

## Bio-based Lubricants: Progress in Research

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Biomass is widely distributed, inexpensive, and easily obtainable. As a transportable and storable organic carbon source, biomass has significant advantages in terms of sustainability, environmental friendliness, resource richness, and versatility. The utilization of biomass resources instead of traditional non-renewable energy is advantageous for addressing issues related to energy, the environment, and product diversity. The conversion of biomass into energy chemicals serves as an effective complement to current energy products. In addition to their role as a protective agent, lubricants play a crucial role in machinery operation. This paper provides a comprehensive review of various plant-based lubricant-based oil synthesis technologies with promising applications, such as olefin metathesis, cross-lactone, plant sugar fermentation, and C-C coupling. It also covers modification techniques including additive, chemical, and biological modifications. Technical process of each synthesis and modification method is summarized, as well as the physical and chemical properties of the obtained lubricating oil products. This technology also overcomes limitations of traditional vegetable oil modification methods. A thorough analysis is provided on the performance and process economics of plant-based lubricant base oil synthesis technology to guide industrial development in this area. Additionally, it includes an analysis of future trends in plant-based lubricant synthesis technology.

DOI: 10.15376/biores.20.3.Hao

**Keywords:** *Bio-based lubricants; Bio-lubricant base oils; Kinematic viscosity; Viscosity index; Solidifying point*

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## INTRODUCTION

Since the industrial revolution, with the continuous development of productivity, mechanical-scale production has gradually replaced traditional handicraft production. This shift has greatly reduced labor intensity and has greatly improved production efficiency. However, in the process of mechanized production, friction loss will inevitably occur. In order to minimize this problem, lubricating oil came into being.

As is well known, lubricating oil plays an important role in mechanical operation and is an indispensable part of maintaining good performance and stable operation of machinery. Lubricating oil mainly acts on the surface of two relatively moving objects, aiming to reduce the friction loss between two objects, transfer the heat generated during the friction process, prevent rust corrosion of objects, prolong the service life of objects,

and ensure the long-term stable operation of machinery. High quality lubricating oil usually has the characteristics of high viscosity index (VI), high boiling point, thermal stability, low solidifying point (SP), corrosion resistance, and strong antioxidant capacity. Traditional lubricating oil is mineral-based lubricating oil. Mineral-based lubricating oil is generally composed of additives and base oil. The proportion of additives is 1 to 30%, and the proportion of base oil is 70 to 90%. Commonly used lubricating oil additives are also mainly inorganic additives, which can be harmful to the environment.

The global strategic goal of “carbon peak and carbon neutrality” has put forward more urgent needs for energy transformation, and it is necessary to accelerate research and development of environmentally friendly low-carbon lubricants (Breda *et al.* 2022). Bio-based lubricants prepared from biomass are environmentally friendly, can achieve zero CO<sub>2</sub> emissions, and have good compatibility with additives. They are green substitutes for mineral-based lubricants (Zhao *et al.* 2020). Environment-friendly lubricating oil not only can meet the requirements of equipment, but it also can be biodegraded in a short time, which has a good ecological effect. However, vegetable oil also has some disadvantages, such as poor low temperature fluidity, narrow range of kinematic viscosity, and C = C and active β-CH structure, which lead to poor oxidation stability of vegetable oil. It is difficult to be directly used as lubricating base oil, so it is necessary to modify it (Negi *et al.* 2021). Common modification methods include additive modification, transesterification, selective hydrogenation, and epoxidation/epoxidation ring opening. Although these methods can improve their low temperature fluidity and oxidation stability to a certain extent, it is still difficult to obtain ultra-low SP lubricating base oil (SP is lower than -40 °C) by this method. There is still a significant gap between the modified lubricating oil and the high-end lubricating oil (Li *et al.* 2020; Mao and Duan 2021). However, with the continuous improvement of environmental awareness and the high attention to renewable resources, the advantages of vegetable oil-based lubricants are becoming increasingly apparent.

In recent years, olefin metathesis, cross-lactone, plant sugar fermentation, and C-C coupling technology have been gradually developed and applied to the preparation of bio-based lubricating base oil. The prepared lubricating oil has excellent performance, and some of the product performance can be comparable to or close to high-end synthetic lubricating oil such as PAO. The oil has natural performance advantages such as biodegradation. The key is that at the end of the service life of the plant-based lubricating oil, the “waste oil” will be decomposed into CO<sub>2</sub> and water by microorganisms. Since the amount of CO<sub>2</sub> released during the production and use of the whole lubricating oil is the same as the amount of CO<sub>2</sub> absorbed, the CO<sub>2</sub> in the whole process is recycled, that is, the lubricating oil is biodegradable. In addition, the VI of plant-based lubricants is higher than that of petroleum-based lubricants, which ensures that they are used in a wider temperature range. Therefore, the development of environmentally friendly vegetable oil-based lubricants is of great significance for improving air quality and ecological environment, increasing the proportion of green and clean lubricants, exploring alternative ways of mineral-based lubricants, and promoting the development of energy agriculture and forestry. It is an important way to solve the problem of environmental pollution caused by waste lubricants and maintain public health.

This paper summarizes the modification technology of plant-based lubricating oil and the synthesis technology of plant-based lubricating oil base oil. The article also puts forward a new prospect for the development of plant-based lubricating oil in the future.

## Vegetable Oil as Environmentally Friendly Lubricant

Lubricating oil is composed of base oil with certain characteristics and a small amount of additives. The base oil accounts for about 90% of the mass fraction. It has a great influence on the basic performance of lubricating oil and is also an important factor affecting the ecological environment. Additives can improve the oxidation stability, anti-wear, anti-friction, and viscosity-temperature characteristics of base oil (Chen *et al.* 2008).

Environmentally friendly lubricants, also known as biodegradable lubricants or green lubricants, refer to lubricants that not only can meet the requirements of equipment use, but also can be decomposed by microorganisms in a short period of time and have favorable ecological effects (Yang *et al.* 2003). The environmentally friendly lubricating oil itself and the products after use can be naturally degraded (more than 60% can be degraded within 28 days under natural conditions), non-toxic or non-ecologically toxic, rich in sources (bio-based carbon is higher than 25%), and renewable (Willing 2001).

Vegetable oil lubricants are renewable and biodegradable, with a wide range of sources, a long history of use, and sustainable production. They are good substitutes for mineral lubricants and can be used as environmentally friendly lubricants (Martin *et al.* 1995).

In recent years, with the increasingly serious situation of resources and energy and the increasing destruction of ecological balance, the research and development of vegetable oil lubricants have attracted people's attention (Gong and Yu 2000). From a technical point of view, more than 90% of the lubricants used today can be prepared from vegetable oils, and vegetable oils such as soybean oil, sunflower oil, rapeseed oil, castor oil, palm oil, jatropha oil and peanut oil have been successfully converted into lubricants and applied (Wilfried 1998).

## Advantages and Disadvantages of Vegetable Oil-based Lubricants

Vegetable oil is derived from a diverse range of sources, primarily in the form of triglycerides. With a VI (VI) exceeding 220, it surpasses mineral oil (VI: 90-120), making it advantageous as a lubricant for reducing friction and minimizing mechanical energy loss by 5 to 15%.

However, due to the abundance of unsaturated carbon-carbon double bonds and active  $\beta$ -H in alcohol components, vegetable oils exhibit poor thermal stability and oxidation resistance, necessitating the addition of numerous antioxidants during use (Fox and Stachowiak 2007; Erhan *et al.* 2008). Furthermore, the hydrolysis stability of glycerides in fats is inadequate, rendering natural fats unsuitable as base oils for lubricants (Fang *et al.* 2005; Arnsek *et al.* 1999, 2000).

Nevertheless, owing to their natural long straight chain carbon structure and abundant oxygen-containing functional groups, these oils can be subjected to hydrogenation, transesterification, and esterification reactions to enhance the performance of bio-based lubricant base oils (Kimberly *et al.* 2016). Table 1 compares the properties of common vegetable oils and ester oils. The kinematic viscosity (as determined at 40 or 100  $^{\circ}\text{C}$ , *i.e.* KV<sub>40</sub> or KV<sub>100</sub>), VI and SP were found to be significantly higher than those of ester oil while the flash point (FP) is notably lower. Research on the impact of ester bond quantity on oil properties has revealed that increasing the number of ester groups enhances lubrication performance.

