is under local high temperature and high-pressure conditions, additives can be decomposed to produce new substances. These new substances can react with metals and yield a film which can prevent the surface from gluing. These are the main processes by which additives play a protective role.

Lubricant additives have a variety of functions being divided into viscosity index modifiers, detergent and dispersant additives, extreme pressure and anti-wear additives, antioxidants, and other additives.

#### Viscosity Index Modifiers

Viscosity index modifiers are linear polymer compounds, which are soluble in hydrocarbon base oils. They are based on the difference in the viscosity of different forms at different temperatures and improve the viscosity performance of the oil [15]. When the polymer shrinks and curls at low temperatures, they have a relatively small effect on the viscosity. However, polymer swells at high temperatures, and the internal friction of the base oil increases significantly, resulting in an obvious increase in the viscosity of the base oil. The addition of the viscosity index modifiers compensates for the disadvantages of decreasing the viscosity of lubricants caused by the rise in temperature. The most commonly used viscosity index improvers are hydrogenated styrene diene polymers, polymethacrylates, ethylene-propylene copolymers, polyisobutylene, polyvinyl *n*-butyl ether, and so on.

#### Detergents and Dispersants

Lubricating oil can be oxidized at high temperatures. Oxidation products form deposits, thus reducing the efficiency of the internal combustion engine. Therefore,

in order to neutralize these substances, detergents are added to the lubricating oil. Detergents are mostly alkaline which can neutralize the acids produced by the oxidation of lubricating oils and prevent them from further oxidative condensation. Detergent has a role in promoting dissolution. Because they can dissolve and wash the materials such as colloidal substances and carbon deposits produced by the oxidation of lubricating oils. Detergents are rarely used singly in oils. They are often used in combination with dispersants [41].

Carbonaceous sludge forms in the combustion chamber due to incomplete combustion. This sludge accumulates to form an oil-insoluble substance. Dispersant additives can disperse the sludge particles and keep them suspended in the oil [39]. The main function of the dispersant is similar to that of the detergent. Both dispersants and detergents play a part in dispersing and solubilizing, but the performance of dispersant is better than that of detergent. This is because the dispersant provides a larger oil-soluble group, which makes carbon deposits and colloidal substances harder to aggregate. The dispersant can directly interact with the carbonyl, carboxyl, hydroxyl, nitro, sulfate of the sludge. These polar groups are dissolved and dispersed in oil in the form of small particles thus preventing the clogging of the screen.

Commonly used dispersants and detergents include metal sulfonate, ash-less sulfonate, overbased sulfonate, salicylates, alkyl phenolates, overbased carboxylate, polyisobutylene succinimides, glycidol modified succinimides, Mannich adducts, polyethylene glycol esters, polyol poly- (12-hydroxy stearic acid), phosphates and phosphonates [39].

## Antioxidants

Lubricants inevitably undergo oxidation during use and storage. Oxidation is the main cause of deterioration of the lubricating oil. In order to solve this problem, it is necessary to add a certain amount of antioxidant to extend the working time of the lubricating oil. Antioxidants have two mechanisms: one is the capture of free radicals generated during the oxidation process to terminate the oxidation process; the other one is decomposing the peroxide and yielding a stable compound. Therefore, according to these two mechanisms, antioxidants can be divided into two categories: free radical trapping agents and peroxide decomposition agents. Among the commonly used antioxidants, the radical capturing agents are mainly phenol antioxidants and amine antioxidants. And the peroxide decomposition antioxidants are mainly dialkyldithiophosphates e.g., dialkyl zinc dithiophosphate and dialkyl dithiocarbamate [36], etc.

## Extreme Pressure and Anti-Wear Additives

Extreme pressure and anti-wear additives play a role in preventing metal surface from abrasion, scratching, and sintering under high load on the metal surface. Chlorine, phosphorus, and sulfur are typically contained in extreme pressure and anti-wear

additives [5]. These elements protect the metal surface with easily sheared layers of chlorines, phosphides, or sulfides, which forbid severe seizure and wear. However, it should be noted that the use of these elements is controlled due to environmental concerns—since these elements lead to corrosion of metal specimens as well as pollution [22]. In the past ten years, nitrogen-containing heterocyclic compounds and their derivatives have become research hotspots for green lubricating oil additives. The reported multifunctional lubricating oil additives containing nitrogen heterocyclic derivatives can be summarized as thiadiazole, thiazole, benzothiazole, benzotriazole, morpholine, imidazoline, and triazine [40, 42]. Kalam investigated that waste vegetable oil-contaminated lubricants with amine phosphate as anti-wear additive reduced wear and friction coefficient as the same time increased viscosity [18, 25].

