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Esterification of high FFA tung oil with solid acid catalyst in fixed bed reactor

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ABSTRACT

The effect of molar ratio of methanol to oil, temperature and space velocity (SV) on pre-esterification of Tung oil was carried out in pilot-scale fixed bed reactor, with solid acid catalysts. The molar ratio results showed the maximum acid value reduction efficiency (90.21%) was obtained at the molar ratio of 8:1, the acid value decreased sharply to 0.70 g kg^{-1} of KOH. And esterification reaction attained balance when space velocity was enough, so 0.029 h^{-1} was optimal space velocity. Furthermore, activity of reactant and rate of reaction increase with temperature increased, and the maximum conversion was achieved at 65 °C, the acid value of Tung oil could be reduced to 1.4 g kg^{-1} of KOH.

1. Introduction

Biodiesel produced from vegetable oil and animal fat, can be blended at any level with petroleum diesel and used in compression-ignition engines with no modification. With a higher cetane number, no aromatics, and 10–11% oxygen content, biodiesel is regarded as a good alternative of fossil-diesel [1].

The feedstock is a bottleneck for biodiesel industry development in China [2]. One way to reduce the cost of biodiesel is to use less expensive feedstock. Residual oils [3], non-domesticated plant oil [4] are promising raw materials for biodiesel production. The problem of processing these oils is that it cannot be converted to biodiesel using an alkaline catalyst because of the high content of free fatty acids. These FFA of oil forms soap with the, and this will inhibit the separation of the ester, glycerin and washing water [5]. An alternative way is to use an acidic catalyst, but acid-catalyzed reaction is much slower and needs higher temperature and pressure than alkali-catalyzed one. Optimum method includes two steps, i.e. the acid pretreatment was followed by the base-catalyzed methanolysis. In the recent years, systematic efforts have been made by several researchers to use homogeneous phase (i.e. liquid) catalysts (H_2SO_4), with some disadvantages such as high reaction temperature, instrument corrosion, and environment contamination. Therefore, for the development of an environmental friendly process and the reduction of the production cost, a new procedure using heterogeneous catalyst should be studied [6].

Tung trees are planted widely in China, especially in the southern mountain areas. The production of Tung oil varies from 300 to 450 kg ha^{-1} [7]. There have been studies of the transesterification of tung oil using immobilized lipase [8], a two step alkali process [9] and an evaluation of the production process with relevance to the degree of unsaturation (84.6% in tung biodiesel) of Tung oil [10]. Tung oil often has

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Table 1 – Physical properties of tested ion-exchange resins.

Functional group	Ionic	Particle size range ≥ 95%, nm	Pore volume, dm kg^{-1}	Specific surface area, m^2 kg^{-1}	Average particle size, A	Maximum operating temperature, °C	Water content, %
SO^{3-}	H^+	400–1250	0.3–0.36	35–40 000	200–500	120	Drier 3–5

high FFA values and this work examines the feasibility of using solid catalysts in the fixed bed conversion of the FFA.

2. Materials and methods

2.1. Material and reagent

KOH and anhydrous methanol were purchased from the chemical companies in China, which can be used without further purification.

Tung oil was supplied from Guangzhou Eastern Time Development Trading Co., Ltd. The free fatty acid content of unrefined Tung oil was about 3.5%, i.e. acid value of 7 g kg^{-1} of KOH. The density, water content of the samples was 0.94 g cm^{-3} and 0.1048%, respectively. Solid strong acid which purchased from the Zhejiang company was selected as catalyst which was firstly dried for 2 h in 105 °C before used. Physical properties of tested ion-exchange resins are listed in Table 1.

2.2. Esterification procedure

The esterification reaction was conducted using a fixed bed reactor packed with the solid acid catalyst which had been tested in the batch experiments. Fig. 1 shows a schematic diagram of the esterification system. A water-jacketed column with inner diameter of 10 cm and length of 80 cm was vertically placed. The feed solution was supplied to the bottom of the column at a constant flow rate using a metering pump. Different temperature (40 °C, 50 °C, 60 °C and 65 °C), methanol to oil ratios (4:1, 6:1, 8:1 and 10:1) and space velocity (0.029 h^{-1}, 0.25 h^{-1} and 0.37 h^{-1}) were used to investigate their influence on the acid value of Tung oil.

2.3. Analytical methods

The acid values (AV) of Tung oil were measured following standards of PRC: GB/T14489.3—93, calculated by the following equation (AV):

$$\mathrm{AV}\ (\mathrm{mg\ KOH\ g^{-1}}) = \frac{V_{\mathrm{KOH}} \times C_{\mathrm{KOH}} \times 56.1}{m_{\mathrm{oil}}} \quad (1)$$

where V_{KOH} is the volume of KOH standard solution (mL), C_{KOH} is KOH standard solution concentration (mol L^{-1}).