**Table 1.** Comparison of the Properties of Mono-, Di- and Polyester Oils and Vegetable Fats

Raw Materials	KV <sub>40</sub> (mm <sup>2</sup> /s)	KV <sub>100</sub> (mm <sup>2</sup> /s)	VI	SP (°C)	FP (°C)
Palm oil	41.9	8.6	189	12	165
Coconut oil	27.9	5.8	155	20	112
Soybean oil	30.3	7.4	224	-12	176
Linseed oil	37.4	—	—	-10	178
Olive oil	45.2	—	—	-15	179
Peanut oil	49.2	—	—	-18	177
Rapeseed oil	44.5	—	—	-20	62
Monoester lubricating oil	4.5-17	2-23	159-233	-46-20	160-230
Diester lubricating oil	11-2035	3-18	126-169	-70-40	280-300
Polyol ester lubricating oil	6-255	2-18	46-229	-64-5	215-331
Polyester lubricating oil	70-40000	11-2000	119-278	-45-6	260-325

## Modification of Vegetable Oil

The disadvantages of vegetable oil make it unable to be directly used as lubricating oil in many applications. It must be modified by certain methods to improve the viscosity-temperature performance, oxidation stability, thermal stability, and hydrolysis stability. At present, the modification of vegetable oil mainly includes additive modification from the outside, chemical modification from the molecular structure, and biological modification from the gene (Erhan and Asadauskas 2000).

### Additive modification

It is found that adding an appropriate amount of additives to vegetable oil can significantly improve the viscosity-temperature performance, anti-oxidation performance, anti-wear, and anti-friction performance of vegetable oil. With the improvement of the requirements for lubricating oil, the requirements for additives are getting higher and higher. The German 'Blue Angel' label stipulates that lubricating oil additives must meet the requirements of ecological and environmental protection (Zeng *et al.* 2015).

Liu *et al.* (2016) proposed a new method to effectively adjust the fluid properties and change the viscosity of lubricating oil by adding high concentration inorganic nanoparticles. In this method, nano-SiO<sub>2</sub>/PAG suspension with stable, high concentration and controllable viscosity is synthesized by in-situ Stober sol-gel method, and the suspension is used as a vegetable oil viscosity modifier. The smaller the nanoparticles of the suspension, the better the thickening effect of the lubricating oil, and the greater the viscosity.

Zhao *et al.* (2016) prepared nano-hybrid poly(methacrylic acid)/graphene oxide(PMA-GO) by free radical polymerization of graphene oxide and methacrylic acid as a solidifying point inhibitor. The addition of 0.2wt%PMA14-6GO can reduce the CFPP of diesel by 14 °C, and 0.2wt%PMA14-9GO can reduce the SP of diesel by 19°C. Given the heterogeneous nucleation mechanism, PMA14-GO increased the crystallization temperature of diesel and modified crystallization behavior of the wax crystals by forming uniform and tiny particle-shaped crystals and hindering the formation of three-dimensional network.

However, studies have shown that the toxicity and adverse effects of additives on the environment often are more serious than those of base oil. Some additives will deteriorate during use, which will have a negative impact on the biodegradability of lubricating oil. Therefore, it is of great significance to add additives that can improve the biodegradability of vegetable oil.

Of course, the proportion of additives in lubricating oil is small (generally below 10% mass fraction). Therefore, it is the base oil itself that plays a decisive role in lubricating oil.

### *Chemical modification*

The disadvantages of vegetable oil are mainly determined by its molecular structure. The ester group in vegetable oil molecules is vulnerable to attack by other molecules, and the  $\beta$  hydrogen atom is also easily oxidized to form acid or precipitate, which leads to corrosion of metal surface. Polyunsaturated bonds in vegetable oils are also easily oxidized and cleaved into corrosive products such as carboxylic acids and / or alcohols.

Chemical modification can change the chemical structure of vegetable oils, thereby improving their poor properties (Shashidhara and Jayaram 2010). For example, a double bond reaction is used to improve the oxidative stability of vegetable oil, or functional groups and / or branched chains are introduced to change its flow properties. At present, the commonly used chemical modification methods include hydrogenation, isomerization, epoxidation, and transesterification (Wagner *et al.* 2021).

### *Hydrogenation modification*

Hydrogenation modification is an effective method to improve the thermal oxidation stability and melting point of vegetable oil. Under the action of the catalyst, hydrogen is added to the unsaturated fatty acid double bonds of the vegetable oil to increase the saturation of the vegetable oil. The hydrogenated vegetable oil is changed from its previous nature, the hardness is increased, and the liquid is changed from liquid to semi-solid or solid, which is called hydrogenated oil or hardened oil.

The hydrogenation of vegetable oil includes selective hydrogenation and non-selective hydrogenation. In order to maintain the low-temperature fluidity of vegetable oils, all unsaturated bonds in the molecule cannot be added to become saturated bonds, and only selective hydrogenation can be performed, such as the conversion of linolenic acid containing three unsaturated double bonds and linoleic acid containing two unsaturated double bonds into monounsaturated oleic acid without increasing the content of saturated acid (Johansson and Lundin 1979; Zaccheria *et al.* 2012).

The catalysts used for selective hydrogenation are generally supported catalysts (such as activated carbon palladium) or metals and metal oxides (such as copper or nickel). However, in recent years, it has been found that copper-based catalysts can accelerate the oxidation of oil and produce trans fatty acids in the hydrogenation process, while nickel-based catalysts are carcinogenic to human body. Therefore, more and more other catalysts have attracted much attention (Qiu *et al.* 2002).

Ravasio *et al.* (2002) used chemical adsorption-hydrolysis method to prepare Cu/SiO<sub>2</sub> vegetable oil selective hydrogenation catalyst with high catalytic activity and selectivity, which can significantly reduce the content of linolenic acid or linoleic acid, without increasing the content of stearic acid, and can maximize the limitation of trans fatty acids (Ravasio *et al.* 2002). The hydrogenated vegetable oil has good oxidation stability

and good low temperature lubricity. It is an environmentally friendly vegetable oil lubricant.

The research of vegetable oil selective hydrogenation catalyst focuses on high activity, high selectivity, low trans structure, and low-cost catalyst systems.

#### *Modification by transesterification*

The transesterification reaction can improve the degree of branching of vegetable oil, which can greatly reduce the SP of vegetable oil. Especially when the branch chain is located in the middle of the molecule, the SP of vegetable oil decreases more, which is attributed to the breaking of the symmetry within the molecule (Freedman *et al.* 1984).

The transesterification method is the use of fats and excess alcohols, such as pentaerythritol, neopentanediol, and other fatty alcohols with long branched chains, in the presence of acids, bases or enzymes to produce fatty acid esters and glycerol. Due to the high boiling point of fatty alcohols, the unreacted alcohol reactants will lead to difficulties in its recovery, and the separation of glycerol is also a problem. The number of oxygen-containing functional groups of the oil prepared by transesterification method does not decrease compared with that of the natural vegetable oils, which made them have some properties, such as poor oxidation stability, high hydrolysis stability, and high acid value. It was found that the properties of ester oils are greatly affected by their structure. Angulo *et al.* (2018) used fish oil residue and triglyceride as raw materials and sodium ethanol as catalyst to conduct transesterification under vacuum conditions of 100 to 140 °C. The research results showed that fish oil residue contained a large amount of fatty acid ethyl ester, and the extent of conversion reached 84%. The kinematic viscosities at 40 and 100 °C of the prepared bio-based lubricating base oil were 3.75 and 1.6 mm<sup>2</sup>/s, respectively. The FP and SP were 176 °C and -11 °C, respectively.

