Biodiesel synthesis by transesterification using coal-based solid acid catalyst

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Abstract. The medium metamorphic degree of bituminous coal with high oxygen content and low ash content is selected as the carbon carrier to prepare an efficient carbon-based solid acid catalyst through partial carbonization and sulfonation approach, and then is employed to catalyze transesterification of palm oil with methanol for biodiesel production. The strength of catalyst is characterized by Hammett inductor method. The reaction parameters are optimized by single factor method. Results demonstrate that the prepared catalyst possesses the Hammett acid strength range of 0.8<\textit{H}<3.3. The maximum biodiesel yield of 97.8% is obtained at catalyst dosage of 6 wt.%, transesterification temperature of 160 °C, molar ratio of methanol to palm oil of 18 and stirring rate of 1000 rpm for 8 h. Moreover, the catalyst exhibits satisfactory activity in catalyzing simultaneous esterification and transesterification when 20 wt.% oleic acid is added to palm oil.

1. Introduction

Due to the depletion of traditional fossil energy and aggravation of environmental pollution, renewable alternative fuels have attracted considerable attentions in recent years. Biodiesel is renewable, biodegradable and environmental benign. It possesses similar physicochemical properties with fossil diesel, such as cetane number, lubricity, viscosity, flash point, and can be directly applied to the engine without mechanical reformation. Biodiesel is composed of alkyl esters of long-chain fatty acids and commonly produced from transesterification technology. As displayed in equation (1), the reaction between triglycerides (TGs, the main components of vegetable oils and animal fats) and short chain alcohols in the presence of catalytic effect to produce biodiesel and by-product glycerol, is referred to as transesterification [1]. Generally, the pricing problem and crucial sustainability issues have become the major hurdle for industrial production of biodiesel when employing alkali-catalyzed (NaOH, KOH or NaOCH3, etc) transesterification using refined feedstock oil. To reduce the production cost, low-quality feedstocks, including waste cooking oils (WCOs) and animal fats also can be used. Nevertheless, a high percentage of free fatty acids (FFAs) presented in these feedstocks would react with the alkali catalyst to form soaps. It not only consumes the alkali catalyst, but also decreases the transesterification efficiency.

A feasible way to solve the FFAs problem is using an acid catalyst. Compared with alkali catalysts, acid catalysts can catalyze FFAs esterification (shown in equation (2)) and not be affected by acidification degree of feedstock oil. Moreover, acid catalysts have been reported to perform well in
catalyzing esterification and transesterification simultaneously when using low-quality feedstocks [2,3]. Conventional mineral acids (e.g. H₂SO₄ or HCl) exhibit strong catalytic activity, but they are subjected to the drawbacks of equipment corrosion, discharge of waste water and non-recyclability. Thus, solid acid catalysts can be adopted to solve the above-mentioned issues.

\[
\begin{align*}
\text{R} & + \text{R'} \rightarrow \text{R}^+ \text{R}^{-} \\
\text{OH} & + \text{OH} \rightarrow \text{HO}-\text{OH}
\end{align*}
\]

To date, numerous researchers have investigated solid acid catalysts [4-7], such as heteropoly acid, cation exchange resin, metal oxides, zeolites as well as sulfonated carbon-based solid acid. Although the operating temperature, pressure range and raw material composition are greatly various, most solid acids exhibit good catalytic activity. Among these catalysts, sulfonated carbon-based solid acid gains increasing attention for advantages of the high catalytic activity, thermal stability and low preparation cost. This kind of solid acid was first introduced by Toda et al. [8] and usually prepared by partial carbonization of carbonaceous material to form polycyclic aromatic carbon sheets and subsequent functionalized with some specific functional groups through sulfonation. Dawodu et al. [9] obtained an efficient carbon-based solid acid catalyst derived from glucose or C. inophyllum seed cake and successfully catalyzed C. inophyllum oil with 15% FFA into biodiesel. Other carbonaceous materials such as bamboo [10] and seed pod [11] have also been studied.

