Original Article

Effect of biodiesel ester structure optimization on low temperature performance and oxidation stability

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The main shortcomings of biodiesel are related to the low-temperature performance and oxidation stability. Hence, this study proposes to investigate the influence of the oleic acid-based esters with various linear and branched chain alcohols on these two properties of biodiesel. The economic impact of biodiesel with various compositions is also evaluated by means of a mathematical model. The results showed that the longer the carbon chain length of the alcohol component, the better the low-temperature performance of the biodiesel. Hence, the cold filter plugging point and solidifying point of methyl oleate were −19 and −24 ºC, respectively, whereas the cold filter plugging point and solidifying point of amyl oleate were −36 and −41 ºC, respectively. The more irregular the molecular structure, the better the low-temperature performance of oleic acid-based lipids. For instance, the condensed point and solidifying point of oleic acid-based esters with branched chain alcohols should be lower than oleic acid-based esters with linear chain alcohols. On the other hand, for the linear esters of oleic acid, the oxidation stability is better as the carbon chain is longer. For instance, the induction period of methyl oleate is 0.07 h while for amyl oleate, it is 0.36 h, which corresponds to an increase of about 5 times. For the branched esters, although they are sensitive to oxidation, the induction period is higher than that of methyl oleate. Finally, the DEA evaluation model was used to analyze the economic aspects of the resulted biodiesel. The results showed that the addition of ethyl oleate to biodiesel significantly improved the low-temperature performance and oxidation stability of biodiesel with good economic benefits.

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1. Introduction

According to BP World Energy Statistical Yearbook (2018 edition), the global energy demand increased by 2.2% in 2017, compared with the year-on-year growth of global energy
demand (1.2%) in 2016. The report of the UN Environment Conference 2017 pointed out that more than 80% of the cities do not meet the UN’s air quality standards. Moreover, it is stated that the global energy reserve and environmental pollution are well-known problems faced by the highly industrialized society [1,2]. Hence, there is an urgent need to develop renewable and clean energy sources. Biodiesel is a renewable energy source obtained by transesterification of animal and vegetable fats or food wastes with short-chain alcohols. It is considered as a good alternative to the traditional energy fuels because of its environmental protection and renewable advantages. Due to the high amount of unsaturated and saturated fatty acid methyl esters [3–5], however, biodiesel has a number of limitations that prevent its widespread use. These performance issues include poor oxidative stability, higher NOx exhaust emissions than petrodiesel, poor filterability and high feedstock cost.

The saturated fraction of biodiesel have a favorable effect on its stability, but they (particularly the long-chain saturates) can potentially compromise the low-temperature performance of the fuel. Long-chain saturated esters have a very high melting point, and they tend to crystallize under conditions of low temperature. Thus, biodiesel containing high levels of long-chain saturated components may not perform ideally under certain climatic conditions. To address the problem of poor low-temperature fluidity, many innovative methods, such as ozone oxidation, winterization, and addition of MgO nanoparticles, were proposed [6–8], blending of biodiesel with petroleum diesel and kerosene [9,10], transesterification with branched chain alcohol [11,12], modification of the fatty acid profile of biodiesel [13,14], which have significantly improved the low-temperature performance of biodiesel. The development of pour point depressants, such as terpolymers (e.g., AMS, polymethacrylate, polyacrylate) [15–22], but depending on the physical or chemical methods, other properties of biodiesel can be changed, which finally will change the quality of diesel fuel, while the time and economic cost of developing new pour point depressants is higher.

The fatty acid oxidation is a classic free radical chain reaction. The olefinic compounds are easily attacked by the initiators and especially in the bis-allylic carbons (present in linoleic and linolenic acids) which are less stable than allylic carbons. The points of unsaturation in biodiesel are readily attacked, leading to a chain of radical-mediated oxidative reactions in which the parent molecule is broken down to a range of small chain compounds. The condition is aggravated under certain conditions of storage, such as exposure to air, sunlight, moisture, metals, and other extraneous materials. To improve the oxidation stability of biodiesel, the most effective approach is to add antioxidants, while other strategies such as blending, hydrogenation, etc. were also applied [23–30]. Although the oxidation performance of biodiesel is improved, the use of such methods is still low due to the complicated and high processes involved in this transformation, as well as the high cost, increased toxicity, and so on.