Vegetable oil is prone to thermal degradation or hydrolysis. Transesterification of vegetable oil with more branched alcohols can be carried out to improve the degree of branching of vegetable oil. Transesterification not only can improve the antioxidant properties of vegetable oil, but it can also improve the low temperature performance of vegetable oil (Schneider 2006). The esterification reaction is also a method to prepare bio-based ester lubricating oil base oil. Glycerol (TMP), pentaerythritol (PE), or neopentanediol (NPG) are often used to esterify C12-C24 fatty acids on an acidic catalyst to build single ester, double ester or triester bio-based lubricating oil base oil. The properties of this kind of bio-based lubricating oil base oil are significantly related to the number of ester groups and the length of carbon chain. The ester group has good polarity and is easy to form an oil film on the contact surface, thus playing a role of anti-wear and anti-wear. The length of carbon chain is mainly related to the viscosity of the oil and the tipping point. Eychenne and Moulougui (1998) studied the high performance neopentyl polyol lubricating base oil and found that it has high thermal stability, high FP, and low volatility. The KV<sub>40</sub> is 40.3 mm<sup>2</sup>/s. It has a VI of 200 and an SP of -17 °C.

Gryglewicz *et al.* (2003) studied the transesterification of rapeseed oil, olive oil, lard with neopentyl glycol (NPG), and trimethylolpropane (TMP). It was found that the KV<sub>40</sub> of NPG synthetic ester and TMP synthetic ester was between 13.5 and 37.6 mm<sup>2</sup>/s, the SP was between -10.5 and -17.5 °C, respectively, and the VI was very high. The FP of NPG synthetic ester is lower than that of TMP synthetic ester, which has higher thermal oxidation stability and less precipitation (Gryglewicz *et al.* 2003).

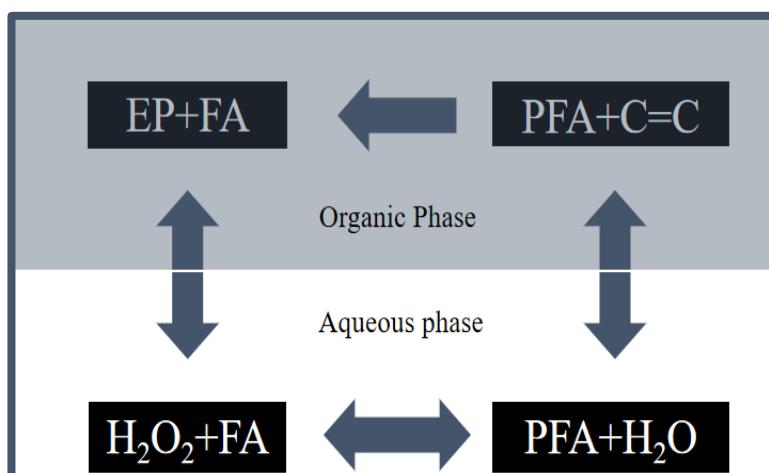
Talib and Rahim (2015) studied the performance of chemically modified jatropha oil-based trimethylpropane (TMP) ester synthesized from jatropha oil (CJO) as a bio-based

multi-walled fat. Modified jatropha oil (MJO) was prepared by transesterification of Jatropha methyl ester (JME) and chemically modified jatropha oil-based trimethylpropane (TMP) at a molar ratio of 3.1:1 and 3.3:1. The viscosity, density and tribological properties of the modified jatropha oil were tested according to the American Society for Testing and Materials (ASTM). The samples were compared with synthetic ester (SE) and jatropha oil (CJO) under orthogonal cutting conditions. The friction coefficient (COF) and wear spot diameter (WSD) were used to compare the lubrication performance of the samples. The results showed that MJO had an obvious lubrication effect and is an ideal choice to replace synthetic esters as processing lubricants.

#### Modification by epoxidation

The C=C in vegetable oil is very vulnerable to attack, so the oxidation stability is poor. The oxidation stability of vegetable oil can be improved by the epoxidation of vegetable oil with in-situ generated percarboxylic acid under the action of catalyst.

The epoxidation reaction is generally divided into aqueous phase reaction and oil-water interface reaction (see Fig. 1).



**Fig. 1.** Epoxidation reaction process

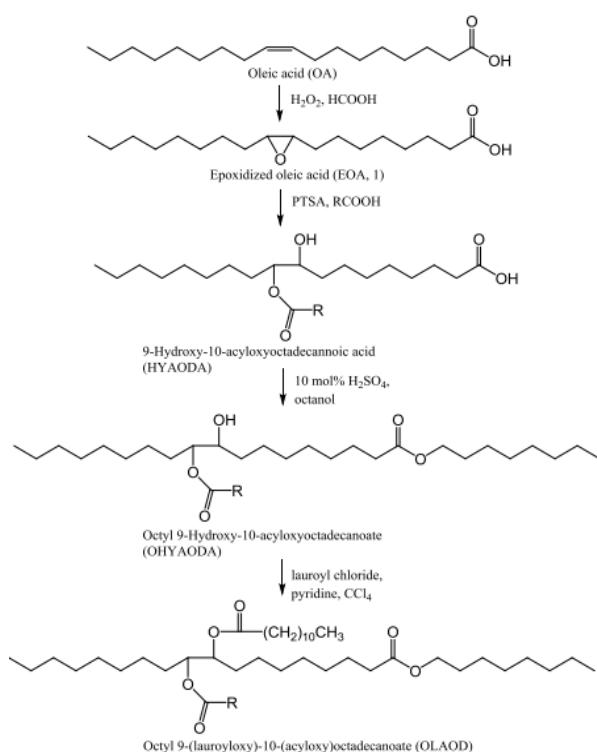
Firstly, hydrogen peroxide and formic acid (FA) react in the aqueous phase to generate the oxidant peroxyformic acid (PFA). Then the generated peroxyformic acid is transferred to the oil-water interface, and the C = C in the oil is attacked under the action of the catalyst to form an epoxy group (Ep), and the peroxyformic acid is reduced to formic acid (Campanell *et al.* 2008).

Epoxidized methyl oleate was prepared by epoxidation of methyl oleate catalyzed by self-made Bronsted acid ionic liquid under solvent-free conditions. The optimum reaction conditions were as follows: the molar ratio of methyl oleate, formic acid and hydrogen peroxide was 1:0.7:2.6, the catalyst was functionalized ionic liquid 1-(3-sulfonic acid) propyl-3-methylimidazolium hydrogen sulfate, the mass fraction was 4.0%, and the reaction was carried out at 80 °C for 1h. The epoxidation extent of the product was 83.4%, and the catalyst could be recycled many times. The thermal oxidation stability of the epoxy methyl oleate was good, and it could be used as lubricating base oil (Yuan 2015).

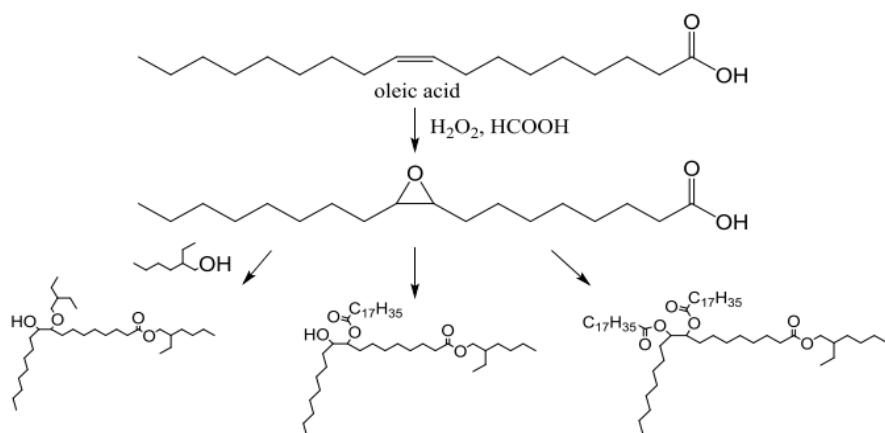
Love and Ankush (2019) prepared olive oil-based lubricants by epoxidation and modified them with Cu and hexagonal boron nitride (h-BN) nanoparticles. After adding Cu nanoparticles and h-BN nanoparticles, the shear stress and shear rate of the epoxidized

olive oil showed a linear relationship. There was a higher viscosity and better lubrication performance. When the concentration of Cu and h-BN was 0.5wt%, the friction coefficient was the smallest.

