A Review of Chemical Modification of Vegetable Oils and Their Applications

Yongjing Zeng 1,†, Zichen Shang 1,†, Zeni Zheng 1, Ning Shi 2, Bo Yang 3, Sheng Han 1,* and Jincan Yan 1,*

1 School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China; 216061108@mail.sit.edu.cn (Y.Z.); 226061105@mail.sit.edu.cn (Z.S.); 226062134@mail.sit.edu.cn (Z.Z.)
2 School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai 201620, China; ningshi_sues@163.com
3 Comprehensive Technology & Service Center of Qinzhou Customs, Qinzhou 535000, China; boyang_ciqqz@163.com
* Correspondence: hansheng554321@sina.com (S.H.); jcyan@sit.edu.cn (J.Y.)
† These authors contributed equally to this work.

Abstract: In order to cope with the shortage of non-renewable energy and the increasingly environmental pollution, sustainable vegetable oils, as competitive alternatives, have widely been held in the good graces of the researchers. Vegetable oils are suitable for a wide range of applications such as biofuels and biodiesel. However, the development of vegetable oils is limited due to the characteristics of unsatisfactory oxidation stability and poor cold-flow properties. Chemical modification is considered as an effective solution to enhance the performance. The research progress of the chemical modification methods and applications of vegetable oils in recent years are summarized in this review. Reducing the content of carbon–carbon double bonds and increasing the degree of saturation are the keys to improve the physicochemical properties of vegetable oils. The prospects for the development direction and challenges of vegetable oils are proposed. Future research may focus on the use of multifunctional catalysts to optimize reaction conditions or to introduce active groups with lubricating properties in epoxidation reactions and explore the combination of chemical and auxiliary methods.

Keywords: vegetable oil; chemical modification; additive; biodegradability; application

1. Introduction

The rising population and limited availability of natural energy sources have accelerated the demand for energy [1]. The development of renewable energy sources has become one of the urgent tasks of researchers. As a substitute for petroleum fuel, vegetable-based oil has been applied in different fields because of its excellent physicochemical properties and environmental friendliness [2]. High biodegradability is one of the most desirable advantages of vegetable oils [3]. At the beginning of the 21st century, a mixture of 20% palm oil and 80% diesel has been successfully used as diesel engine oil [4]. The addition of vegetable oils reduces the risks of machine failures and maintains optimal machine operation [5]. The performance of vegetable-based diesel is similar to conventional fuels while the emissions of CO, NOx, and smoke are significantly reduced which can be attributed to the lower production of harmful gases [6]. Vegetable oil molecules formed an adsorption film on the metal surface, and then fatty acids react with the metal surface to form a monolayer film of metal soap which play a vital role in anti-wear and anti-friction. Sajeeb and Rajendrakumar [7] studied the tribological performance of mineral oil (SAE20W-40) and the blend of coconut and mustard oil (the latter ratio is 10–50%). It can be found that the wear diameter of the mixed oil decreased by 18.45% which demonstrates the excellent lubricating performance. The advantages and disadvantages of vegetable
oils and mineral oils are summarized in Table 1. At present, mineral oils hold an unshakable dominant share because of the mature technique and sufficient feedstocks. From a long-term perspective, green vegetable oils are available to replace mineral oils when their physical and chemical properties can be improved and the synthesis process can be continuously optimized.

Table 1. Summary of the advantages and disadvantages of vegetable oils and mineral oils.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Classification</th>
<th>Vegetable Oils</th>
<th>Mineral Oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advantages</td>
<td>High biodegradability</td>
<td>Excellent lubricity</td>
<td>Sufficient materials</td>
</tr>
<tr>
<td></td>
<td>Long service life</td>
<td>Easy extraction</td>
<td>Low price</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Poor oxidation stability</td>
<td>Easily corroded</td>
<td>Non-renewable</td>
</tr>
<tr>
<td></td>
<td>Easily contaminated</td>
<td></td>
<td>Easily contaminated</td>
</tr>
</tbody>
</table>

In recent years, waste vegetable oil or used cooking oil products have also been utilized in biofuel [8], biodiesel [9], lubrication [10], and other fields after green processing. Due to the low economic benefit and complicated secondary processing, there is still a long way to go. Therefore, the modification of vegetable oil to improve the physicochemical properties is regarded as a potential solution [11]. Chemical modification is the most widely used modification method at present. Among various modified conversion methods, selective hydrogenation, transesterification, and epoxidation addition are currently the preferred choices for the production of biodiesel and biofuels. There is a lack of summary of the methods and applications of chemically modified vegetable oils in recent years. It is necessary to understand and summarize the effects of chemical modification methods. Therefore, this paper aims to review recent applications of vegetable oils obtained via chemical modification in different fields. The intention of this review is related to the emergent necessity of promoting the use of vegetable oils in bio-production. The use of auxiliary methods to further obtain the multi-circulating and high-performance vegetable oils is also discussed.