Coal is a polycyclic aromatic hydrocarbon polymer composed of carbon-based organic compounds. It also has fatty side chains, oxygen-containing functional groups such as -OH and -COOH, and bridge bonds such as -O- and -CH₂- in the coal structure. As reported by Shen et al. [12], bridge bonds could increase the flexibility of the carbon skeleton and reduce the steric resistance. So, coal is an ideal carrier for the preparation of carbon-based solid acid except for combustion, gasification and liquefaction, etc. However, studies on the preparation of carbon-based solid acid derived from coal and further application in catalyzing transesterification for biodiesel production are still very limited.

Yulin coal in Shaanxi province, China, is characterized by extremely low contents of ash, phosphorus, sulfur and medium to high calorific value. It is a kind of relatively clean and high-quality coal with abundant reserves. Palm oil, a tropical woody vegetable oil, is the largest vegetable oil variety in the world in terms of production, consumption and international trade. In this study, a carbon-based solid acid is prepared from bituminous coal and used in catalyzing transesterification of palm oil with methanol for biodiesel production. And the reaction parameters of catalyst dosage, molar ratio of methanol to palm oil, transesterification temperature and transesterification duration are concerned. Moreover, the ability of prepared solid acid in catalyzing simultaneous esterification and transesterification is also explored. The overall objective of this study is to provide some theoretical basis and experimental data for the development and application of coal in biodiesel industry.

2. Experimental

2.1 Materials
The original coal with volatile of 32.56% (air dried basis) is obtained from an electric power plant. Analytical grade chemical reagents of methanol, ethanol, potassium hydroxide and sodium hydroxide are purchased from Kermel Chemical Co. Ltd, Tianjin, China. Concentrated sulfuric acid is purchased from Laiyang Fine Chemical Plant, Shandong, China. Commercial palm oil is purchased from local...
market and the composition is quantitatively analyzed by 7890A-GC coupled with 5975C-MS, Agilent Technologies Co., Ltd, USA. The main components are myristic acid (C14:0, 1.26%), palmitic acid (C16:0, 39.51%), lauric acid (C17:0, 0.27%), stearic acid (C18:0, 7.79%), oleic acid (C18:1, 39.71%), linoleic acid (C18:2, 11.13%) and arachidic acid (C20:0, 0.33%). Also, the main physicochemical indices of palm oil are determined, which are the acid value \((AV=0.42 \text{ mgKOH/g})\) and the saponification value \((SV=182.60 \text{ mgKOH/g})\). Accordingly, the mean molecular weight is calculated to be 923.98 g/mol using equation (3) as follows.

\[
M_{\text{palm oil}} = \frac{M_{\text{KOH}} \times 3 \times 1000}{SV - AV}
\]

Where, \(M_{\text{KOH}}\) is the mean molecular weight of KOH, 56.1 g/mol.

2.2 Catalyst preparation and characterization
Coal-based solid acid is prepared according to the procedure reported previously by our group in the literature [13]. Firstly, the coal is crushed and screened through a 0.125 mm sieve. Then, the coal powder is carbonized at 400 °C under nitrogen flow for 60 min. In the sulfonation process, five grams of carbonized product are digested by 75 ml of concentrated sulfuric acid in an oil bath, stirred under the conditions of 105 °C for 120 min. After cooling to the room temperature naturally, the mixture is washed repeatedly with warm distilled water until to be neutral. Subsequently, the sample is kept overnight in an oven at 105 °C for drying and labelled as \(\text{SO}_3\text{H-Coal}\). And the acid strength of \(\text{SO}_3\text{H-Coal}\) is calibrated by Hammett indicator method as reported literature [14].

2.3 Transesterification reaction and product determination
The mixtures of palm oil, \(\text{SO}_3\text{H-Coal}\) and methanol are accurately weighed and successively added into the 100 mL autoclave. After sealing, the magnetic stirring is started and the rotating speed is set at 1000 rpm. As a transesterification terminates, the autoclave is allowed to cool to the room temperature. Then, \(\text{SO}_3\text{H-Coal}\) is separated from the liquid products through centrifugation and the filtrate is kept in the funnel separator for overnight.