Ester bio-based lubricating oil base oil can also be prepared by epoxidation of carbon-carbon double bonds and then ring-opening esterification, which can not only reduce the number of carbon-carbon double bonds, but also increase the content of ester groups in lubricating oil base oil, so as to improve the polarity of oil. Salih *et al.* (2011) used renewable oleic acid as raw material, hydrogen peroxide as oxidant for epoxidation, and then ring-opening esterification (as shown in Fig 2) to construct a triester lubricating oil base oil.



**Fig. 2.** The synthesis scheme for the formation of triesters

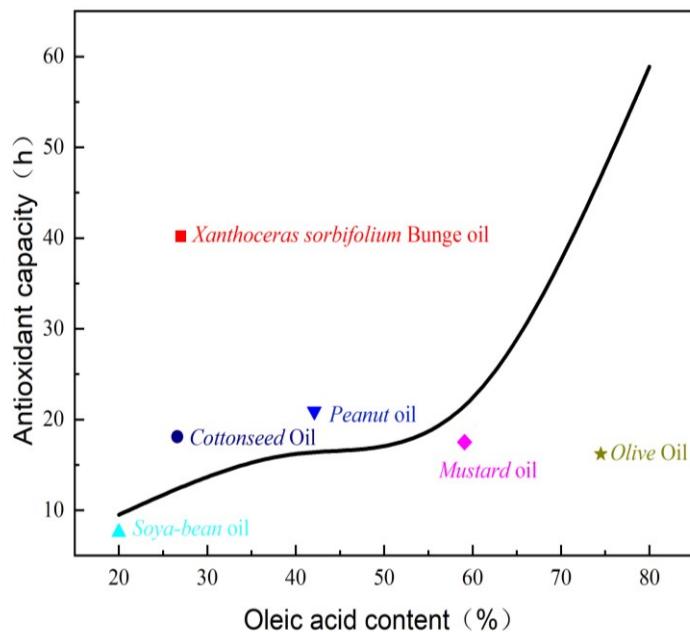


**Fig. 3.** The synthesis scheme for monoester, diesters and triesters

After performance test, the prepared oil had a density of 0.846 g/cm<sup>3</sup> and a volatility of 0.62% at 120 °C. The SP is -34.2 °C, the coagulation is -30.3 °C, the VI is 132, the abrasive spot diameter is 0.53 mm, and the friction coefficient is 0.33. Ob-eye *et al.* (2021) also used unsaturated fatty acids as raw materials. First, hydrogen peroxide was used to epoxidize carbon-carbon double bonds, and then ring-opening esterification or etherification was used to build single ester, double ester or even triester lubricating oil base oil (see Fig. 3). It was found that with the increase of the number of ester groups, the VI of the prepared oil declined. The kinematic viscosity of the oil increases.

### Biological Modification

There are many kinds of vegetable oils, and their composition and structure are quite different. Oleic acid is the main component of vegetable oil. Compared with other polyunsaturated fatty acids, it has better antioxidant properties. At the same time, the higher the content of oleic acid, the better the low temperature fluidity of vegetable oil. Therefore, the goal of biological modification is to increase the proportion of oleic acid. Figure 4 shows the relationship between oleic acid content and oxidative stability in different vegetable oils (Han and Liu 2008).



**Fig. 4.** Relationship between antioxidant properties and oleic acid content of vegetable oil

The goal of biological modification of vegetable oil is to breed plants that can produce high oleic acid vegetable oil through biotechnology. For example, the mass fraction of linoleic acid in sunflower seed oil is as high as 50% to 70%, which determines that sunflower seed oil is easily oxidized. However, the mass fraction of oleic acid in sunflower seed oil can be increased to more than 90% by using invisible genetic modification. The obtained high oleic acid sunflower seed oil has excellent lubrication performance and still has good biodegradability (Miller *et al.* 1987). The content of oleic acid in rapeseed oil was also significantly increased by gene technology. The obtained rapeseed oil had excellent oxidation stability and could be used as lubricating base oil.

## Synthesis of Vegetable Oil Base Oil

Biomass-based lubricant base oils are derived from renewable biomass, such as lignin. These include biodegradable products, cellulose downstream products, carbohydrates, natural oils, and other materials that are biodegradable and have low-toxic or non-toxic properties. They are considered green products. The production process involves carbon-carbon coupling reactions, esterification reactions, polymerization reactions, and other methods for directly producing oil products or oil intermediates. These intermediates can undergo hydrodeoxygenation to produce esters, ethers, or hydrocarbon-based lubricating oil base oils. Through complex physical and chemical processes, the carbon chains of biomass are recombined to meet the structural and performance requirements of lubricating oil base oils (as shown in Fig. 4). Willing (2001) believed that at the end of the service life, the 'iste oil' would be decomposed into CO<sub>2</sub> and water by microorganisms. Because the amount of CO<sub>2</sub> released during the production and use of the whole lubricating oil is the same as the amount of CO<sub>2</sub> absorbed, the CO<sub>2</sub> in the whole process is recycled. In other words, the lubricating oil is biodegradable.

### *Olefin metathesis*

The olefin metathesis reaction is a process in which olefins are converted into new unsaturated compounds by C=C cleavage and reforming under the action of transition metal carbene catalysts. The process mainly includes cross metathesis, ring-opening metathesis, closed-loop metathesis, and so on. In the olefin metathesis process, the metal carbene complex is the active center of the reaction, and the olefin and the transition metal carbene complex form an unstable metal cyclobutane intermediate by [2+2] cycloaddition reaction. Then through the reverse cycloaddition reaction, the cracking produces new metal carbene complexes and olefins, so that the catalytic process continues to cycle until an equilibrium mixture of olefins is obtained (Benedikt *et al.* 2022).

The development of transition metal carbene catalysts has made olefin metathesis one of the important C=C construction methods in organic synthesis. Schrock (1999) reported a highly active molybdenum carbene catalyst-Schrock catalyst. The catalyst requires mild reaction conditions, but it is highly sensitive to oxygen and water, and its application is limited.

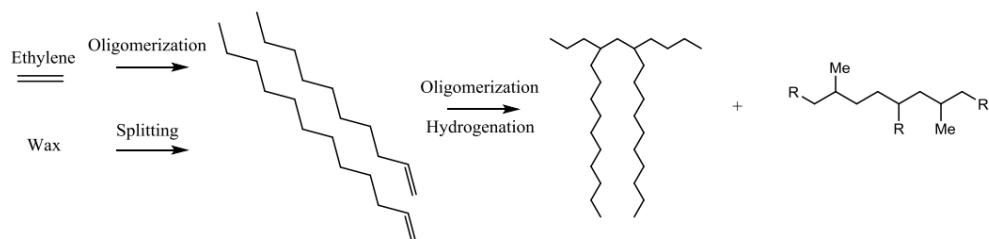
Jawiczuk *et al.* (2020) found that ruthenium carbene complexes not only can efficiently catalyze olefin polymerization, but it also can achieve low sensitivity to oxygen and water. The first generation of Grubbs catalysts containing tricyclohexylphosphine ligands has been developed. However, the first generation of the catalyst has exhibited low catalytic activity and short service life for compounds with large steric hindrance such as p-toluenesulfonamide, so it has not been widely used. Later, the researchers replaced the phosphine ligand in the first-generation Grubbs catalyst with N-heterocyclic carbene to obtain the second-generation Grubbs catalyst. The catalytic activity and selectivity of the second-generation Grubbs catalyst were improved, and the sensitivity to the functional groups of the reaction substrate is lower (Choi and Grubbs 2003). Garber *et al.* (2000) introduced the opropoxy structure into the Grubbs catalyst structure and synthesized the first-generation Hoveyda catalyst and the second-generation Hoveyda catalyst. The stability of Hoveyda catalyst was further improved on the basis of retaining the high catalytic activity and selectivity of Grubbs catalyst.