2. Chemical Modification

The fundamental constituents of vegetable oils are higher fatty acid glycerides, and the types of fatty acids vary from source to source. The structure of saturated fatty acids is generally stable. There are unsaturated double bonds in the molecular structure of vegetable oils. The existence of double bonds leads to poor thermal oxidation stability [12]. The oxidation of vegetable oils is prone to acidification during storage, which leads to corrosion. Therefore, vegetable oils often need to be modified to improve their oxidative stability [13]. The content of carbon–carbon double bonds and allyl carbons in vegetable oil is reduced by chemical modification, and the oxidative stabilities of vegetable oils are improved [14]. Commonly used chemical modification methods include selective hydrogenation [15], transesterification [16], epoxidation [17], and so on.

2.1. Selective Hydrogenation

Unsaturated fatty acids in vegetable oils are converted into higher stable saturated fatty acids by reducing single or multiple carbon–carbon double bonds via selective hydrogenation. As shown in Figure 1, the four-step hydrogenation mechanism [18], including diffusion, adsorption, reaction, and desorption, is a commonly recognized hydrogenation model. In this method, a suitable high-efficiency catalyst is selected to adjust the oxidation stability and low temperature properties.
The hydrogenation activity of the catalysts depends on both the type of metal and support. Metal catalysts such as Pt [19], Pd [20] and Ni [21] are commonly used as supported catalysts in selective hydrogenation. Pt was supported on TiO₂ and ZrO₂ by impregnation to evaluate its catalytic behavior in the selective hydrogenation [22]. In the process of the partial hydrogenation of soybean oil, the catalysts exhibited better activity and lower trans-isomer selectivity. Compared with the catalytic behavior of Raney Ni, the Pt/ZrO₂ catalyst could be a potential substitute for reducing the formation of trans-fatty acids, while maintaining the physicochemical properties of hydrogenated soybean oil. The Pd supported catalysts were used to prepare soybean oil-based biodiesel through CTH in supercritical methanol [23]. Under the optimum condition with 0.5 mg Pd/g oil for 30 min, the FAMEs yield for Pd/ZSM-5 was 97.1%. Numwong [24] investigated the effect of Pd particle size on catalytic activity and cis-trans selectivity with 0.5 and 1 wt% Pd loadings. The C18:1 FAMEs were more easily selected by the smaller Pd/MCM-41 catalyst. The C18:2 and C18:3 FAMEs could be adsorbed on the metal surface by the Pd/SiO₂ catalyst, and the original TOF was improved. The performance of different Al₂O₃ supported metal catalysts was evaluated in the selective hydrogenation of sunflower oil [25]. It was shown that Pt/Al₂O₃ was more active in selective hydrogenation than Ni/SiO₂. The activity and selectivity of Pd/Al₂O₃ could be effectively balanced and the outstanding comprehensive performance was obtained. Papageridis et al. [26] investigated the influence on the selective catalysis of palm oil over Al₂O₃, ZrO₂ and SiO₂ supported Ni catalysts. The characterization revealed that the materials were evenly dispersed on the Ni/ZrO₂ and Ni/Al₂O₃ catalyst, while the best reduction effect was obtained by Ni/SiO₂ samples due to that part of Ni participated in the reaction. The effect of Pd, Pt and Ni catalysts on the partial hydrogenation of FAMEs in soybean oil was investigated [27]. The presence of sulfur influenced the activity of the as-prepared catalyst. Among the sulfur-free compounds, the best hydrogenation was obtained using a Pd/SiO₂ catalyst. This is mainly due to the formation of more conjugated dienes that decreased the rate of isomerization, thereby increasing the hydrogenation efficiency. Regardless of the influence of sulfur compounds, the priority of catalytic activity was Pd/SiO₂ > Pt/SiO₂ > Ni/SiO₂. The oxidation stability of biodiesel was increased by 30.4 h, 5 h, and 3.6 h, respectively.