The content of fatty acid methyl ester (FAME) in the oil phase is analyzed by a GC9790 gas chromatography, fitted with a flame ionization detector (FID) and a polar HP-INNOWAX chromatographic column (30 m×0.25 mm×0.25 μm). The initial oven temperature is 140 °C (held for 4 min), and then increased to 240 °C (held for 8 min) with a heating rate of 10 °C/min. Meanwhile, the feasible injector and the FID detector temperature are found to be 250 and 260 °C, respectively. The carrier gas is \(\text{N}_2\) and the split ratio is 26:1. FAME content of the samples is determined according to the internal reference method with methyl salicylate as internal standard.

The formula for calculating the biodiesel yield is shown in equation (4) [15].

\[
yield = \frac{\text{weight of biodiesel} \times \%\text{FAME}}{\text{weight of oil}} \times 100% \tag{4}
\]

Where, \(\%\text{FAME}\) is the FAME concentration analyzed by GC.

3. Results and Discussion

3.1 Characterization of \(\text{SO}_3\text{H-Coal}\)

| Indicator       | Acidic form | Basic form | Observed color |
|-----------------|-------------|------------|----------------|
| Neutral red     | Red         | Yellow     | Red            |
| Methyl red      | Red         | Yellow     | Red            |
| Dimethyl yellow | Red         | Yellow     | Red            |
| Methyl violet   | Yellow      | Blue       | Blue           |
The acid strength of SO$_3$H-Coal is examined using Hammett indicators, neutral red ($H_0 \leq +7.2$), methyl red ($H_0 \leq +4.8$), dimethyl yellow ($H_0 \leq +3.3$) and methyl violet ($H_0 \leq +0.8$). As shown in Table 1, SO$_3$H-Coal changes the color of dimethyl yellow from yellow to red while cannot change the color of methyl violet. Namely, Hammett acid strength is $0.8 < H_0 < 3.3$ for SO$_3$H-Coal, which demonstrates that the catalyst possesses acidic peculiarity and is expressly suitable for transesterification [16].

### 3.2 Catalytic activity for transesterification

In order to comprehensively investigate the catalytic performance of SO$_3$H-Coal, the reaction parameters including transesterification temperature (from 80 to 180 °C), molar ratio of methanol to palm oil (from 6 to 21), catalyst dosage (from 0 to 8 wt.%) and transesterification duration (from 2 to 10 h) are evaluated.

![Figure 1](image1.png)

Figure 1. Effect of transesterification temperature on biodiesel yield (molar ratio of methanol to oil 15, catalyst dosage 6 wt.%, transesterification duration 6 h)

The effect of different transesterification temperatures on biodiesel yield is shown in figure 1. Acid-catalyzed transesterification requires activation of the carbonyl groups by proton to start the reaction. However, macromolecular structure of triglycerides is unfavorable for activation effect. Therefore, the acid-catalyzed transesterification usually needs a higher reaction temperature. Increasing the temperature not only reduces the mass transfer limitations between the reactants and solid acid, but also promotes the transesterification positive movement due to its reversible and endothermic properties. As can be seen from figure 1, when the temperature is set as 80 or 120 °C, the biodiesel yield is just 2.8% or 15.1%. And then, the biodiesel yield significantly increases to 87.6% as transesterification temperature rises to 160 °C. Further increasing the temperature makes no sense because of the equilibrium.