The development of ruthenium catalysts has made olefin metathesis break through the application limitations in oil chemistry. At present, olefin metathesis technology has become an important means of functionalization of chemical intermediates derived from

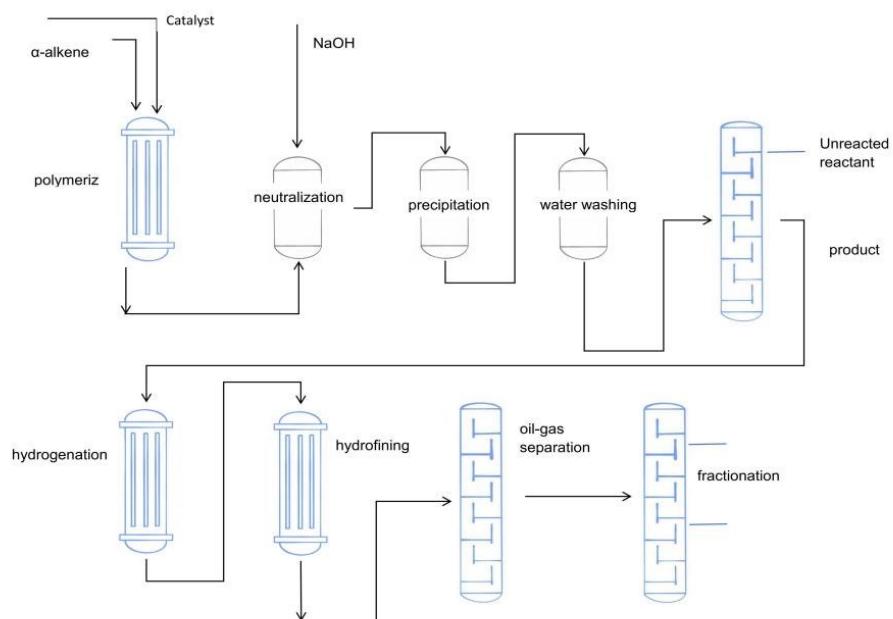
vegetable oil. Schrödi *et al.* (2008) studied the catalytic activity of ruthenium catalyst in the metathesis reaction of methyl oleate and ethylene. The results showed that the N-heterocyclic carbene ruthenium catalyst had good activity and selectivity in the formation of terminal olefins, and the turnover number of the catalyst was up to 35000. Keitz *et al.* (2015) improved and adjusted the structure of N-heterocyclic carbene ruthenium catalyst, and the turnover number of the final catalyst was up to 10  $\Omega$ . This was much higher than the catalyst turnover requirement proposed by Dow Company, (Burdett *et al.* 2004), indicating that the preparation of terminal olefins by olefin metathesis has economic feasibility and industrialization prospects.

The excellent performance of PAO base oil is mainly due to its molecular structure and composition. It is mainly composed of alkanes with narrow molecular weight distribution and high degree of branching, as shown in Fig. 5. The synthesis process of PAO lubricating base oil is shown in Fig. 6. Elevance Renewable Sciences Inc. (Elevance Inc.) successfully commercialized olefin metathesis technology by using olefin metathesis reaction of vegetable oils to prepare lubricants, coatings, and fuel additives. Aria WTP40 bio-based lubricating base oil is synthesized by Elevance Company using 1-decene and methyl 9-decanoate as raw materials. Compared with commercial poly- $\alpha$ -olefin (PAO) base oil, the viscosity value and SP of the two are similar at 100 °C. However, the viscosity of Aria WTPN40 base oil at 40 °C is much lower than that of commercial PAO 40 base oil, and its VI is as high as 165 (see Table 1) (Lu *et al.* 2018). It can be seen that Aria WTPN40 base oil has excellent viscosity-temperature performance and low temperature performance. Different from PAO base oil, the introduction of ester functional groups makes Aria WTP 140 base oil form a stronger adsorption film on the metal surface (Perera *et al.* 2022). The modification not only improves its anti-wear performance, but also improves the solubility of chain hydrocarbon base oil and additives and the poor compatibility of rubber. In addition, 1-decene is an important raw material for the synthesis of PAO base oil in industry. The preparation of 1-decene by olefin metathesis technology can reduce fossil energy consumption and environmental pollution. It can effectively replace ethylene oligomerization process, which is a green and feasible technical route. Nomura *et al.* (2019) used  $\text{BF}_3$ /alcohol as catalyst to polymerize 1-decene and 1-dodecene. When the mass ratio was 75/25, the KV<sub>100</sub> of the product was 5.85 mm<sup>2</sup>/s, the VI was 139, and the SP was -57 °C. Kitphaitun *et al.* (2021) also employed a  $\text{BF}_3$ /alcohol catalytic system for polymerization of 1-decene and 1-dodecene, with a mass ratio of 30/70. The resulting product transport KV<sub>100</sub> was 6.25 mm<sup>2</sup>/s, the VI was 141, and the SP was -21 °C. Seo *et al.* (2017) used C<sub>12</sub>-C<sub>18</sub> internal olefins as raw materials and  $\text{BF}_3$  as a catalyst. They found that the kinematic viscosity (KV<sub>100</sub>) of the resulting product was 4.15 mm<sup>2</sup>/s, the viscosity index (VI) was 137, and the solidifying point was -26 °C. These observations indicate that oil viscosity tends to increase while the VI decreases with higher carbon numbers in raw materials. Although previous studies have investigated  $\text{AlCl}_3$  and  $\text{BF}_3$ , it is important to note their potential environmental and reactor hazards (Cai and He 2003). Immobilizing  $\text{AlCl}_3$  on carriers such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or polystyrene would minimize environmental impact while enhancing active site dispersion. Currently favored carriers include  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, polystyrene molecular sieves, SiO<sub>2</sub>, and graphite. Yu *et al.* (2013) experimented with an  $\text{AlCl}_3$ /TiCl<sub>4</sub> bimetallic catalyst using decene-1 under optimized conditions. This yielded a 73% precursor for lubricant base oil with kinematic viscosities at 40 and 100 °C of 54.8 and 8.8 mm<sup>2</sup>/s, respectively, along with a high VI of 138 and a low SP of -51 °C.  $\text{BF}_3$  has a good performance in the presence of water, alcohol, ether, and so on. The prepared lubricant base oil has a high VI, but  $\text{BF}_3$  will release strong acid gas

HF, which also has the ability to do great damage to the human body, the environment, and the reactor. Li (2014) prepared  $\text{AlCl}_3\text{-TiCl}_4/\gamma\text{-Al}_2\text{O}_3$  catalyst by using coal-based activated carbon and  $\gamma\text{-Al}_2\text{O}_3$  loaded with  $\text{AlCl}_3$  and  $\text{TiCl}_4$ , and the properties of the oil obtained reached the performance index of commercial PAO 40. Moreover, 1-decene and 9-decanoic acid methyl ester can also be used to prepare lubricant base oil. Performance can be improved with additives and surfactants by chemical methods such as polymerization, anhydride and subsequent ring-opening esterification, which has high economic benefits and broad development prospects.



**Fig. 5.** Synthesis route of PAO lubricant base oil



**Fig. 6.** The process of PAO production

**Table 2.** Performance of Aria WTPTM 40 and PAO 40

Base Oil	KV <sub>40</sub> (mm <sup>2</sup> /s)	KV <sub>100</sub> (mm <sup>2</sup> /s)	VI	SP (°C)
Aria WTP <sup>TM</sup> 40	304	40	165	-34
Commercial PAO 40	396	39	143	-33

### *Cross-lactoneation*

Zygalactone is obtained from the oligomerization of fatty acids, and its molecular structure and molecular weight are related to the structure and degree of polymerization (EN) of fatty acids (Soni and Agarwal 2014). Cross-linked lactone base oil not only has high VI, low evaporation loss, and high biodegradation rate, but it also has excellent thermal oxidation stability and hydrolysis stability (García-Zapateiro *et al.* 2013b). The oligomerization of fatty acids is generally divided into a condensation reaction and addition reaction. In the condensation reaction, the hydroxyl group in one fatty acid reacts with the carboxyl group of another fatty acid to remove a molecule of water to form a fatty acid ester with hydroxyl group (García-Zapateiro *et al.* 2013a). In the addition reaction, in the presence of hydrogen ions, the carboxyl group of one carboxylic acid molecule attacks the double bond of another carboxylic acid molecule for addition, and then it generates a fatty acid polymer (Cermak and Isbell 2009).