It was shown that noble metals (Pt and Pd) are able to be supported on oxides such as Al₂O₃ [25,27] and give high hydrogenation efficiency. Base metals (Ni) are more suitable for producing hydrogenated oils with fewer trans isomers [26].
2.1.2. Catalyst Supports

The support materials, as the framework of the active components of catalysts, provide a suitable surface area and pore structure which can meet the requirement of mechanical stability. Al₂O₃, as one of the well-known support materials, possessed a variety of crystal forms (α, β, γ, δ, θ, etc.) [28]. Among them, γ-Al₂O₃ has been widely used in the field of catalysis owing to its rich pore structure, excellent adsorption performance, and high surface area. Toshtay et al. [29] investigated the influence of Pt/γ-Al₂O₃ prepared by adsorption on the formation of trans isomers in the hydrogenation of sunflower oil. The content of trans isomer was decreased from 5.6% to 3.5% at a low concentration of 0.2 wt% as-prepared catalyst. The unsupported and γ-Al₂O₃ supported Ni-Mo catalysts on palm oil hydrogenation were compared [30]. The H-NiMoS₂/γ-Al₂O₃ supported catalyst exhibited higher dispersibility than the unsupported catalyst. When the reaction was performed at 300 °C for 3 h and the catalyst/palm oil ratio was 0.1, 67.0% of C14-C18 alkanes was yielded.

SiO₂ can be easily available and ordered mesoporous silica with good extensibility is generally used as a catalyst carrier; therefore, it has been verified as an effective catalyst support in selective hydrogenation reaction [31]. A mesoporous silica-supported nano catalyst offers key advantages over homogeneous catalysts for in vivo applications of parahydrogen-based hyperpolarization. Rungsi et al. [32] reported the influence of a mesoporous MCM-41 silica support on the Pd particle catalyst for the partial hydrogenation of vegetable oil. The results showed that the adsorption of polyunsaturated FAMEs was enhanced on the metal surface due to the incorporation of Pd. When 2 wt% of Pd was loaded on the catalyst carrier, the Pd/MCM-41-SiO₂ catalyst system obtained the best TOF performance.

It is undoubtable that tunable carbon-based materials with different physical forms are novel catalyst supports that cannot be ignored, especially Pt-based catalysts. The influence of diverse catalysts such as Pt/C, Pd/C, Co-Mo, Pd/Al₂O₃ and Pd/ZSM-5 was studied in rapeseed oil [33]. When using noble metal catalysts (Pd, Pt) on active carbon, the highest heating value and the lowest acid value of the products can be achieved, and Pt/C was the most potential catalyst for the production of hydrogenation cracking oil after process optimizations.

In recent years, mixed oxide supports with synergistic effects have also attracted the attention of researchers. Ni/ZnO/Al₂O₃ and Ni/Al₂O₃ composite catalysts were prepared by co-precipitation, and their performance in the hydrogenation of sunflower oil was evaluated [34]. The pore size of the Ni/Al₂O₃ catalyst was promoted by the addition of ZnO. The pore characteristics of the catalyst were changed and the diffusion limit of the large triglyceride molecules was reduced, and then the hydrogenation activity of the catalyst was improved. Furthermore, the catalytic functions of vegetable oil with Ni-Cu catalysts supported by different oxide materials were studied [35]. The outstanding qualities were obtained when the Ni-Cu/ZrO₂-SBA-15 catalyst was used, and the supported catalyst retained a hydrodeoxygenation reactivity of 87.3% after reusing for five reaction cycles.

To summarize, efficient catalysts and green reaction systems are involved in the hydrogenation modification method of vegetable oils. However, during the hydrogenation of vegetable oil molecules, the positional isomerization generated trans-fatty acids in the molecules, thereby reducing biodegradability.

2.2. Transesterification

Transesterification is an effective method to improve the oxidative stability of vegetable oils by eliminating glycerol groups and introducing short-chain alcohols in order to reduce molecular viscosity, thereby improving the cold flow properties [14]. The factors that need to be considered in the transesterification reaction are alcohol-to-oil molar ratio, reaction temperature, catalyst type (basic or acidic), catalyst concentration, reactant purity, and FFA content. The transesterification of FAME is shown in Figure 2.
2.2.1. Acid Catalysis

Conventional catalysts are liquid acid catalysts, and the drawbacks of liquid acid catalysts can be equipment corrosion, environmental pollution, complex purification and separation, and catalyst recycling. Therefore, investigators are focused on environmentally friendly and efficient solid acid catalysts, such as ion-exchange resins with sulfonic acid and aluminate groups [36], heteroatoms mesoporous molecular sieves [37], heteropoly acids [38], metal-organic frameworks-based solid acids [39], zeolites [40] and so on. Among them, eco-friendly sulfonic and aluminate acid-modified solid acid catalysts are widely used in transesterification reactions due to their superior acid strength, higher surface area, advantageous pore space, and advanced thermal stability. Para-toluenesulfonic acid was considered to be a talented lubricant which can be utilized in the transesterification of sunflower oil, linseed oil, and jatropha oil [41]. The synthesis and application of sulfonic acid functionalized solid acid catalysts for transesterification reactions have been integrated over past 20 years [42].