![Figure 2](image2.png)

Figure 2. Effect of molar ratio of methanol to oil on biodiesel yield (transesterification temperature 160 °C, catalyst dosage 6 wt.% , transesterification duration 6 h)
The influence regularity of methanol to palm oil molar ratio on the biodiesel yield is exhibited in figure 2. For an exhaustive transesterification, the excess methanol is obligatory to drive the reaction towards to the formation of biodiesel, although the stoichiometric molar ratio value of methanol to oil is 3. From figure 2, only 46.9% of yield is achieved when the molar ratio is set as 6. As the molar ratio gradually raises from 9 to 18, the biodiesel yield is correspondingly increased from 60.5% to 92.4%. Nevertheless, the yield slightly decreases with a further increment of molar ratio over 18, because the superfluous methanol may cause the dilution of transesterification system or even shield the triglyceride molecules from the catalyst active sites [17]. Therefore, the optimal molar ratio of methanol to palm oil is 18.

![Figure 3. Effect of catalyst dosage on biodiesel yield (transesterification temperature 160 °C, molar ratio of methanol to oil 18, transesterification duration 6 h)](image)

The amount of catalyst exhibits great influence on biodiesel yield. In general, the catalyst can lower the activation energy needed for any reaction to take place [9]. More active sites are available with increasing of the catalyst dosage then a higher biodiesel yield could be achieved. As illustrated in figure 3, the non-catalyzed transesterification is pretty slow, where only 8.1% of biodiesel yield is obtained. As the catalyst dosage raises from 0 to 2 wt.%, the biodiesel yield is found to be increased drastically and produces a value of 71.7%. Then, it is gradually increased while enhancing the catalyst dosage and the maximum biodiesel yield of 92.4% is attained at 6 wt.%. When the catalyst dosage keeps on increasing to 8 wt.%, the yield is slightly heightened from 92.4% to 92.7% due to the equilibrium limit. Hence, 6 wt.% could be regarded as a proper catalyst dosage.

![Figure 4. Effect of transesterification duration on biodiesel yield (transesterification temperature 160 °C, catalyst dosage 6 wt.%, molar ratio of methanol to oil 18)](image)

In consideration of the mass transfer limitation caused by three immiscible phases of palm oil, methanol and SO₃H-Coal, sufficient reaction duration is normally requisite to ensure the completion of
transesterification. Figure 4 depicts the influence of transesterification duration on biodiesel yield. In the primary stage, the reaction rate is fast because the large concentration of reactants is favorable for the process of positive direction transesterification. So, after 2 h of transesterification, the biodiesel yield could be rapidly climbed to 68.2%. With the prolongation of duration, transesterification is carried on continuously and the yield is increased gradually. For the duration of 8 h, the biodiesel yield of 97.8% is obtained and then basically remained almost unchanged even further prolonging duration to 10 h. Based on the above results, the selected transesterification duration is 8 h.

Table 2. The ability of different solid acids to catalyze transesterification

| Catalyst | Feedstock oil | Reaction conditions | yield/% | Ref |
|----------|---------------|---------------------|---------|-----|
| TiO$_2$- SO$_4^{2-}$ | Cottonseed oil | $\zeta=2$ wt.%、 $\gamma=12$ | 90% | [18] |
| SiO$_2$- SO$_4^{2-}$ | Waste cooking oil | $\zeta=5$ wt.%、 $\gamma=20$ | 87.57% | [19] |
| Sulfonated pyrolyzed rice husk | Soybean oil | $\zeta=3$ wt.%、 $\gamma=30$ | 90% | [20] |
| Sulfonated pyrolyzed glucose | Cinnamomum camphora | $\zeta=0.2$ wt.%、 $\gamma=18.2$ | 89.93% | [21] |
| Sulfonated vegetable oil asphalt | Tripalmitin | $\zeta=30$ wt.%、 $\gamma=120$ | 78% | [22] |
| Nb$_2$O$_5$/SO$_4$ | Macaw palm oil with FFAs | $\zeta=30$ wt.%、 $\gamma=120$ | 98.65% | [23] |

Note: $\zeta$ is catalyst dosage, $\gamma$ is molar ratio of methanol to oil, $T$ and $\tau$ are reaction temperature and duration, respectively.