At present, there are many kinds of catalysts that can be used in the cross-lactone reaction, and each has its own characteristics. The lipase catalyst has mild reaction conditions and few side reactions, but the selectivity of the lipase catalyst is closely related to the position of the hydroxyl group in the hydroxyl fatty acid chain, and the reaction yield is low (Todea *et al.* 2015). Ionic liquids have the advantages of low volatility, high activity and environmental friendliness, but the recycling efficiency is not high (Wang and Sun 2017). The catalytic activity of concentrated sulfuric acid is high, and the yield is about 60%. However, in the catalytic process, it is often accompanied by side reactions such as sulfonation. These can easily produce by-products, which is not conducive to the purification and separation of products (Borugadda and Dalai 2018). Perchloric acid is a commonly used catalyst at present. The conversion rate of raw materials under its catalytic reaction is high, and the yield of the obtained cross-lactone product can reach more than 70%, but its strong corrosivity can easily lead to equipment corrosion.

Cross-linked lactone lubricants are usually derived from vegetable oils such as oleic acid, castor oil, coconut oil and sunflower seed oil, and their physical and chemical properties and lubricating properties are closely related to the introduced structural units. Cermak and Isbell (2001) and Cermak and Isbell (2002) synthesized fatty acid oligomers with oleic acid as the structural monomer under the catalysis of perchloric acid. The results show that the unsaturated double bond in the oleic acid structural monomer will significantly affect the thermal oxidation stability of the lactone. The saturated fatty acid-terminated fatty acid cross-lactone obtained by introducing saturated fatty acid into the cross-lactone structure has improved low-temperature performance and thermal oxidation stability. In addition, by introducing the C<sub>4</sub>~C<sub>6</sub> saturated acid structure unit at the top of the fatty acid lactone, it was found that the SP of the lactone gradually decreased with the increase of the length of the fatty acid carbon chain, and the minimum could reach -39 °C. With the increase of the chain length to C<sub>1</sub>, the SP gradually increased to -15 °C. Hoong *et al.* (2019) capped the synthesized oleic acid lactone with different fatty acids, and then the product was reacted with alcohols with different molecular structures to obtain a lactone product with good low temperature performance and thermal oxidation stability. The experimental results show that the SP of the cross-lactone product is related to the carbon chain length of the fatty acid, which is consistent with the conclusion of Cemark and Isbell (2001).

Hoong *et al.* (2020) synthesized fatty acid lactones from oleic acid and acetic acid under the catalysis of hydrogen peroxide. In order to improve the oxidation stability of the product, the hydroxyl group of the product was blocked with lauric acid, and it was finally

reacted with alcohol to obtain the cross-lactone base oil. The KV<sub>40</sub> and KV<sub>100</sub> of the synthesized lactone product were 110 and 17 mm<sup>2</sup>/s, respectively, the VI was 169, the SP was -36 °C, and the initial oxidation value was 201 °C. Sammaiah *et al.* (2016) synthesized cross-lactones from dicarboxylic acids with different carbon chain lengths and methyl ricinoleate under solvent-free conditions. The results showed that the synthesized products have excellent low temperature performance and high VI. The SP of the representative products can reach below -60 °C, the VI was 176, and the biodegradation extent was more than 0%. The low temperature fluidity and thermal oxidation stability of base oil can be improved by changing the structure and polymerization degree of fatty acid monomer. At the same time, it is renewable and highly biodegradable, which is also in line with the current sustainable development trend of energy.

The United States Department of Agriculture and Biosynthetic Technologies have developed high-performance cross-lactone products – SE7B and SE15B lubricating base oils – which are used for the development of various lubricant product formulations, and the cross-lactone technology has been commercialized. Table 2 shows that compared with synthetic ester oil and PAO, SE7B and SE15B lubricants have higher VI and lower evaporation loss (Jones *et al.* 2016). SE7B and SE15B lubricants have good viscosity-temperature properties and thermal oxidation stability. Biosynthetic Technologies also synthesized 5W-20 and 5W-30 cross-lactone engine oils based on high oleic acid soybean oil. The bio-based engine oil is certified by the American Petroleum Institute (API). The performance indicators meet or even exceed most of the high-quality petroleum-based lubricants currently sold on the market. After use, the sludge deposition is less and has good biodegradability.

**Table 3.** Performance Comparison of Estolide Lubricant with Other Synthetic Oils

Base Oil	KV <sub>40</sub> (mm <sup>2</sup> /s)	KV <sub>100</sub> (mm <sup>2</sup> /s)	VI	SP (°C)
SE7B	30.3	6.3	164	-18
SE15B	90.8	14.7	154	-18
synthesis of esters	53.0	8.6	135	-51
PAO	38.0	7.0	146	-43

#### *Plant sugar fermentation*

Sugars in nature are abundant and renewable. They are usually divided into monosaccharides, disaccharides, and polysaccharides. Unlike high-fiber sugar crops, sugar beets, sugar cane, and corn have high sucrose content and are easy to obtain. Their syrup juices can be directly bio-fermented to produce chemicals such as bioethanol, lubricants, and farnesene without thermochemical pretreatment (Eggleson and Lima 2015).

The traditional method for preparing farnesene is through the polymerization of isoprene, but the purity of farnesene prepared by this method is low and there are many by-products (McPhee 2013).  $\beta$ -Farnesene with high purity (95%) was prepared by Amyris Biotechnology Company using sugar cane and beet as sugar sources, with the application of a yeast fermentation process. Amyris Company selectively hydrogenated  $\beta$ -farnesene and polymerized with  $\alpha$ -olefins, and then it was hydrogenated again to improve the oxidation stability of the product. Finally, farnesene-derived base oils with different viscosity levels were obtained by fractionation (Jones *et al.* 2016). This process eliminates the conjugated diene structure and partial unsaturated sites in  $\beta$ -farnesene by selective

hydrogenation, which not only can regulate the branching degree and molecular weight of comonomers, but also can reduce the production of by-products.

$\beta$ -Farnesene can also be hydrogenated by introducing a protective group, and then it can be converted into branched  $\alpha$ -olefins by eliminating the protective group, and then polymerized with other  $\alpha$ -olefins to obtain high-performance hydrocarbon base oil (Arnsek and Vizintin 2000). In addition, the process steps of preparing base oil with  $\beta$ -farnesene as raw material are basically the same as those of  $\alpha$ -olefin polymerization. Therefore, the synthesis process equipment and device of farnesene-derived base oil can be extended to equipment for poly- $\alpha$ -olefin synthesis, which saves the cost for the industrial synthesis of farnesene-derived base oil and further improves the market competitiveness.

**Table 4.** Physicochemical Properties of Farnesene-derived Base Oil

Base Oil	KV <sub>40</sub> (mm <sup>2</sup> /s)	KV <sub>100</sub> (mm <sup>2</sup> /s)	VI	SP (°C)
PDBO 3	13.8	3.3	108	-57
PDBO 4	19.2	4.2	122	-42
PDBO 7	44.0	7.2	125	-48
PDBO 12	104.3	13.3	125	-27
PDBO 15	137.6	15.7	118	-42
PDBO 32	32.8	6.1	134	-42

Table 4 shows that the farnesene-derived base oil has a high VI and a low SP. The viscosity-temperature performance and low temperature performance are better than the mineral base oil, and the comprehensive performance is close to that of PAO. Farnesene-derived base oil is derived from plant sugars and does not contain any harmful substances such as aromatic hydrocarbons and sulfur. It is renewable and non-toxic, and it has significant environmental benefits. At the same time, the base oil derived from farnesene contains a polymethyl branched chain structure, which makes it have good biodegradability. The biodegradability extent is greater than 60%, which is much better than that of mineral base oil and PAO (<40%).

