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Procedia Environmental Sciences 11 (2011) 757 – 762
Procedia Environmental Sciences

Biodiesel Fuel Production through Transesterification of Chinese Tallow Kernel Oil Using KNO_3/MgO Catalyst

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Abstract

In this study, biodiesel was product by transesterification of Chinese tallow kernel oil with methanol in a heterogeneous system, using magnesium oxide loaded with potassium nitrate as a solid catalyst. After calcination, the dependence of the conversion of Chinese tallow kernel oil on the reaction variables such as the catalyst loading, reaction temperature, the molar ratio of methanol/oil, the reaction time was studied. The conversion was over 94% under the conditions of 340K, the molar ratio of methanol/oil 8:1, reaction time 3h. Catalyst reusability was also studied.

Keywords: Transesterification; Chinese tallow kernel oil; biodiesel; Saponification; catalyst

1. Introduction

As an alternative resource, biodiesel (fatty acid methyl esters) derived from the transesterification of vegetable oil or animal fats with methanol are potential substitutes for petrolrum-base diesel fuel. Biodiesel can be used in its pure form or mixed with petroleum diesel and has lower emissions. In addition, biodiesel is non-toxic, bio-degradable [1]. 10 percent of biodiesel must be used in diesel fuel in some provinces of China. This will reduces reliance on oil imports. In addition, petroleum-based products are one of the main causes of anthropogenic carbon dioxide (CO_2) emissions to the atmosphere. Today, the transportation sector worldwide is almost entirely dependent on petroleum-derived fuels. One-fifth of global CO_2 emissions are created by the transport sector [2], which accounts for some 60% of global oil consumption [3]. Biodiesel can help to reinforce energy security and reduce the emission of both greenhouse gases and urban air pollutants [4]. Biodiesel had been produced using various oils, such as soybean oil [5,6], palm oil [7], cottonseed oil [8], sunflower oil [9], jatropha oil [10], waste cooking oil [11,12], and Chinese tallow kernel oil[13].

doi:10.1016/j.proenv.2011.12.117

It is well known that oil and grain are in short supply in many countries. Thus, it is necessary to develop non-edible oil as raw material of biodiesel. Chinese tallow kernel oil is woody plant oil containing 40-70% fatty acid and has more than 100,000 metric tons of production in China. The acid value (2-8mg KOH/g oil) [14] of Chinese tallow kernel oil is higher than soybean oil and Chinese tallow kernel oil, as a result, it causes intoxication and saponification using homogeneous catalyst such as NaOH and KOH. Therefore, KNO_3/MgO as solid base catalyst was used in transesterification of Chinese tallow kernel oil. The catalyst can be recovered from the reactor and isn't disposed of as a waste stream. Reusability test were also studied.

2. Experimental

Chinese tallow kernel oil used in the present study were provided from Jiangsu Suyang, Co.,Ltd, China. Some of its physical and chemical properties were determined and summarized in Table1. N-hexane (99%) and methanol (99.8%) were procured from Tianjin Kermel Chemical Reagent Co.,Ltd, China. Methyl oleate which was used as internal standard for gas chromatography (GC) was purchased from Westingarea Co.,Ltd, China.

Table.1. Physicochemical properties of Chinese tallow kernel oil

Properties	**Chinese tallow kernel oil**
Physical	
Acid value(AV)/(mg KOH/g oil)	4.369
Saponification value/(mg KOH/g oil)	206.35
Iodine value (IV)/(g/g oil)	137.52
Moisture content/%	1.445
Viscosity(25℃，mPa·s)	46.92
molecular mass(g/mol)	833
Chemical	%
$C_{11}H_{22}O_2$ (11:0)	0.162
$C_{12}H_{22}O_2$ (12:1)	4.022
$C_{13}H_{28}O_2$ (14:0)	0.313
$C_{15}H_{32}O_2$ (16:0)	5.937
$C_{17}H_{36}O_2$ (18:0)	2.049
$C_{18}H_{34}O_2$ (9c-18:1)	15.238
$C_{18}H_{34}O_2$ (11c-18:1)	1.027
$C_{18}H_{32}O_2$ (9c,12c-18:2)	29.773
$C_{18}H_{30}O_2$ (18:3 n-6)	0.278
$C_{18}H_{30}O_2$ (18:3 n-3)	41.201