This work is an attempt to address the identified problems associated with the currently prepared biodiesels. Hence, this paper is focused on the study of low-temperature and oxidation performances of biodiesel enriched with an unsaturated fatty acid methyl ester. The n-butylpyridine hydrogensulfate ionic liquid was used as a catalyst for the synthesis of olate esters [31–34]. To provide a cost-effective product, with high potential for real applications, several ester-based structures with various liners and branched chain alcohols were studied. This screening process allowed optimizing the low-temperature performance and oxidation stability of the biodiesel. Moreover, this study provides fundamental knowledge for a large-scale commercial development of biodiesel.

## 2. Experimental

### 2.1. Materials and instruments

The materials and reagents used in this work are n-butylpyridine hydrogen sulfate ion (homemade), ultrapure water (homemade), 1 mol/L phenolphthalein solution (homemade), KOH-ethanol solution (0.1 mol/L), oleic acid, methanol, ethanol, propanol, isopropanol, butan, isobutan, pentanol, isoamyl alcohol, petroleum ether, ethyl acetate, absolute ethanol, 95% ethanol, potassium hydroxide, concentrated sulfuric acid (97%), n-bromobutane, etc., purchased from Aladdin are all analytically pure. The main instruments used in this work are listed in Table 1.

### 2.2. Preparation of Jatropha biodiesel

The biodiesel was prepared through transesterification. 100 ml of Jatropha oil was mixed with 220 ml of methanol. There action temperature was controlled at 75 °C and 3 g of KOH was used as the catalyst. The reaction time was 2 h. The crude biodiesel oil is washed several times with distilled water, the glycerin and alkaline catalyst therein are washed away, and then dried and filtered to obtain refined biodiesel. The basic physicochemical parameters are presented in Table 2.

### 2.3. Preparation n-butylpyridine hydrogen sulfate ionic liquid

Pyridine and n-bromobutane (Molar mass ratio of 1:1.2) were added to a three-necked flask under nitrogen and magnetically stirred for 30 h to obtain a white precipitate as ionic liquid intermediate. The obtained solid was dissolved in anhydrous ethanol and reduced stress under at 95 °C. The mixture was washed three times with ethyl acetate and petroleum ether,
and then vacuum dried at 80 °C for 6 h to give a pale yellow viscous liquid. The yellowish viscous liquid was distributed into three flasks, and an appropriate amount of concentrated sulfuric acid was added. The liquid was magnetically stirred at room temperature and allowed to reacting with nitrogen for 6 h to generate viscous yellowish or red-brown liquid. Then, the liquid was washed three times with ethyl acetate and petroleum ether. After that, it was vacuum dried at 80 °C for 6 h, and finally cooled to obtain a pale yellow or orange yellow viscous liquid, denoted as n-butylypyridine hydrogensulfate ionic liquid. The main reactions involved in the synthesis of the catalyst are shown in Fig. 1.

### 2.4. Test method for catalyst cycle characteristics

Ionic liquid was recovered by extracting the reaction mixture with petroleum ether and washed several times with water. The aqueous solution was collected for recovering the branched alcohol starting material, and the water and alcohol were removed by concentrating the aqueous solution under reduced pressure using a rotary evaporator at 80 and 95 °C. Finally, the residue was dried at 80 °C for 5 h to recover the ionic liquid.

### 2.5. Synthesis of oleic acid esters

In a typical synthesis (Fig. 2), a mixture containing a suitable ratio between oleic acid, alcohol, and ionic liquid catalyst was placed in a three-neck flask equipped with a thermometer, a stirrer, and a reflux condenser. The flask was placed in a water bath heated. After the completion of the reaction, the product was washed several times with ultrapure water and then was placed in a rotary evaporator for distillation under reduced pressure to recover the unreacted alcohol. The reaction product was placed in a vacuum drying oven (the temperature maintained at 80 °C) for several hours.