In 2015, Novvi Company of the United States industrialized the process of farnesene-derived base oil, introduced NovaSpec renewable synthetic base oil, and applied it to hydraulic oil, transformer oil, compressor oil, and industrial gear oil uses. Novvi has also partnered with Korea's Gardners (GS) to develop engine oils from NovaSpec renewable base oils. The company has launched Kixx 0W-20 and 5W-30 bio-based engine oils (see Table 4 for specific physical and chemical parameters). The Kixx engine oil has been certified by the United States Department of Agriculture to meet API SP and ILSAC GF-6A specifications. Compared with traditional API SP engine oil, Kixx BIO1 engine oil not only has excellent viscosity-temperature performance and low temperature performance, but it also has less sludge deposition.

**Table 5.** Physicochemical Parameters of Kixx BIO1 Engine Oil

Base Oil	KV <sub>40</sub> (mm <sup>2</sup> /s)	KV <sub>100</sub> (mm <sup>2</sup> /s)	VI	SP (°C)
0W-20	44.9	8.6	175	-46
5W-30	61.8	10.4	157	-43

### *C-C coupling*

Lignocellulose is a cheap and readily available biomass resource, and its main components include cellulose, hemicellulose, and lignin (Menon and Rao 2012). In recent years, biomass platform compounds derived from lignocellulose, such as alkylfurans, furan, furfural, 5-hydroxymethylfuran, and other carbonyl compounds, have achieved carbon chain growth through C-C coupling, realizing the conversion from low-carbon small molecules to high-carbon chemicals. However, because the active small molecule compounds containing furan rings have simple molecular structure and small molecular weight, and usually the carbon number of lubricating oil base oil can reach C<sub>30</sub> to C<sub>50</sub>, it is usually necessary to carry out multiple carbon-carbon coupling reactions, resulting in an increase in the separation cost of each step and a decrease in synthesis efficiency. There are many kinds of active small molecules that can participate in carbon-carbon coupling, and their structures are different, so the structure of hydrocarbon lubricating oil base oil can be controlled by targeting design, and then different raw materials can be used for synthesis, so as to accurately regulate the molecular weight and oil structure of the prepared hydrocarbon lubricating oil base oil, and then adjust the properties of the oil. Therefore, compared with conventional lubricating oil base oil, biomass hydrocarbon lubricating oil base oil has the characteristics of controllable structure and adjustable properties.

### *Hydroxyl alkylation/alkylation*

Hydroxyl alkylation/alkylation is an important way to construct carbon chains in the synthesis of hydrocarbon lubricating base oil. It mainly entails the electrophilic aromatic substitution reaction of alkyl furans with carbonyl compounds such as aldehydes and ketones under the catalysis of Bronsted acid. In this process, the carbonyl reactant is protonated and added to the furan ring active reaction site, and then the alcohol intermediate is generated by the hydroxylation process. After the alkylation step, the alcohol intermediate loses a molecule of water to obtain a carbocation and combines with a molecule of furan compound to form a long-chain compound containing a furan ring. Finally, it is hydrode oxygenated to form a hydrocarbon lubricating base oil.

Liu *et al.* (2019a) studied the effect of structure on properties of biomass-based hydrocarbon lubricating oil base oil. First, an alkylation reaction is employed on perfluorinated resin PW98 to facilitate the carbon-carbon coupling of 2-alkylfuran and aliphatic aldehydes, as depicted in Fig 5. This process allowed for the one-step production of a biomass-based lubricating base oil containing furan rings. Alternatively, a Pd/C catalyst can be utilized to hydrogenate furan rings and construct epoxy-ether biomass-based lubricating oil. Furthermore, the carbon chain length of 2-alkyl furan and fatty aldehyde can be adjusted to regulate the total carbon number of the lubricating oil and the length of branch chains, thereby fine-tuning the properties of the prepared oil. The C<sub>30</sub> lubricating oil base oil exhibited KV<sub>100</sub> and KV<sub>40</sub> values of 3.47 and 13.58 mm<sup>2</sup>/s respectively, an oxidation temperature of 170°C, VI of 105, and SP lower than -48°C. However, due to its "T" structure with only one branch chain, it displayed a higher SP compared to commercial PAO-based lubricants. To increase the carbon branch chains, diene long-chain aldehydes with conjugated structures were further used for alkylation with 2-alkylfuran on PW98 catalyst to achieve carbon chain extension. Subsequently, this process led to obtaining a biomass-based all-hydrocarbon lubricating oil base oil with three branch chains after hydrodeoxidation (Liu *et al.* 2019b). The resulting product demonstrated KV<sub>100</sub> and KV<sub>40</sub> values of 3.14 and 12.91 mm<sup>2</sup>/s respectively; an initial oxidation temperature is at 181°C; VI is at 138; and SP is below -63°C. It should be noted

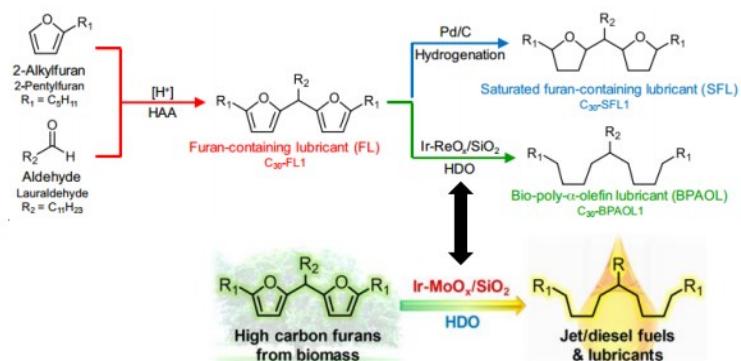
that due to steric resistance and weak polarity characteristics inherent in molecules used for constructing lubricating oil intermediates, the reaction rate may be slow. Liu *et al.* (2019c) selected alkyl furans and aldehydes with different chain lengths and structures as reaction raw materials to precisely control the molecular structure and molecular weight of the products. They prepared C hydrocarbon lubricating oil base oil containing three molecular structures of aromatic furan ring, saturated furan ring and branched alkanes. The KV<sub>40</sub> and KV<sub>100</sub> had values of 17.9 and 3.91 mm<sup>2</sup>/s, respectively. The VI was 140, and the SP was lower than -60°C. The synthesized lubricating base oil exhibited excellent viscosity-temperature performance and volatility, and the low temperature performance of branched alkanes was close to that of commercial PAO4. Due to the lower carbonyl electrophilicity of ketones, the reactivity was lower than aldehydes. Liu *et al.* (2020) used thiol as a catalytic additive to study the hydroxyl alkylation/alkylation reaction of alkylfurans derived from lignocellulose with ketones. The yield of the final product can reach 90%. Experiments showed that thiols can reduce the barrier of the rate-limiting dehydration step and can significantly increase the reaction rate of alkylfurans and ketones. The SP of the product can reach below -60 °C, and the low temperature performance and viscosity-temperature performance of the synthetic base oil were better than those of the commercial alkyl naphthalene base oil.

Elvis *et al.* (2021) used phenolic compounds and aldehydes derived from lignin as raw materials and selected P-SiO<sub>2</sub> and Ir-ReO/SiO<sub>2</sub> as catalysts to synthesize aromatic and naphthenic lubricating oils by hydroxyl alkylation/alkylation and hydrodeoxygenation. The yield of the product reached 80%. The performance index of naphthenic lubricating oil was close to that of commercial PAO 3.6, and its KV<sub>40</sub> and KV<sub>100</sub> values were 12.6 and 3.18 mm<sup>2</sup>/s, respectively. The VI was 118, but the evaporation loss rate was high.