Table 2 lists a comparative analysis of reaction conditions and biodiesel yield catalyzed by recently developed solid acid catalysts from the reported literatures [18-23]. Generally, the high temperature, alcohol/oil molar ratio and longer reaction duration are required to obtain excellent productivity for the solid acid-catalyzed transesterification. In this study, the optimal reaction parameters of palm oil with methanol catalyzed by SO$_3$H-Coal are determined as transesterification temperature of 160°C, methanol to palm oil molar ratio of 18, catalyst dosage of 6 wt.% and transesterification duration of 8 h, where 97.8% of biodiesel yield could be achieved. The relatively mild reaction conditions and satisfactory catalytic activity make the SO$_3$H-Coal comparable with other reported solid acid catalysts. In addition, the physicochemical properties of palm oil biodiesel produced under optimal conditions are determined to assess its quality. As shown in Table 3, the density, viscosity, acid value, water content, carbon residue and ash content indexes of refined biodiesel satisfy the requirement of ASTM D6751.

Table 3. Physical and chemical indexes of refined palm oil biodiesel

| Biodiesel property | ASTM D6751 | Purified biodiesel |
|--------------------|------------|--------------------|
| Density (15 °C, g/cm$^3$) | 0.86-0.90 | 0.87 |
| Kinetic viscosity (40 °C, mm$^2$/s) | 1.9-6.0 | 4.20 |
| Acid value (mgKOH/g) | 0.50 Max | 0.21 |
| Carbon residue (wt.%) | 0.05 Max | 0.04 |
| Ash content (wt.%) | 0.02 Max | 0.01 |
| Water content (wt.%) | 0.05 Max | 0.02 |
3.3 Activity in catalyzing simultaneous esterification and transesterification

Considering that the oleic acid is an important FFA component in saponin acidified oil, model mixtures of TGs and FFA (20 wt.% oleic acid added to palm oil) are employed to simulate the low-quality grade greases. The simultaneous esterification of FFA (i.e., oleic acid) and transesterification of TGs (i.e., palm oil) catalyzed by SO$_3$H-Coal are conducted under conditions of catalyst dosage of 6 wt.%, temperature of 160 °C, methanol to acidified oil molar ratio of 18 and stirring rate of 1000 rpm for 6 h. The FFA conversion is labelled by the rate of acid value reduction before and after the esterification [24], and the total biodiesel yield is determined by GC. At this condition, the FFA conversion and the total biodiesel yield are observed to reach 91.7% and 94.8%, respectively. A sulfonated vegetable oil asphalt catalyst was prepared by Shu et al. [25] and employed to simultaneously catalyze esterification and transesterification when the acidified oil (cotton seed oil mixed with 50 wt.% oleic acid) was used as feedstock. 94.8% of FFA conversion and 80.5% of TGs conversion were obtained respectively after 4.5 h at 220 °C, with 16.8 molar ratio of methanol to oil and 0.2 wt.% of catalyst dosage. The solid acid-catalyzed simultaneous esterification and transesterification has been confirmed to be the highly economic value and development potential technology for biodiesel production when using low-quality grade greases as feedstocks. The coal-based solid acid prepared in this study also has good catalytic performance in catalyzing the simultaneous esterification and transesterification of acidified oil, so it can be considered as a kind of solid acid catalyst with high research value and development potential.

4. Conclusions

SO$_3$H-Coal prepared by partial carbonization and sulfonation shows strong catalytic activity in catalyzing transesterification of palm oil with methanol. The optimal conditions for the reaction are transesterification temperature of 160 °C, molar ratio of methanol to oil of 18, catalyst dosage of 6 wt.% and transesterification duration of 8 h, where the biodiesel yield could reach up to 97.8%. Moreover, SO$_3$H-Coal could be employed as a promising solid acid catalyst for simultaneous esterification and transesterification. FFA conversion and total biodiesel yield are observed to reach 91.7% and 94.8%, respectively, when the palm oil containing 20 wt.% oleic acid is used as feedstock. Above research achievements can expand resources for the development and utilization of carbon-based solid acids, and realize the high value-added utilization of coal in the biodiesel industry.

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