2.2.2. Base Catalysis

Compared with acid catalysts, base catalysts, such as NaOH, and KOH, are more widely adopted by researchers owing to their high reaction conversion rate (>90%), high catalytic activity, and wide availability [11]. The transesterification of blended soybean oil and palm oil can be catalyzed by natural diatomite and the NaOH system [43]. It was found that the catalyst performed similar to zeolite with 98% and 98.4% conversion peaks at 63 °C and 70 °C. The temperature-dependent kinetics of the transesterification reaction in excess methanol could be well fitted to the first-order kinetics model, and the first-order rate constant had a good correlation with the Arrhenius equation. Kumar, S. et al. [44] investigated the successful transesterification of Jatropha oil with methanol using potassium hydroxide (0.5 wt%) as the alkaline catalyst at 70 °C.

However, the base is sensitive to water and then soap can be formed in the reaction system. Therefore, a solid base catalyst replaces the traditional liquid base catalyst and plays a critical role in the transesterification [45]. Solid base catalysts based on metal oxides are popular due to their low cost, high efficiency and wide variety [46]. The yield of biodiesel prepared using the transesterification reaction under UV light was 96.67% when employing palm oil as the raw material and TiO$_2$-modified CaO as a catalyst [47]. A similar study had been reported that the as-prepared CaO catalyst with a porous hollow cage-like structure was employed to the transesterification [48]. The yield was 97.80% under the optimal reaction conditions and can be 90.30% after the fifth recycle. Yadav and Sharma [49] revealed that the conversion of methyl ester was 93.28% by the catalyst of BaAl$_2$O$_4$ in transesterification, and the conversion can be maintained as high as 80% after five reaction cycles.

The metal oxides can be also loaded on some support and an active K$_2$CO$_3$ with a Al$_2$O$_3$/SiO$_2$ support has been reported [50]. The production of biodiesel based on sunflower oil at 120 °C and a 15:1 molar ratio of methanol to oil were the optimal conditions.
It was shown that the conversion rate reached 93% after 15 min of reaction. Furthermore, a composite base catalyst or so-called multifunctional catalysts were developed. The CaO-MgO/Al$_2$O$_3$ catalyst synthesized by co-precipitation achieved a cottonseed oil conversion rate of 97.62% at 95.63 °C when the molar ratio of ethanol to cottonseed oil was 12.24 and the CaO-MgO loading was 14.4 wt% [51]. A favorable interaction between Al and other metals was recognized to improve the defects of the catalysts. The active sites on the surfaces are enhanced by the interaction of Sr, Al and Zn oxides [52]. The SrO-CaO oxide was loaded on the Al$_2$O$_3$ support to prepare the SrO-CaO-Al$_2$O$_3$ trifunctional catalyst. The yield of biodiesel prepared from palm oil remained at 92.61% after five cycles [53].

The base catalysts used in the transesterification of various vegetable oils are summarized in Table 2.