The lower remaining free fatty acid content after esterification indicated that esterification reaction is complete. AV refers to the number of milligrams of KOH needed for the neutralization of 1 g free fatty acids in fat. Therefore, the lower the acid value, the higher the AV reduction efficiency. The AV reduction efficiency (α) was calculated by the following equation:

$$\alpha = \frac{\mathrm{AV_r} - \mathrm{AV_E}}{\mathrm{AV_r}} \times 100\% \quad (2)$$

where AV_r is the acid values in raw material (mg KOH g^{-1}), AV_E is the acid values after esterification (mg KOH g^{-1}).

The water content was measured by Karl Fisher Titrator (787 KF Titrino, Metrohm). The density was determined following standards of GBT 1884-2000.

3. Results and discussion

3.1. Effect of methanol to oil molar ratio

The molar ratio of methanol to oil is one of the important variables that affect the esterification efficiency. The influence of methanol to oil ratio on acid value and AV reduction

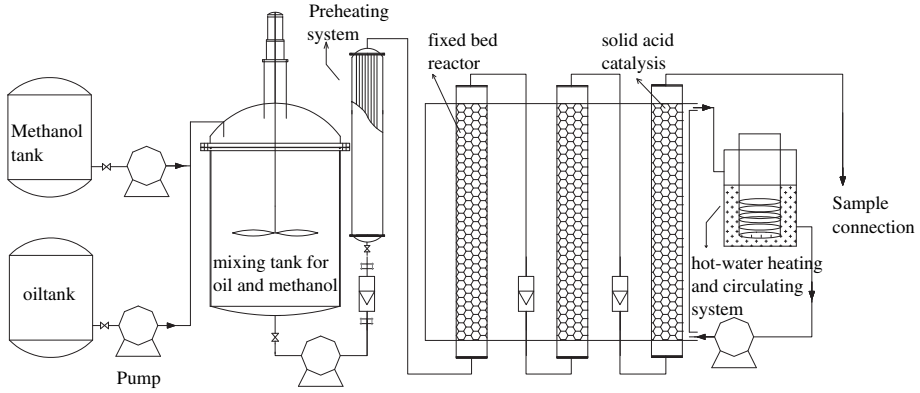

Fig. 1 – Schematic diagram of continuous experiment system using fixed bed reactor.

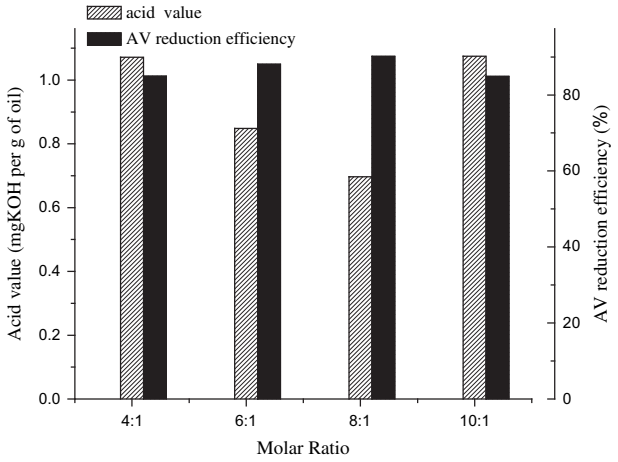

Fig. 2 – Effect of molar ratio of methanol to oil on acid value and reduction efficiency.

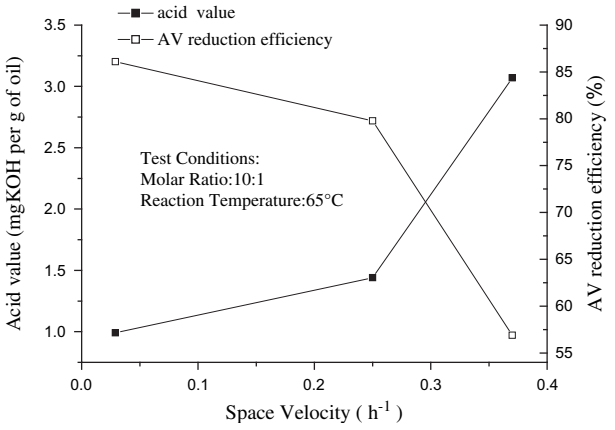

Fig. 3 – Effect of SV on acid value and reduction efficiency.