Figure1. Pretreatment of Chinese tallow kernel oil

Initially, Chinese tallow kernel oil was heated above 323K for 0.5 h to remove solid particles by filtration. The free fatty acid content was determined by titration according to GB/T5530. The amount of potassium hydroxide was calculated based on the titration result, and then an aqueous solution of KOH (2N) was added to neutralize the free fatty acids in the oil. The oil was heated to 358K and then cooled to room temperature. The precipitated solids were settled and then centrifuged. The oil was further washed by agitation with 5% water and centrifuged again. Finally, diatomaceous earth (1%, w/v) was mixed into the oil. The mixture was stirred continuously for 30 min by a magnetic stirring apparatus at temperature of 393K to remove water for further use. The free fatty acid content of the clear oil was determined and the value was 0.1565 mg KOH/g oil. The result of pretreatment of Chinese tallow kernel oil is shown in Fig.1.

Magnesium oxide was purchased from Hongxing chemical plant (Beijing, China). Potassium nitrate was purchased from Beijing chemical plant (China). The catalyst was prepared by impregnation of magnesium oxide with an aqueous solution of potassium nitrate. For this purpose, 20ml of (10%, 20%, 30%, 40% and 50%) potassium nitrate was loaded onto 10 g of magnesium oxide by an impregnation method, followed by drying at 373K. Before the each reaction, the catalysts were calcined in tubular furnace at desired temperature (at 1073K) in N_2 flow for 3h.

Reaction experiments were carried out in a 500 ml three-necked reactor equipped with a reflux condenser. The magnetism blender rate was 600 rpm. The reactor was heated in a constant-temperature heating controlled by a temperature controller. The reaction procedure was as follows: First, 3wt% catalyst was added into the methanol in the reactor which was heated by water circulation together. Then 100g Chinese tallow kernel oil was added into mixture after achieving the setting reaction temperature. After the specified reaction time was reached, the catalyst was separated by filtration. The filtrate was laid aside for 24h. It formed two phases, the lower layer was mixture of glycerol and a small amount of solid catalyst, the upper layer was biodiesel which was analyzed by gas chromatographic equipped with flame ionization detector.

3 Results and discussion

In order to study the effect of KNO_3 loading amount on KNO3/MgO, a series of samples with the loading amount of KNO_3 ranging from 10 to 50 wt% were prepared and used as catalyst (3 wt %) in transesterification reaction for 3 h with the methanol/oil molar ratio of 8:1 at 67 °C. The results are presented in Fig.2. As seen in Fig.2, increasing the amount of KNO_3 the conversion enhances from 10 to 30 wt%. The maximum value is 94%. More loading of KNO_3 on catalyst cannot improve conversion, on the contrary, the value declines.

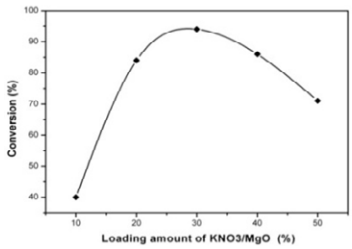

Figure 2. Different loading amount of KNO3/MgO on the conversion. Reaction conditions: Chinese tallow kernel oil 100g, methanol/oil molar ratio 8:1, catalyst amount 3 wt%, reaction time 3h, reaction temperature 340K.

Stoichiometrically, the methanolysis of Chinese tallow kernel oil requires three moles of methanol for each mole of oil. However, in practice, the methanol/oil molar ratio should be higher than that of stoichiometric ratio in order to drive the reaction towards completion and produce more methyl esters as product. As is evident from Fig.3, when the methanol amount was increased, the conversion of Chinese tallow kernel oil was increased considerably. The maximum conversion of Chinese tallow kernel oil of 94% was obtained when the methanol/oil molar ratio was close 8:1. However, there was only little change in the conversion using excessive methanol. Therefore, we can conclude that methanol/oil molar ratio was important factor to elevate the conversion of Chinese tallow kernel oil a certain extent.