### Other Additives

Plant oils and synthetic esters are easily hydrolyzed to produce acidic substances that can cause metal rust. To achieve a good rust-proof effect, rust inhibitors need to be added. The main types of lubricating oil rust inhibitors are sulfonates, carboxylic acids/carboxylates, alcohols, esters, organic amines, phosphoric acid, and phosphates.

Thickeners that are commonly known for increasing viscosity can be used for biodegradable greases. Although inorganic thickeners such as clay and silica cannot be biodegraded in the environment, they do not pose a hazard to the environment therefore still be used. Because soap-based greases such as lithium/calcium-based mixed soaps,  $C_{18}H_{35}O_3Li$  or  $(C_{18}H_{35}O_3)_2Ca$ , and composite aluminum soaps have good heat resistance and water resistance, they can also be used as thickeners. Of course, the choice of thickener can also be determined by the properties such as viscosity, toxicity, and degradability of the grease.

Other lubricant additives include corrosion inhibitors such as fatty acid derivatives, amines, imidazolines, and triazoles for preventing corrosion of equipment; anti-foaming agent such as polysiloxanes and methacrylates to prevent foaming; biodegradation accelerators such as phosphor-nitrogen modified fatty acid [7], etc.

### 7.2.3.2 Bio-Lubricant Blending Technology

#### Bio-Lubricant Blending Process

Lubricant blending is mostly a homogenous phase mixing process. When the lubricant additive is a solid, it is a heterogeneous phase mixing process, during which solid additives will eventually dissolve and form a homogeneous phase. It is generally believed that the liquid-liquid homogenous mixing is a combination of three diffusion mechanisms: molecular diffusion, eddy diffusion, and convection diffusion.

The blending of lubricant has two methods: intermittent and continuous blending. During intermittent blending process, the material is blended under the effect of

**Table 7.1** Additives in antirust oil

| Ingredients                        | Quality/g | Effect                         |
|------------------------------------|-----------|--------------------------------|
| Barium petroleum sulfonate         | 5.00      | Corrosion inhibitor            |
| Benzotriazole                      | 0.02      |                                |
| Diisooctyl sebacate                | 5.00      | Solubilizers                   |
| Dibutyl phthalate                  | 0.10      |                                |
| 2,6-di-tert-butyl <i>p</i> -cresol | 0.20      | Antioxidants                   |
| Methyl paraben                     | 0.20      | Preservatives and antioxidants |
| Propylparaben                      | 0.10      |                                |
| Silicone oil                       | 0.10      | Defoamer                       |

mechanical stirring or pump circulation stirring. Continuous blending requires that base oils and additives are fed into the mixer in a defined ratio. When the process is completed, the physical and chemical properties of mixed oil can meet the demands, and the oil can be directly filled or entered into the product tank for storage. Compared with continuous blending, the intermittent blending process equipment is relatively simple. This blending process eliminates the need for accurate flow meters, highly reliable automatic controls, and online quality inspection methods. Therefore, the investment required to build such a blending device is low and it is easy to implement. The production capacity of such a blending device is limited by the capacity of the tank. As long as a suitable blending tank is selected, it can meet a certain demand for production capacity, but the labor intensity is huge. Continuous blending requires meters and controls to accurately measure and control the flow of each component, as well as on-line quality analysis instruments and computer control systems. Since this method of blending has advanced equipment and means mentioned above, continuous blending can achieve optimal control, rational use of resources, thereby reducing costs. Continuous blending production capacity depends on the size of the blending tank. The efficiency of equipment and the quality of components in the blending process directly affect the quality of the oil.

### Bio-Lubricant Blending Examples

With the development of environment-friendly lubrication antirust oil as the starting point, L-RD-4-2 lubricant antirust oil that has been developed is used for steel corrosion protection.