efficiency in the present study is shown in Fig. 2. The acid value decreased sharply from initial value to 1.07 mg KOH g^{-1}, 0.85 mg KOH g^{-1}, 0.70 mg KOH g^{-1} with the increasing of methanol to oil ratio from 4:1 to 8:1, and the AV reduction efficiency increased from 84.95% to 90.21%. The maximum AV reduction efficiency was obtained at the molar ratio of 8:1. With the further increasing of molar ratio to 10:1, the AV reduction efficiency decreased to 84.9%. The reason is the maximum positive accelerating effect of methanol concentration to esterification reaction was obtained at the molar ratio of 8:1, and this effect decreases with the increasing of methanol concentration, moreover the esterification reaction is reversible and more excess methanol lead to the increasing of polarity of entire reaction system, finally affect the reaction rate and decrease the AV reduction efficiency. Freedman et al. [11] found that the oil acid value should be less than 1 g kg^{-1} of KOH and all raw materials should be anhydrous (water content < 0.3%), reaction yield would be reduced due to the deactivation of catalyst and the formation of soaps, and finally lower conversion efficiency resulted if these requirements are not met. Otherwise, acid value is one of the most important properties of biodiesel [12]. Free fatty acid (FFA) contents both could meet the requirement of transesterification at the ratio of 6:1 and 8:1, but taking the recovery of methanol, power consumption and financial cost into account, 6:1 methanol to oil ratio was selected as an optimum value for the esterification of Tung oil.

3.2. *Effect of reaction time*

The variation of acid value with the SV is shown in Fig. 3. The acid value was reduced rapidly from 3.07 mg KOH g^{-1} to 1.44 mg KOH g^{-1} when the SV was changed from 0.37 h^{-1} to 0.25 h^{-1}, and the AV reduction efficiency was increased from 56.88% to 79.78%. The reduced trend of acid value became slow when continually changed SV to 0.029 h^{-1}, and the AV reduction efficiency changed from 79.78% to 86.10%, only 7.3% increased. As can be seen, esterification reaction attained balance when SV was enough, so an optimum of 0.029 h^{-1} was necessary for acid value reduction.

3.3. *Effect of reaction temperature*

The effect of reaction temperature on esterification is shown in Fig. 4. Reaction temperature is one of the major factors affecting the catalytic activity of solid acid. The higher temperature was used, the more acid value was reduced and the higher AV reduction efficiency was achieved. Only 29.07% conversion efficiency was achieved at 40 °C the acid value was reduced to 5.05 mg g^{-1} of KOH. As the temperature raised to 65 °C, the acid value of Tung oil could be reduced to 1.4 mg g^{-1} of KOH, and AV reduction efficiency was increased to 80.34%. It can be seen that activity of reactant and rate of reaction increase with temperature increased, and finally lead to the increasing of AV reduction efficiency. There have been studies of esterification of high FFA polanga seed oil [13] and mahua oil [14] as material at 60 °C. Therefore, there was an optimum temperature for esterification, which was the temperature very close to boiling point, this could avoid the loss of methanol and the waste of power [15]. For methanol, its boiling point is 64.5 °C according to this experiment, the optimum temperature was 65 °C.

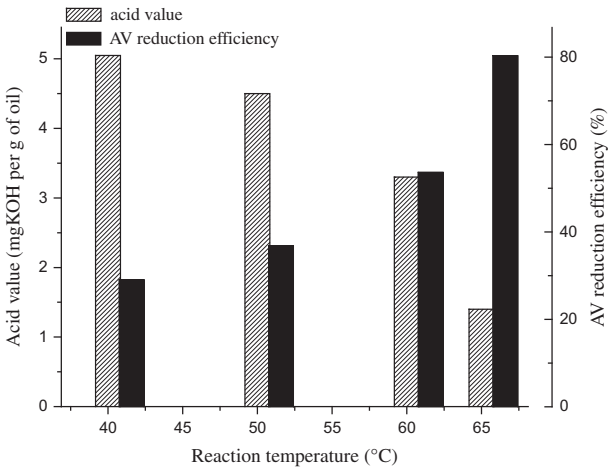

Fig. 4 – Effect of temperature on acid value and reduction efficiency.

4. Conclusions

Molar ratio of methanol to oil, reaction temperature and SV are the three important factors, having considerable effect on the esterification reaction. When molar ratio of methanol to oil was 6:1, the temperature of the fixed bed was 65 °C and SV was 0.029 h^{-1}, the maximum AV reduction efficiency was achieved, the acid value of the oil could be reduced to 0.8 mg g^{-1} of KOH. This process can achieve high conversion of FFA using solid catalyst, while the cost of reactor was decreased and the reaction time was shortened. Furthermore, this study developed a promising and environmental friendly method to deal with feedstock with high acid value.

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