However, the yield of each product is calculated based on the acid value before and after the reactants, so the yield of esterification reaction was calculated using Eq. (1):

$$\text{Esterification conversion} = \frac{AV_0 - AV}{AV_0} \times 100\%$$ (1)

where $AV_0$ and $AV$ are the acid values of the initial raw material and of the reaction product, respectively.

#### 2.6. Oxidation stability test and low-temperature fluidity test

The oxidative stability of biodiesel was determined by the Rancimat method using the European standard method EN 14112-2003 [35]. The cold filter plugging point method used herein refers to the national standard GB/T 510–2018 [36] for diesel fuel blending. The method used for measuring the solidifying point refers to the national standard SH/T 0248 [37] for diesel fuel blending.

#### 2.7. GC–MS detection of biodiesel components

Gas chromatography–mass spectrometer (GC–MS) manufactured by Finnigan, USA. GC–MS test sample parameters: DB-WAX column, injection volume 0.1 μL, the gas used is H2 carrier gas; when starting the temperature program, the initial temperature is 150 °C, keep 1 min and then heat up to 5 °C/min to at 210 °C, the temperature is raised to 240 °C at a rate of 3 °C/min for 10 min; the system will use the software to process the results, before using GC–MS samples, pre-treatment with n-hexane. After testing, the fatty acid concentration of Jatropha biodiesel are: Methyl palmitate (C16:0)–6.51%, Methyl stearate (C18:0)–3.68%, Methyl oleate (C18:1)–55.22%, Methyl linoleate (C18:2)–20.18%, Methyl linolenic acid (C18:3)–6.93%.

#### 2.8. Computational methods

The Bond Dissociation Energy (BDE) and bond length between oleic acid straight chain ester and oleic acid branched chain ester have been calculated using Gaussian 09 software [38]. Structural optimization has been done at Density Functional Theory (DFT) level with B3LYP functional and 6–31 G(d,p) basis set, and the BDE for the bond cleavage reaction $AB \rightarrow A + B$ is calculated by Eq. (2) [39]:

$$\Delta E_{\text{BDE}} = E_A + E_B - E_{AB}$$ (2)

where $\Delta E$ is Hartree–Fock (HF) energies and unit is KJ/mol.
Fig. 2 – Schematic representation of the experimental setup used for the synthesis of esters.

Fig. 3 – Effect of catalyst recycle times on esterification rate.

3. Results and discussion

3.1. Catalyst recycling characteristics

The more times the catalyst can be used, the lower its industrial cost; therefore, the recycling characteristics of the catalyst are one of the important indicators to measure the performance of the catalyst. The reaction time was 60 min using ionic liquid as the catalyst at 100 °C with 5:1 molar ratio of catalyst to alkyl. The catalyst was recycled for 6 times and reused, as shown in Fig. 3, indicating that with increasing number of cycles, the esterification rate decreased slightly, but still maintained high catalytic activity. The esterification rate was 90.1% after six cycles of use, showing good stability of the catalyst.

3.2. Preparation of oleate esters

To determine the optimum reaction conditions for the oleate esters synthesis, single factor experiments were carried out. In this regard, different reaction conditions (i.e., temperature, time, catalyst mass and alcohol to acid molar ratio) influencing the product yield were studied. The optimized conditions were as shown in Table 3.

As seen in Table 3, the optimal conditions are different for each ester. As the size of the alkyl group increases, the reaction temperature and reaction time seem to show an upward trend in order to achieve high conversion. However, under the optimal reaction conditions, the yield is above 97% for each of the prepared esters.

3.3. Analysis of low-temperature performance and oxidation stability

The low-temperature properties and oxidation stability of oleic acid esters with linear and branched chain alcohols were studied. The results are displayed in Fig. 4.

3.3.1. Analysis of low-temperature performance of oleic acid esters with linear chain alcohols

As the experimental results displayed in Fig. 4 show, as the length of the carbon chain increases (In the process of increasing the alkyl headgroup from one to five), cold filter plugging point and solidifying point decrease, and low-temperature performance are improved, the solidifying point and cold filter plugging of methyl oleate are −19 °C and −24 °C, while the solidifying point and cold filter plugging of amyl stearate are −36 °C and −41 °C, respectively. Performance has improved by 89.47% and 70.83%, which is a considerable improvement.