The base oil and additive are confected using the polar corner design method. The base oil in the lubricant is a mixture of hydraulic oil, rapeseed oil, castor oil, and Span-85, and was mixed at a ratio of 1:1:1:1, accounting for about 80–95% of the total content of bio-lubricant. The remaining part is the functional additives (Table 7.1). This ratio is assigned based on the product's performance requirements. For example, L-RD-4-2 lubricant antirust oil products are required to meet several

**Table 7.2** Product quality index

| Items   | National standard requirements   | Result    | Testing method |           |
|---|----------------------------------|-----------|----------------|-----------|
| Flash point (°C)                                  | ≥170                             | 212       | GB/T 3536      |           |
| Pour point (°C)                                   | ≤-25                             | -30       | GB/T 3535      |           |
| Dynamic viscosity(mm <sup>2</sup> /s, 100 °C)     | 9.3-12.5                         | 10.1      | GB/T 265       |           |
| Low-temperature dynamic viscosity (mPaos, -18 °C) | ≤2500                            | 2000      | GB/T 6538      |           |
| Viscosity index                                   | ≥75                              | 83        | GB/T 1995      |           |
| Viscosity ratio                                   | ≤2.0                             | 1.4       | -              |           |
| Increased total acid number (mg KOH/g)            | ≤3.0                             | 2.6       | -              |           |
| Volatile content (m/m)                            | ≤2.0%                            | 0.9%      | SH/T 0660      |           |
| Foam volume (mL)                                  | 24 °C                            | Qualified | GB/T 12579     |           |
|   | 93.5 °C                          |           |                |           |
| Acid neutrality                                   | Qualified                        | Qualified | SH/T 0660      |           |
| Removability (wet heating)                        | Removable                        | Removable | SH/T 0212      |           |
| Rust prevention                                   | Hot and humid (Grade A)(h)       | ≥480      | 500            | SH/T 2361 |
|   | Salt spray (Grade A)(h)          | -         | -              | SH/T 0081 |
|   | Saline impregnation (Grade A)(h) | ≥20       | 24             | SH/T 0025 |

demands: viscosity in a range of 9.3-12.5 mm<sup>2</sup>/s, price is lower than 20 yuan/kg and plant base oil content not less than 50%.

After nearly one year of storage under natural conditions (high temperature and humidity in summer; large temperature difference between day and night in autumn; cold and wet in winter), the testing results showed that the quality index (Table 7.2) of L-RD-4-2 lubricant antirust oil meets the requirements of the SH/T 0692-2000 standard.

The lubricant antirust oil has the characteristics of stable quality, excellent performance, and easy use, and is a product with broad application prospects.

The properties of bio-lubricant can be improved by the introducing additives such as viscosity modifiers, detergent and dispersant additives, extreme pressure and anti-wear additives, antioxidants and other additives, depending on the requirements of the application. The main blending mechanism of lubricating oil is summarized, and the intermittent and continuous blending of lubricating oil is compared. L-RD-4-2 lubricant antirust oil blended by plant-based oils and additives has excellent performance. With people's attention to the environment, bio-lubricants will be widely studied.

**Table 7.3** Fire-resistant hydraulic oils-pentaerythritol oleate

| Items   | National standard requirements | Result | Testing method |
|---|--------------------------------|--------|----------------|
| Dynamic viscosity (mm <sup>2</sup> /s, 40 °C) | 62–68                          | 63     | GB/T 265       |
| Acid value (mg KOH/g)                         | ≤0.8                           | 0.47   | GB/T 7304      |
| Iodine value (g I <sub>2</sub> /100 g)        | 85–100                         | 102    | AOCS CD1-25    |
| Hydroxyl value (mg KOH/g)                     | ≤10.0                          | 6.2    | GB13482        |
| Flash point (°C)                              | ≥300                           | 338    | GB/T 3536      |
| Pour point (°C)                               | ≤−21                           | −23    | GB/T 3535      |
| Demulsibility                                 | ≤25                            | 19     | GB/T 7305      |
| Chroma  | ≤2                             | 1      | GB/T 1722      |
| Moisture                                      | ≤0.05                          | 0.05   | 07033.053      |

**Table 7.4** Fire-resistant hydraulic oils-trimethylolpropane oleate

| Items   | National standard requirements | Result | Testing method |
|---|--------------------------------|--------|----------------|
| Dynamic viscosity (mm <sup>2</sup> /s, 40 °C) | ≤53                            | 46     | GB/T 265       |
| Acid value (mg KOH/g)                         | ≤1.0                           | 0.42   | GB/T 7304      |
| Iodine value (g I <sub>2</sub> /100 g)        | 75–90                          | 86.4   | AOCS CD1-25    |
| Hydroxyl value (mg KOH/g)                     | ≤7                             | 6.6    | GB13482        |
| Flash point (°C)                              | ≥300                           | 324    | GB/T 3536      |
| Pour point (°C)                               | ≤−39                           | −45    | GB/T 3535      |
| Demulsibility                                 | ≤25                            | 18     | GB/T 7305      |
| Chroma  | ≤2                             | 1      | GB/T 1722      |
| Moisture                                      | ≤0.1                           | 0.03   | 07033.053      |

Different bio-based lubricants have different physical and chemical properties and are used in different occasions. Here we list the detection indicators of fire-resistant hydraulic oils—pentaerythritol oleate (Table 7.3), trimethylolpropane oleate (Table 7.4) and some bio-based lubricants produced by Heda (Table 7.5) for reference.