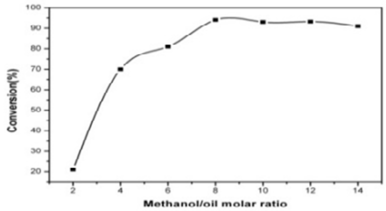

Figure 3. Influence of methanol/oil molar ratio on the conversion. Reaction conditions: Chinese tallow kernel oil 100g, catalyst amount 3 wt%, reaction time 3h, reaction temperature 340K.

In Figure 4, the influences of catalyst loading amount are presented. The optimum catalyst amount was found to be 3 wt%, and the yield reached 94%. The extra loading of the catalyst did not lead to an obvious increase inconversion. This was probably because the slurry became too viscous, giving rise to a problem of mixing and a demand of higher power consumption for adequate stirring.

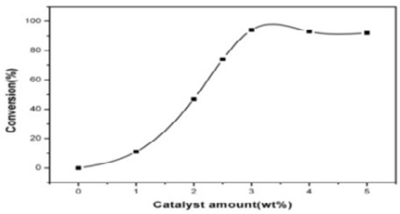

Figure 4. Influence of catalyst amount on the conversion. Reaction conditions: Chinese tallow kernel oil 100g, methanol/oil molar ratio 8:1, reaction time 3h, and reaction temperature 340K.

In Fig.5, the conversion of Chinese tallow kernel oil versus reaction time is presented. The experiment was carried out at three different temperatures. The conversion is lower in the first hour. It can be seen that the conversion of Chinese tallow kernel oil was increased in the reaction time range between 1 and 3 h, and thereafter remained nearly constant as a representative of nearly equilibrium conversion. The nearly equilibrium conversion of Chinese tallow kernel oil was found to be about 94% at 3h of reaction time.

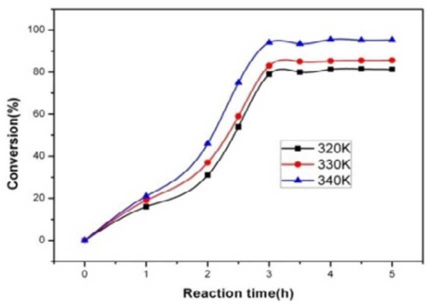

Figure 5. Effect of temperature. Reaction conditions: Chinese tallow kernel oil 100g, methanol/oil molar ratio 8:1, and catalyst amount 3 wt%.

Reusability tests were also performed. The catalyst calcined at 600 ℃ under N_2 flow reused without re-calcination would achieve 61.8% conversion for the second round, and 44.9% for the third round. Otherwise, the catalyst calcined at 600 ℃under N_2 flow before each cycle was used for four cycles. The yield was 88.5%, 83.5%, 75.6%, and 60.1% in Fig.6. It is reasonable that calcination is very important for the catalyst's reusability.

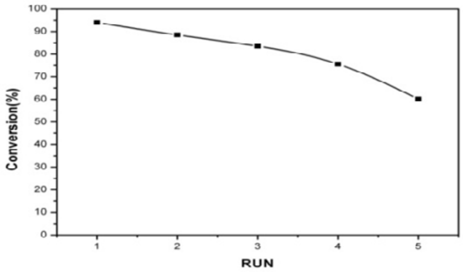

Figure 6. Reusability study. Reaction conditions: Chinese tallow kernel oil 100g, methanol/oil molar ratio 8:1, catalyst amount 3 wt%, reaction time 3h, reaction temperature 340K.

4. Conclusions

Magnesium oxide loaded with potassium was found be strong solid base catalyst for transesterification of Chinese tallow kernel oil with methanol. The catalyst with 30 wt% KNO_3 loaded on MgO and calcined at 1073K for 3h. The highest conversion reached 94% at 340k for 3h, when methanol/oil molar ratio is 8:1. The catalyst was recycled to study the reusability. Catalyst may be used at least for four times. As a non-edible oil, Chinese tallow kernel oil may be transform biodiesel by pretreatment before reaction.

Acknowledgment

The authors gratefully acknowledge the support of Key Laboratory of Coal Science Technology of Taiyuan University of Technology to carry out this study.

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