This phenomenon is explained by the interactions established between the esters in composition of biodiesel (Fig. 5 and Fig. 6 as examples for methyl oleate and ethyl oleate, respectively). Hence, it is obvious that the methyl and ethyl oleates have each of them an ester group containing a carbonyl oxygen and a methoxy or ethoxy group. According to the electronic effect theory [40,41], used to explain the intermolecular interactions and molecular packing model of these esters, the oxygen atom is a negatively charged atom and attracts a positively charged methyl/ethyl group leading to a crystalline solid. However, unlike the methyl ester of oleic acid, the ethyl oleate contains an additional CH₂ groups, which increase the hydrophobic interactions, the hydrogen atoms on −CH₂− will mutually repel each other. These attractive interactions will generate additional resistance, which is more difficult when the oleic acid methyl esters condense with each other, and as the carbon chain grows, the −CH₂− structure between the ester group and the methyl group will increase. The repulsive force will become greater, and the condensation more difficult. Therefore, the solidifying point and solidifying point gradually decrease as the length of the carbon chain increases (C₁₉−C₂₃), whereas the low-temperature performance improve.
3.3.2. **Analysis of low-temperature performance of oleic acid esters with branched carbon chains**

On the basis of the results displayed in Fig. 4, it can be stated that the low-temperature properties of the branched esters follow a similar tendency as for the linear esters. As the carbon chain grows, the cold filter plugging point and the solidifying point of the oleic acid esters with branched chains gradually decreases and the low-temperature fluidity increases. At the same carbon chain length, the branched ester has lower freezing and solidifying points than the corresponding linear ester while the low-temperature performance is superior. The low-temperature flow properties of isoamyl oleate are 17.14% and 15.38% higher than those of isopropyl oleate, respectively, and the low-temperature fluidity of branched oleate is generally better than that of linear oleate.

Taking propyl oleate and isopropyl oleate as examples, it can be seen from Fig. 7 and Fig. 8 that the isopropyl oleate terminal has two positively charged methyl groups, so it attracts negatively charged ester groups attract. At the time, there is a selectivity problem. Once the ester group is combined with the attraction of other ester groups, the combined ester group can form a greater ability to absorb heat. This is why the isopropyl oleate has a lower freezing point than the propyl oleate, which has one methyl group at the terminal. Fig. 5 gives the schematic representation of the intermolecular interaction between methyl oleate molecules.
with one of the methyl groups, the other free methyl group attracts the other free ester groups, causing them to pull each other. Secondly, according to the theory of intermolecular forces, the interaction between molecules is related to the spatial configuration of the molecule, and it has the characteristics of non-directionality and saturation. Compared with propyl oleate, Linear propyl oleate has a tighter, more compact molecular structure and is more likely to accumulate with each other, resulting in low temperature poor fluidity of linear esters.

3.3.3. Oxidation stability analysis
It can be clearly seen from Fig. 4 that both the linear oleic acid ester and the branched oleic acid ester significantly increase the induction period with the increase of the carbon chain length. The worst oxidative stability was methyl oleate with an induction period of only 0.07 h, and the best oxidative stability was with pentyl oleate with an induction period of 0.36 h, a difference of 4.14 times.

It is acknowledged that the oxidation of fats and oils follows a free radical mechanism, which involves three steps, i.e., induction, propagation, and termination. The period between the induction and oxidation stages is a measure of oil's resistance to auto-oxidation, known as oxidative stability. Oxidation chain reactions involving free radicals suggest that the oxidation of unsaturated fatty acid esters starts with a dehydrogenation reaction to produce a carbon based free radical, as shown in Fig. 9. The indicators usually used to evaluate how easy the dehydrogenation reaction occurs include C-H bond length (BDH), the bond orders, C-H bond dissociation energy (BDE). Among them, BDE is the most widely used evaluation index [42,43]. The lower the BDE value, the more stable the generated radicals are. Likewise, a weaker C-H bond is easier to oxidize.