### 7.3 Outlook

The requirements for lubricants are varied with the development of the industry and technology. During the 1950s, appropriate viscosity and the absence of acidic components of the base oil was of great importance. While from 1990s, base oil development was influenced not only by the demands of lubricant performance but also by environment, health, and safety criteria. Taking these into consideration, bio-lubricants are more attractive than mineral-based lubricants. Bio-lubricants exceed

**Table 7.5** Some bio-based lubricants produced by Heda

|  | Priolube<br>1414 | Priolube<br>1446 | Priolube<br>1851 | Priolube<br>1936 | Priolube<br>2089 | Priolube<br>3987 |
|--|------------------|------------------|------------------|------------------|------------------|------------------|
| Dynamic<br>viscosity<br>(mm <sup>2</sup> /s, 40°C)     | 6.0              | 30               | 495              | 26               | 44               | 138              |
| Dynamic<br>viscosity<br>(mm <sup>2</sup> /s,<br>100°C) | 2.3              | 7.0              | 49               | 5.3              | 8.7              | 18.2             |
| Viscosity index  | 229              | 207              | 153              | 139              | 181              | 140              |
| Pour point (°C)  | −21              | −24              | −36              | −54              | −54              | −33              |
| Flash point<br>(°C)                                    | 195              | 295              | 300              | 244              | 315              | 320              |
| <b>Biodegradable<br/>OECD 301B<br/>(%)</b>             | <b>&gt; 60</b>   | <b>84</b>        | <b>65</b>        | <b>74</b>        | <b>99</b>        | <b>70</b>        |
| Renewable<br>ingredient (%)                            | 79               | 85               | 87               | 0                | 85               | 85               |

the performance of mineral lubricants in terms of viscosity, low carbon-forming tendency, stability, volatility, response to additives, and biodegradability. Bio-lubricants are now widely accepted as offering a number of inherent performance advantages over conventional petroleum-based oils to formulate modern automotive engine oils [25]. Using bio-lubricants as a replacement of mineral oil can reduce the discharging of harmful gases and may remit the greenhouse effect.

Among various bio-lubricants, castor oil-based lubricants are the most promising one as castor oil is non-edible and has excellent physical and chemical properties. By using castor oil-based lubricants instead of mineral-based lubricants, we can achieve the goal of reducing carbon emission, increasing energy efficiency and increasing carbon sink. Besides bio-lubricants, castor oil can also be used to produce other high value-added products, thus has a great economic benefit. For example, Tianjin Nankai University Castor Engineering Technology Co., Ltd. has developed a series of high value-added products based on castor oil, such as biodegradable lubricants, bio-jet fuel, bio-materials, and so on [17]. Currently, industrial uses of castor oil are largely limited by its supply [3]. The problem associated with castor oil production is that its seeds contain the toxin ricin and hyper-allergenic 2S albumins, which are detrimental to growers as well as processors [27]. Furthermore, the current production of castor oil-derivatives generally suffers from high energy consumption and heavy environmental pollution. Therefore, eco-friendly and sustainable technologies are highly desirable in the improvement of castor crop to develop high oil and low toxin or toxin-free castor oil for the production of castor oil-derived lubricants, biodiesel, bio-plastics, and other value-added bio-chemicals.

Although there have been some achievements in bio-lubricants industry, further improvements are inevitable and are already being recorded with an increasing number of studies directed toward such areas. Firstly, new extraction method should be developed for large scale production in order to produce castor oil with high quality effectively. Secondly, lower power-consuming and more efficient modification methods are needed to achieve a better performance of bio-lubricants [13, 14]. And more and more bio-lubricants should be developed to meet various lubrication demands [17]. The cost of modification should also be decreased. Thirdly, additives which can change the chemical and physical properties of bio-lubricants may also have unknown negative effects on bio-lubricants such as a drop in viscosity or a decrease in biodegradability [5, 15, 35]. Hence, development of high-performance, multi-functional, and environmental friendly additives with less side effects will become research hotspot. Additionally, further systematic research of interactions between bio-lubricants and additives should be conducted. Bio-based high-performance green lubricants are good for energy-saving and emission-reducing. By accelerating the application of high-performance green lubricants, improving power, saving fuel, reducing emissions, and preventing gray skies can be achieved.

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