<table>
<thead>
<tr>
<th>State</th>
<th>Types of Catalyst</th>
<th>Concentrations of Catalyst (wt%)</th>
<th>Methanol to Oil Molar Ratio</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Types of Vegetable Oil</th>
<th>Yield (%)</th>
<th>Yield after Five Cycles (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid NaOH</td>
<td>14.2</td>
<td>/</td>
<td>70</td>
<td>6</td>
<td>Palm</td>
<td>98.4</td>
<td>/</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>1</td>
<td>6:1</td>
<td>64.7</td>
<td>0.75</td>
<td>Flaxseed</td>
<td>94</td>
<td>/</td>
<td>[44]</td>
<td></td>
</tr>
<tr>
<td>Solid Diatomite</td>
<td>10.04</td>
<td>/</td>
<td>63</td>
<td>6</td>
<td>Soybean</td>
<td>98</td>
<td>/</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>3</td>
<td>15:1</td>
<td>65</td>
<td>2</td>
<td>Soybean</td>
<td>97.8</td>
<td>90.3</td>
<td>[48]</td>
<td></td>
</tr>
<tr>
<td>BaAl$_2$O$_4$</td>
<td>4</td>
<td>21:1</td>
<td>65</td>
<td>2.5</td>
<td>Used vegetable oil</td>
<td>93.28</td>
<td>&gt;80</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$-CaO</td>
<td>2.52</td>
<td>15:1</td>
<td>65</td>
<td>2.5</td>
<td>Palm</td>
<td>96.67</td>
<td>&gt;80</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$-SiO$_2$</td>
<td>2</td>
<td>15:1</td>
<td>120</td>
<td>12</td>
<td>Sunflower</td>
<td>93.5</td>
<td>/</td>
<td>[45]</td>
<td></td>
</tr>
<tr>
<td>CaO-MgO</td>
<td>14.4</td>
<td>12:1</td>
<td>95.63</td>
<td>8.5</td>
<td>Cottonseed</td>
<td>97.62</td>
<td>/</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>SrO-ZnO</td>
<td>15</td>
<td>10:1</td>
<td>75</td>
<td>5</td>
<td>Corn</td>
<td>95.7</td>
<td>/</td>
<td>[52]</td>
<td></td>
</tr>
<tr>
<td>SrO-CaO</td>
<td>7.5</td>
<td>18:1</td>
<td>65</td>
<td>3</td>
<td>Palm</td>
<td>98.16</td>
<td>92.61</td>
<td>[53]</td>
<td></td>
</tr>
</tbody>
</table>

2.2.3. Enzyme Catalysis

Enzyme catalysis is known as having a high specificity, high efficiency, having mild reaction conditions and being able to easily purify by-products, which plays an indispensable role in the transesterification process. It was found that the addition of methanol could effectively maintain the activity of lipase [54]. The recombinant Rhizopus oryzae lipase was used in the transesterification of olive oil and palm oil and resulted in a product loss of less than 30% under six reuses. A similar enzyme catalysis method was reported by Yu et al. [55], Pseudomonas cepacia lipase was applied to the biodiesel, and the enzyme can be recycled and reused by a magnetic field, retaining 80% of the initial FAME conversion rate.

To summarize, the catalyst for the esterification process can be selected from inorganic salts, metal oxides, ion exchange resins, and lipase. Restaurant waste oil can be also used as the vegetable oil, and the esterification method has been widely used in the preparation of biodiesel. The elimination of glycerol groups in vegetable oil molecules can improve the oxidative stability of vegetable oil, but the double bonds still remain in the molecules, and therefore the activity of double bonds cannot be neglected.

2.3. Epoxidation

The carbon–carbon double bonds in vegetable oils can be reduced by epoxidation with peroxycarboxylic acid to generate epoxy vegetable oils, so as to improve the oxidation stability. The double bond in the molecule is vulnerable to attack from the epoxidation reagent to form epoxy groups [28]. The introduction of functional groups with lubricating or antioxidant properties to the vegetable oil through epoxidation and the ring-opening method is proved to be an effective method to prepare vegetable lubricant with excellent performance. The schematic diagram of the peroxidation and epoxidation reaction is shown in Figure 3.

The Prileshajev oxidation method is the most popular method for vegetable oil epoxidation [56]. Peroxycarboxylic acid formed in situ is considered to be superior because it is more environmentally friendly than the use of halogenated hydrocarbons, safer than oxygen molecules, and more effective than inorganic peroxides. The catalysts used in the epoxidation of vegetable oils is summarized in Table 3.
The epoxidation is of great significance in the treatment of waste oil to prepare environmentally friendly lubricants and biodiesel. Kurańska et al. [62] studied the in situ reaction of CH₃COOH, H₂SO₄, H₃PO₄, and H₂O₂ to generate peroxycetic acid in the epoxidation reaction. The conversion was found to be associated with the acid strength of the catalyst used. The H₂SO₄ catalysis achieved the highest reaction conversions (81%), while the highest selectivity was obtained by using H₃PO₄. Solving waste oil pollution by recycling and reusing UCO is an important method, which is in accordance with the development philosophy of the clean energy strategy.