Modern Density Functional Theory (DFT) is based on a remarkable result by Hohenberg and Kohn [44], in which without loss of rigor the ground state expectation values of all quantum mechanical observables are written as functional...
of the electronic ground-state density \( \rho(r) \) [45]. Through the application of the variational principle Hohenberg and Kohn proved that, up to a trivial constant, there exists one-to-one mapping between the external potential and the ground-state electron density. In order to present a summary of DFT, we suggest that the reader to follow the approach of Scuseria [46]. The DFT is well known for its accuracy and economy in regard to computational effort, all calculations were performed using Gaussian 09 software [45] for calculation, the DFT algorithm was applied to select the 6–31G (d, p) basis set for the optimization of the structure of parent and free radical molecules. First, BDE calculation was performed for each C-position of methyl oleate to determine the position at which the hydrogenation can occur. The results are shown in Fig. 10.

As can be seen in Fig. 10, the bond lengths and BDEs at different positions vary greatly, showing a wavy pattern. C8 and C11 are the points with the lowest bond energy, the bond energy of both is 368.6 kJ/mol, and the maximum of the BDEs of C9 and C10 is 471.8 kJ/mol, the BDEs of C8–C10 and C8–C11 allyl groups at the ortho position to the double bond is at least 47 kJ/mol less than the BDE at other positions.

This is due to the formation of free radicals after dehydrogenation of allyl C8 and C11 in the ortho position of the double bond, which is relatively stable due to the C9–C10–C11 and C8–C9–C10 resonance forms, as shown in Fig. 11. Therefore, the energy required for dehydrogenation is relatively low.

According to the literature reports, the BDEs of C4–C9 and C9–C11 allyl groups are almost identical. In the calculations of the bond dissociation energy of other acid oleic-based lipids, only the BDEs of C8 and C11 were calculated, and the results are shown in Table 4.

According to the data in Table 4, the BDE values of C8 and C11 of oleic acid-based esters with linear and branched chain alcohols gradually increase with the increase of carbon chain length, which is consistent with the trend of the induction period of the oleic acid oleic acid linear ester and the oleic acid branched chain ester in Fig. 3 and Fig. 4, it can be seen that the length of the carbon chain and the relative position of the double bond influence the induction period of both types of esters, i.e., linear and branched. The longer the carbon chain length, the larger the molecular mass, and the greater the energy of the BDE of C8–C10 and C9–C11 allyl groups, the more unstable the radical is, the stronger the C–H bond is, and the less likely it is to be oxidized. At the same time, for the branched oleic acid-based esters, the structural irregularity leads to the more unstable the intermolecular force. The BDE value of C8–C10 and C9–C11 allyl groups are smaller than that of the branched ester, and the CH bond is weaker. It is relatively easy to be oxidized, and its induction period is smaller.

3.3.4. Comprehensive economic analysis

Data Envelopment Analysis (DEA) is a nonparametric method used to evaluate the economic systems [47]. By studying the effectiveness of production frontiers, the results of the analysis are verified, and more outputs are obtained with relatively less input. In this method, multiple inputs and outputs are considered and not just one input and one output. A DEA value of 1 is considered relatively valid while a DEA value less than 1 is relatively ineffective. The smaller the DEA value, the lower the efficiency.

In this study, the cold filter plugging point, solidifying point, and the induction period were selected as output indicators to investigate the combined effects of oleic acid-based esters on the low temperature performance and oxidation stability of biodiesel. From an economical perspective, the analysis of oleic acid-based esters used to improve the low-temperature performance and oxidation stability of biodiesel, the cost of the reagent is treated as an input indicator. Biodiesel is selected from rapeseed oil biodiesel. This biodiesel is characterized by a cold filter plugging point of –11.5 °C, a solidifying point of –4 °C, an oxidation induction period of 5.28 h. For the DEA calculations, 10% oleate was added. The results are shown in Table 5.