Chen and Zhao (2021) synthesized a highly branched intermediate with a furan ring by hydroxyalkylation/alkylation using 5-hydroxymethylfurfural and alkylfuran as raw materials and Pd/c-Pt/HZSM-5 as a catalyst. The yield was as high as 98%. Highly branched epoxy ether lubricating oil and T-type hydrocarbon lubricating oil were prepared by selective hydrogenation and deoxygenation hydrogenation. The KV<sub>40</sub> and KV<sub>100</sub> ranges of epoxy ether lubricating oil were 54.5 to 58.8 and 8.2 to 9.9 mm<sup>2</sup>/s, respectively. The VI was 121 to 155, the SP was -33 to -21 °C, and the initial oxidation temperature was 125 to 142 °C. The KV<sub>40</sub> and KV<sub>100</sub> of T-type hydrocarbon lubricating oil ranged from 13.2 to 15.5 mm<sup>2</sup>/s and 3.4 to 3.8 mm<sup>2</sup>/s, respectively. The VI was from 133 to 136, the SP was from -47 to -36 °C, and the oxidation starting temperature was 151 to 192 °C. By adjusting the carbon chain structure of the reaction raw materials, the molecular size and molecular weight of the bio-based lubricating oil could be effectively changed to meet different performance requirements. However, the highly active bimetallic catalyst Ir-ReO/SiO<sub>2</sub> used in the hydrodeoxygenation process of the synthesized lubricating oil precursor is expensive and the industrial technology economy is low. Recently, Liu *et al.* (2019) found that use of Ir-Mox/SiO<sub>2</sub> and Ir-Rex/SiO<sub>2</sub> catalysts hydrodeoxygenation of furan ring to build 'T' type hydrocarbon bio-based lubricating oil. Ir-Mox/SiO<sub>2</sub> was judged to be more cost-effective than Ir-Rex/SiO<sub>2</sub> (Liu *et al.* 2019).

From the above studies, it is found that the construction of lubricating oil molecules from small molecule compounds by alkylated carbon-carbon coupling usually requires two or more steps. The process is cumbersome, and the separation of intermediates is time-consuming and labor-intensive, and it is difficult to get moistened in one step. The oil contains natural long carbon chain structures. If these long carbon chains can be reorganized to achieve the carbon chain structure required for lubricant molecules, and

simultaneously undergo complete deoxygenation, biomass-based hydrocarbon lubricant base oil can be obtained. Xue *et al.* (2019) used castor oil, which contains conjugated double bonds in its molecular chain, as the raw material. Through a one-pot method on a  $\text{MoO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$  catalyst, they carried out transesterification, dehydration, and polymerization of conjugated olefins, achieving the synthesis of biomass-based hydrocarbon lubricant base oil in a single step. Structural testing revealed that the yield of dimer oil was 70.8%. Property testing showed that the prepared lubricant base oil had a KV<sub>40</sub> of 27.9 mm<sup>2</sup>/s, the solidifying point of -42 °C, and it exhibited good boundary lubrication performance. The natural long carbon chain structure of castor oil was fully utilized through carbon chain reorganization, enabling the one-step process of transesterification, dehydration, polymerization, and hydrogenation on an acidic catalyst.



**Fig. 7.** Synthetic route of "T" type cyclic ether and hydrocarbon bio-based lubricant base oil

#### *Aldol condensation*

Aldol condensation is mainly the nucleophilic addition of furfural and 5-hydroxymethylfurfural with carbonyl compounds containing  $\alpha$ -H, such as aldehydes and ketones under base catalysis, forming a new C=C in the molecule to achieve carbon chain growth. Gu *et al.* (2017) used furfural and acetone derived from lignocellulose as raw materials,  $\text{Pd}/\text{y-Al}_2\text{O}_3$  and  $\text{Pd}/\text{NbOPO}$  as catalysts, through aldol condensation, selective hydrogenation, secondary aldol condensation, and hydrodeoxygenation four-step reactions to synthesize highly branched C<sub>23</sub> alkanes, with a yield of 50.6%. The route achieves carbon chain growth by aldol condensation strategy, but multiple reaction steps lead to low yield, and a large amount of reaction solvents are required, which greatly increases the production cost. In this regard, Norton *et al.* (2019) used furfural and 12-triketone as raw materials, selected Ir-ReO/SiO<sub>2</sub> as catalyst, and prepared C<sub>2</sub> and C<sub>Δ3</sub> branched alkane base oil through two steps of aldol condensation and hydrodeoxygenation, with an overall yield of 61%. The KV<sub>40</sub> and KV<sub>100</sub> of the base oil were 14.37 and 3.43 mm<sup>2</sup>/s, respectively, and the VI was 115. The viscosity was lower than that of commercial PAO 3.6, and the overall performance was better than that of Phillips 66 Mineral oil. The above aldol condensation reaction conditions are relatively mild, and the solid base catalyst can shorten the reaction time and is easy to separate and recover. However, the yield of the synthetic product is not high when the lubricating oil base oil is prepared by this strategy. Therefore, it is necessary to develop catalysts with high activity and high efficiency.

#### *Self-condensation of ketones*

Arab *et al.* (2016) used alkyl ketones and furan ketones as raw materials, and they self-condensed the corresponding cyclic trimers under the catalysis of solid acid (such as

$\text{Ta}_2\text{O}_5/\text{SBA-15}$ ) or solid base (such as  $\text{MgAlO}$ ). The condensation product was subjected to hydrodeoxygenation to prepare naphthenic bio-based lubricating oil with a yield of more than 90%. The synthesized naphthenic lubricating base oil exhibited excellent SP, VI, and thermal oxidation stability, and the overall performance index was close to that of commercial PAO base oil. The  $\text{KV}_{40}$  and  $\text{KV}_{100}$  range of the product was 15.2 to 106.5  $\text{mm}^2/\text{s}$  and 3.4 to 11.5  $\text{mm}^2/\text{s}$ , respectively. The VI was 40 to 146, the minimum SP was  $-75\text{ }^\circ\text{C}$ , and the initial oxidation temperature was greater than  $200\text{ }^\circ\text{C}$ . Experiments show that the structure of the synthesized product is related to the properties of the catalyst. Under the catalysis of solid bases such as  $\text{MgAlO}$ , the reaction mainly produces cyclic trimers. Under the catalysis of solid bases such as  $\text{Ta}_2\text{O}_5/\text{SBA-15}$ , the reaction mainly produces aromatic cyclic trimers. In addition, through the performance-structure relationship, it is concluded that the VI of the naphthenic lubricating base oil is proportional to the length of the alkyl side chain, and the volatility is inversely proportional to the length of the alkyl chain.

## SUMMARY AND PROSPECTS

Driven by the global energy transition and carbon neutrality strategy, vegetable oil-based lubricants are emerging as a key development direction to replace petroleum-based lubricant products due to their renewability, excellent biodegradability, and low ecotoxicity. The existing vegetable oil modification technologies have formed a progressive technical architecture of "basic modification - deep synthesis". The basic modification layer comprises three main pathways: additive modification, chemical modification, and biological modification. Additive modification maintains its fundamental application status owing to its simple process and low cost; chemical modification significantly enhances thermal oxidation stability through reactions such as transesterification, yet faces challenges in waste liquid treatment; biological modification achieves green transformation through enzymatic catalysis, but urgently needs to overcome the bottleneck of conversion efficiency. In the field of deep synthesis, using biomass as raw material and advanced catalytic technologies such as olefin metathesis and intramolecular lactonization as the core, combined with biosynthetic strategies like plant sugar fermentation and C-C coupling, a molecular engineering platform for precise regulation of carbon chain structures has been constructed. Despite the high cost of catalysts and separation difficulties, the utilization of diverse functional groups in biomass platform molecules for carbon chain construction enables precise control of the molecular structure and size of target products, allowing the synthesis of bio-based lubricant base oils that meet various performance requirements. This approach is highly innovative and sustainable. Therefore, future efforts should focus on developing low-cost catalysts with high activity and selectivity, improving the recycling efficiency of catalysts, and utilizing downstream derivatives of biomass to precisely construct long-chain alkanes through pathways such as hydroxyalkylation and aldol condensation, followed by hydrodeoxygenation to produce hydrocarbon-based bio-lubricants.

## ACKNOWLEDGMENTS

This work is supported by the Natural Science Foundation of Inner Mongolia (No.2024MS03068); Inner Mongolia Agricultural University 2024 Innovation and

Entrepreneurship Training Project (202410129031); Inner Mongolia Agricultural University 2023 Innovation and Entrepreneurship Training Project (202310129045); and Science and technology projects of Jungar Banner (No.2023YY-12).

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Article submitted: June 28, 2024; Peer review completed: July 31, 2024; Revised version received: August 19, 2024; Further revised version received and approved: March 13, 2025; Published: July 16, 2025.

DOI: 10.15376/biores.20.3.Hao