The epoxidation modification of vegetable oil as a lubricating oil base oil is a practical modification method, but the epoxide group itself has a high activity, and therefore...
epoxidized vegetable oil is not the final product. Therefore, the ring can be further opened by nucleophiles that include alcohols, carboxylic acids, acid anhydrides, and amines, although numerous others can also lead to valuable functionalized fatty derivatives [63]. Biolubricants obtained from fatty acids of castor oil were synthesized by epoxidation and oxirane ring opening reactions using 2-ethylhexanol as nucleophilic agents, and it has a lower friction coefficient when compared to the commercial mineral oil [64]. The oleic acid was esterified with 1-octanol, followed by epoxidation. The oxirane ring opening reaction was performed using different alcohol structures (linear, branched, and cyclic), in order to evaluate their influence on the final physicochemical properties with the synthesized samples [65]. The chemical modification of pure rice bran oil via epoxidation and ring opening process can also be helpful for the improvement of lubricating properties [66]. Soybean and jojoba oil were chemically transformed by epoxidation followed by the transesterification, ring-opening and acetylation of the hydroxylated obtained products. The rheological and tribological characteristics of the compounds demonstrate the possibility of an environmentally sustainable method for producing bio-lubricants [67].

To summarize, epoxidation is commonly carried out using peracetic acid, peroxy-mosulfuric acid, hydrogen peroxide, etc. as oxidants, with the temperature at 60–80 °C. Inorganic acids, organic acids, heteropoly acids, ion exchange resins, alumina, phase transfer agents, and silica molecular sieves have been used as catalysts for the epoxidation. Modifying epoxidized plant oil through an epoxide-opening reaction is a more effective modification method.

2.4. Estolide Formation

The estolide formation method can be also used in the modification of vegetable oil. Chemical modification in the form of estolide synthesis from oleic acid can lead to increased oxidative and hydrolytic stability and better cold flow properties [68]. Estolides were synthesized and showed similar tribological performance to epoxidized Jatropha oil [69]. A comparative physicochemical property assessment of biolubricants produced using chemical modification was performed, and it was found that the oxidative stabilities of chemically modified biolubricants followed the order of epoxidation > triesterification > estolide probably due to the content of C=C bonds in the molecules [70].

3. Auxiliary Methods

3.1. Modeling

In recent years, modeling was regarded as a more effective method, and it can be used to compare with the experiments, to determine the data conditions consistent with the experimental data, and to verify the accuracy of the dynamic model through continuous optimization [71]. Jalil [72] analyzed the optimal conditions for the catalytic epoxidation reaction optimization of palmitic oleic acid and other oleic acids, formic acid and mixed acid with different proportions, and verified the accuracy of the model through modeling data simulation experiments.

3.2. Thermal Induction

On account of the high content of FFAs and other impurities, the use of acid-base transesterification to prepare biodiesel from BHO is technically and economically challenging in terms of yield and economics. Under high acidity conditions, the in situ transesterification of FFAs and glycerides can also be carried out in porous media without slowing down the reaction rate [73]. Jung et al. [74] reported the feasibility of thermally induced transesterification from BHO to biodiesel. When the molar ratio of methanol to BHO reached 200, the reaction optimally yielded 58 wt%. Without changing the components of C6-22, the yield was proportional to the reaction temperature, and this method provided a new direction for biomass recovery.
3.3. Microalgae

Photosynthesis can be used as a carbon storage product to achieve lipid accumulation. Triacylglycerol could be transformed into biodiesel via transesterification technology, where the utilization rate of light energy of microalgae was 18% higher than that of ordinary crops [75]. Qu et al. [76] discussed the distinction of the microwave-assisted in situ transesterification of various algae with ethanol. The catalytic performance evaluation results showed that the highest yield of biodiesel could reach 95.8% under the optimum reaction condition.

3.4. Ultrasonic

Ultrasound can be used in hydrogenation to improve the selectivity. Sancheti and Gogate [77] discussed the benefits of ultrasound assistance in the synthesis of hydrogenated soybean oil. In total, 5 wt% of Pd/C was applied to the soybean oil, and the hydrogenation reaction effect was the best under the condition of 22 kHz frequency and 100 W irradiation power. In comparison to the traditional hydrogenation reaction under high pressure and high temperature, the ultrasonic-assisted reaction obtained high selectivity, and the ultrasonic-assisted soybean oil CTH reaction generated less trans-isomers at normal temperature. Tan et al. [78] summarized the influencing factors of the ultrasonic-catalyzed transesterification reaction. Under the control of the alcohol–oil ratio, catalyst dosage, reaction time and reaction temperature under certain conditions, ultrasound as an auxiliary method could not only improve the conversion rate and yield of the reaction, but also strengthen the production process of biodiesel.