As can be seen in Table 5, the nature of oleate ester impacts the economical parameters. Hence, the use of propyl oleate has the worst effect, with a DEA value of 0.7590 while the enrichment of biodiesel with the ethyl ester leads the maximum DEA value of 1. Therefore, the use of ethyl oleate as an additive for biodiesel does not only improve the low-temperature performance of biodiesel, but also a positive impact on the oxidation stability of biodiesel, preparation cost, which promote the industrial production of such a biodiesel.
Table 4 – BDE and BDH of oleic acid-based lipids.

<table>
<thead>
<tr>
<th>Methyl oleate</th>
<th>Ethyl oleate</th>
<th>Propyl oleate</th>
<th>Butyl oleate</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDE</td>
<td>BDH</td>
<td>BDE</td>
<td>BDH</td>
</tr>
<tr>
<td>C₆</td>
<td>368.6224</td>
<td>1.088</td>
<td>368.7339</td>
</tr>
<tr>
<td>C₁₁</td>
<td>368.4097</td>
<td>1.087</td>
<td>368.7050</td>
</tr>
<tr>
<td>Amyl oleate</td>
<td>Isopropyl oleate</td>
<td>Isobutyl oleate</td>
<td>Isoamyl oleate</td>
</tr>
<tr>
<td>BDE</td>
<td>BDH</td>
<td>BDE</td>
<td>BDH</td>
</tr>
<tr>
<td>C₁₁</td>
<td>370.1828</td>
<td>1.087</td>
<td>369.3334</td>
</tr>
</tbody>
</table>

Note: The unit of BDE is “kJ/mol” and the unit of BDH is “nm”.

Table 5 – DEA operation results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cost/¥</th>
<th>SP/°</th>
<th>CFPP/°</th>
<th>IP/h</th>
<th>DEA value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl oleate</td>
<td>56.5</td>
<td>−7.5</td>
<td>−14</td>
<td>4.24</td>
<td>0.9833</td>
</tr>
<tr>
<td>Ethyl oleate</td>
<td>57</td>
<td>−8.5</td>
<td>−15</td>
<td>4.35</td>
<td>1.0000</td>
</tr>
<tr>
<td>Propyl oleate</td>
<td>77</td>
<td>−10</td>
<td>−17</td>
<td>4.46</td>
<td>0.7590</td>
</tr>
<tr>
<td>Butyl oleate</td>
<td>64</td>
<td>−11</td>
<td>−18</td>
<td>4.78</td>
<td>0.5787</td>
</tr>
<tr>
<td>Amyl oleate</td>
<td>77</td>
<td>−12</td>
<td>−18.5</td>
<td>4.96</td>
<td>0.8440</td>
</tr>
<tr>
<td>Isopropyl oleate</td>
<td>63</td>
<td>−13.5</td>
<td>−19.5</td>
<td>4.54</td>
<td>0.9442</td>
</tr>
<tr>
<td>Iso-butyl oleate</td>
<td>65.3</td>
<td>−15</td>
<td>−21</td>
<td>4.81</td>
<td>0.9652</td>
</tr>
<tr>
<td>Iso-amyl oleate</td>
<td>77</td>
<td>−16</td>
<td>−23</td>
<td>5.02</td>
<td>0.8542</td>
</tr>
</tbody>
</table>

Note: SP, CEEP and IP represent freezing point, cold filtration point and induction period respectively.

4. Conclusions

1. Using the self-made ionic liquid with good cycle characteristics as a catalyst, the best reaction conditions for each oleic acid ester were obtained through single factor experiments. Under the optimal reaction conditions, the yields above 97% were obtained for the studied esters.

2. The low-temperature flow properties and oxidation stability properties of branched and linear esters are optimized with increasing carbon chain length. The reasons for the optimization of performance are the mutual attraction of free radical electrons and the relationship between the molecules and the carbon chain length and the relative position of the double bond are changed, and the irregularity of the molecular structure leads to the instability of the force between the molecules.

3. The results of the DEA model algorithm revealed that only the ethyl oleate is an appropriate additive for biodiesel with the best economic benefit (DEA value is 1).

Conflicts of interest

The authors declare no conflicts of interest.

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