4. Applications

4.1. Surfactant

Surfactant, as an effective additive for IFT reduction, is able to significantly refine the reservoir rock wettability and emulsion formation. Contamination could be produced after using traditional sulfur- and phosphorus-containing surfactants [79]. Therefore, the preparation of eco-friendly surfactants from vegetable oils has attracted research attention. Surfactants are widely applied in chemical enhanced oil recovery as it reduces the IFT to an ultra-low value and also alters the wettability of oleophilic rocks. The effectiveness of surfactants could generally be assessed by calculating the IFT between the crude oil and the surfactant solution. Saxena et al. [80] investigated alpha-sulfonated ethyl ester surfactants via transesterification. The wettability of oil-wet carbonate and quartz surfaces were changed to water-wet by the surfactants with outstanding thermal stability.

4.2. Hydraulic Fluid

Hydraulic fluid transmits power and energy, and acts in the role of lubricating, cooling, and sealing parts. Due to the good lubricating property, extreme pressure abrasion-resistant properties, and an eco-friendly performance, vegetable oil-based hydraulic fluid is widely applied to the agriculture field. Fanigliulo et al. [81] prepared semi-refined crambe abyssinica oil as a bio-hydraulic fluid and applied it in agriculture so as to relieve food contamination. Nogales-Delgado, Encinar, and Cortés [82] proposed a hydraulic oil prepared from high oleic safflower oil, and the hydraulic oil showed higher oxidative stability than rapeseed or cardoon. By avoiding the use of antioxidant additions, it revealed a cleaner and more sustainable production. Olszak et al. [83] studied the working fluids which are generated from vegetable oils. Compared to raspberry seed oil, blackcurrant seed oil was considered as a better option for hydraulic couplings.

4.3. Cutting Fluid

Traditional cutting fluids are non-biodegradable mineral oil-based fluids, and they are detrimental to workers’ health and the natural environment. Compared to oil-based cutting fluids, Debnath, Reddy, and Yi [84] proposed the potential feasibility of plant-based cutting fluids in green machining. The bio-cutting fluids exhibited excellent biodegradability and
similar lubricating properties. The rice bran oil-based cutting fluid formulated by Edla et al. [85] exhibited lower cutting force, higher thermal stability, and similar lubricating properties in the tests, and was considered as an alternative solution for commercial mineral oil cutting fluids. The applicable scope of different types of vegetable oils is summarized in Table 4.

Table 4. Application scope of vegetable oils.

<table>
<thead>
<tr>
<th>Types of Vegetable Oils</th>
<th>Advantageous Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rapeseed oil</td>
<td>Recycling and Biodegradation</td>
</tr>
<tr>
<td>Almond oil</td>
<td>Natural corrosion inhibitors</td>
</tr>
<tr>
<td>Castor oil</td>
<td>Turning hardened stainless steels</td>
</tr>
<tr>
<td>Karanja oil</td>
<td>Extending the life of tools</td>
</tr>
<tr>
<td>Sunflower and palm oil</td>
<td>Assisting the machining operations</td>
</tr>
<tr>
<td>Soybean oil</td>
<td>Improving surface finish</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>Reducing the flank wear</td>
</tr>
</tbody>
</table>

4.4. Biodiesel

As a fuel for combustion engines, the consumption of diesel increases year by year because of its high operating power and economic efficiency [86]. For decades, researchers put emphasis on the production of biofuels through the addition, modification and doping of vegetable oils. Vegetable oils have been updated to the second generation (non-edible oil) as a feedstock in order to reduce dependence on food crops up to now [87]. The function of vegetable oils on engine performance and emissions was investigated compared to the results without vegetable oil [88]. It is shown that the blend oil with 10% wild mustard oil maintained similar engine performance while decreasing the CO, CO₂, O₂, and SO₂ emissions in a continuous 200 hours experiment.

Biofuels, prepared from chemically modified CPO blended with diesel, also demonstrated similar results to commercial diesel [89]. It was shown that biofuel blended with 30% CPO was the best to balance diesel performance and reduce emissions. HVO is a popular method to prepare ester-type biodiesel. The potential of HVO blends as promising biofuels on fuel consumption reduction in contemporary automotive diesel engines was evaluated and confirmed [90]. Dobrzyönska et al. [91] further analyzed the effect of HVO on commercial B7 fuel. It was reported that HVO can be a promising alternative to conventional diesel engine vehicles and it can meet the requirements of upcoming emission standards (EURO 7). Emissions reductions by fuel modifications were more practical and effective than abandoning higher-emitting engine vehicles.

4.5. Flame Retardant Plasticizer

The majority of the traditional flame retardants in the market are still based on halogen-containing compounds. Bio-based flame-retardant plasticizers have become more and more popular over the past years. A method for preparing flame retardant PVC material with a castor oil-based flame-retardant plasticizer was developed [92]. The as-prepared flame-retardant PVC materials possessed high thermal stability and flame-retardant performance. Epoxidation is one of the most proficient ways for synthesizing plasticizers from vegetable oils. Jia et al. [93] investigated the progress of epoxidized soybean oil on PVC plasticizers. It was shown that soybean oil-based polyol ester plasticizers were beneficial to strengthen the stability of PVC blends. Chang et al. [94] studied the performance of a sustainable flame-retardant plasticizer prepared via the epoxidation of corn oil. The blends maintained good plasticizing properties and effectively retarded flame propagation, which revealed that the sustainable bio-based flame-retardant plasticizers could be a desirable alternative to halogen-based flame-retardant plasticizers.
5. Conclusions and the Outlook

The research progress of the chemical modification methods and applications of vegetable oils in recent years are summarized in this review. Hydrogenation modification has been widely used and regarded as an effective method when efficient catalysts and green reaction systems are involved in the method. However, during the hydrogenation of vegetable oil molecules, the positional isomerization generated trans-fatty acids in the molecules, thereby reducing the biodegradability. Transesterification is used to eliminate glycerol groups in vegetable oil molecules, and low-chain alcohols are introduced to reduce viscosity and strengthen cold flow properties. However, the double bonds still remain in the molecules after transesterification, and therefore the activity of double bonds cannot be neglected. The number of double bonds is reduced by the epoxidation reagent attacking the double bonds to form epoxy groups, improving the oxidation stability of vegetable oil in the epoxidation process. However, the epoxide group itself has a high activity, and therefore epoxidized vegetable oil is not the final product. Modifying epoxidized plant oil through an epoxide-opening reaction is a more effective modification method. It is not difficult to see that reducing the content of carbon–carbon double bonds and increasing the degree of saturation are fundamental to improve the physicochemical properties of vegetable oil. The comparison of the modification methods is shown in Table 5.

Table 5. Comparison of the modification methods.

<table>
<thead>
<tr>
<th>Modification Methods</th>
<th>Low Temperature Performance</th>
<th>Oxidation Stability</th>
<th>Biodegradability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selective hydrogenation</td>
<td>Moderate</td>
<td>Good</td>
<td>Poor</td>
</tr>
<tr>
<td>Transesterification</td>
<td>Moderate</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Estolide formation</td>
<td>Moderate</td>
<td>Poor</td>
<td>Good</td>
</tr>
<tr>
<td>Epoxidation</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Good</td>
</tr>
<tr>
<td>Epoxidation + other methods</td>
<td>Good</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

The improvement of the oxidative stability and cold flow properties of vegetable oils by chemical modification is the main direction of future work. Looking back on the past few years, modification with a single method is not satisfactory; therefore, the combination of different methods can improve the performance of vegetable oil. Auxiliary methods combined with chemical modification are beneficial to obtain better performance from both experiments and simulations. This multidisciplinary approach may allow UCO to be used as a latent feedstock in various areas.

In terms of application, the use of modified vegetable oil can achieve stable production capacity, high economic efficiency, and environmental friendliness [95,96]. Biofuel and bio-lubricants can be the main applications for vegetable oil. Biofuel is used for combustion with high heat density but almost zero SO₂ and low CO₂ emission. Bio-lubricants can be directly used to reduce friction and wear, and then the energy loss and consumption can be reduced. Although waste oil is still generated after the use of bio-lubricants, it can be easily degraded in the environment. Therefore, biofuel and bio-lubricants still have a prospect in the future.

It is extremely urgent to speed up basic research on vegetable oils and cease the dependence on crude oil. Unfortunately, the price and regulations can be a challenge of the application of vegetable oil. Therefore, conducting research on the degradation mechanism of modified vegetable oil, establishing experimental methods for biodegradability testing, and formulating a set of evaluation standards for biodegradable lubricants are of a great practical significance, as they can promote the development of biodegradable lubricants and their application in equipment.
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List of Abbreviations

- UCO: Used Cooking Oil
- CTH: Catalytic Transfer Hydrogenation
- TOF: Turnover Frequency
- FAME: Fatty Acid Methyl Ester
- BHO: Bio-Heavy Oil
- IFT: Interfacial Tension
- CPO: Crude Palm Oil
- HVO: Hydrogenated Vegetable Oil
- PVC: Polyvinyl Chloride
- FFAs: Free Fatty Acids

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