

Synthesis of biodiesel using KOH/Borax as suitable mixed catalyst via transesterification of waste sesame oil

Sahar Belyani¹, Mahdi Behzad^{1,*} and Fatemeh Tamaddon²

¹Department of chemistry, Semnan University, Semnan, Iran

²Department of chemistry, Yazd University, Yazd, Iran

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Abstract

The catalytic activity of KOH/borax as homogeneous mixed catalyst was evaluated for the synthesis of biodiesel via transesterification of sesame oil extracted from waste sesame seeds with n-hexane. The effects of catalyst loading, methanol to oil ratio, temperature and reaction time in transesterification were investigated. The highest yield of 87% for biodiesel production was obtained at optimized conditions including 0.4 wt.% KOH and 10 wt.% Na₂B₄O₇·10H₂O of mixed catalyst loadings, methanol to oil molar ratio of 8:1, reaction time of 2.5 h and reaction temperature of 65 °C.

Keywords: Transesterification; Biodiesel; KOH/Borax.

1. Introduction

Nowadays, with the depletion of fossil fuels, increasing world population and wide demands for a possible substitute for conventional diesel; biodiesel has attracted great amount of attention [1-4]. Compared to conventional diesel, biodiesel is biodegradable, renewable, non-toxic, and has reduced emissions of CO₂, SO₂, and poly aromatic hydrocarbons [5-6]. Biodiesel is alkyl ester of vegetable oils or animal fats that can be used in diesel engines without engine modifications because its properties are very similar to traditional petroleum-based diesel. Some of the main methods for biodiesel production include esterification of free fatty acids [7-10], transesterification of triglycerides [11-14], and deoxygenative ecofining of triglycerides in a non-alcohol environment [15]. Various kinds of homogeneous and heterogeneous catalysts such as acid, base and enzyme catalysts have been used for biodiesel production [16-24]. Base catalysts including KOH or NaOH, produce highest yield of biodiesel via transesterification of edible and non-edible oils with low-molecular-weight alcohols. Although homogeneous base catalysts such as sodium and potassium hydroxide have several problems which include the use of more alcohol, recoverability after

the reaction, washing requirement, and generating toxic waste-water [25] but transesterification via homogeneous base catalysts is still the conventional industrial process used for biodiesel production. The optimized range for catalyst loading by using KOH and NaOH in transesterification reaction is 0.75 wt.% and 1 wt.% respectively according to the previous literatures [26].

Borax is a naturally occurring fine, white, and water soluble sodium salt of boric acid with LD₅₀ 2660 mg/kg which its aqueous solutions in water show pH value in the range of 9.3-9.5. Hydrated borax as Na₂B₄O₇·10H₂O contains [B₄O₅(OH)₄]²⁻ anion dehydrates at high temperatures to give anhydrous borax as two tetrahedral and two triangles of BO₄ and BO₃. Borax has been used as catalyst or co-catalyst for promotion of various organic transformations because of its interesting properties such as water compatibility, its buffered base media with controllable pH and its dual Lewis acid/Bronsted base properties [27].

From another point of view, the price of feedstock is also a major difficulty that affects the mass production of biodiesel fuel, so finding a cheap feedstock with high percentage of oil is considerable. Sesame oil used extensively as a superior source of essential oil for human nutrition and health proposes.

* . Corresponding Author: E-mail:mbehzad@semnan.ac.ir; Tel:+98-23-33383195

Traditionally, sesame oil is extracted at high pressure by use of mill from roasted or crude sesame seeds which is an oilseed herbaceous crop. Increasing the consumption of sesame oil has resulted in the production of a large amount of waste sesame seeds containing approximately 10% oil which cannot be extracted by traditional ways. Because of the nutrition uses of sesame oil, waste sesame seed oil is more desirable source for biodiesel production.

Due to the environmental advantages of biodiesel production from waste oil using a mild base catalyst; the unique properties of borax and to reduce the amount of KOH catalyst, in this study, we studied the transesterification of extracted oil from waste sesame seeds in the presence of KOH/borax as mixed catalyst. The results showed that up to 87 % of biodiesel was obtained in the optimized conditions which is comparable to previously studied catalysts while lower amounts of KOH was used.

2. Materials and methods

2.1. Characterization of waste sesame oil

The waste sesame seeds (WSS) used for extracting waste sesame oil (WSO) in the present research was obtained from the Abe Hayat Oil Extraction Co (Yazd, Iran). Waste sesame oil was extracted from cylindrical tubes of waste sesame seeds using 300 mL chloroform for 300g waste sesame seeds. $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and KOH were purchased from Merck Co. (Germany). MeOH with purity of 99.8% was supplied by Iranian Petrochemical Co. Table 1 shows the fatty acid composition of WSO determined by GC/Mass analyses. The physical properties of WSO and the produced biodiesel were determined according to ASTM and EN methods D 6751 and 14214 respectively.

Table 1. Fatty acid composition of waste sesame oil

Fatty acid	WSO(%)
Palmitic	10.4
Stearic	5.5
Oleic	42.3
Linoleic	41.98
Linolenic	0.37
Arachidic	0.49
Eicosenoic	0.16
Lignoceric	0.02

Characterization of catalyst

A series of $\text{KOH}/\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ mixed catalysts with varying KOH loadings (0.1, 0.2, 0.3, 0.4, and 0.5 wt. %) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ loadings (5, 10, 20, 30, and 40 wt. %) were prepared.

Transesterification procedure

Mixture of $\text{KOH}/\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (0.4 wt. %/10 wt. % of oil) and alcohol in a two-neck flask equipped with a condenser and magnetic stirrer at controlled temperature of 65 °C was added to waste sesame oil. After a desired time, the mixture was distilled to remove the excess of methanol and the remained liquid was washed with brine (50 mL for each 10 mmol) and water (50 mL for each 10 mmol) to remove the mixture of catalyst and glycerol. The produced biodiesel was dried over Na_2SO_4 . Dichloromethane or chloroform was used as extractor in the small lab scale reactions.

3. Results and discussion

3.1. Properties of WSO

Some properties of waste sesame oil used in this work, such as saponification value, iodine number, amount of Fe, Cu, Pb, and As, free fatty acid content (acidic number), and moisture content were determined and are shown in Table 2 which are in the desirable range values [11-12].

Table 2. Properties of waste sesame oil

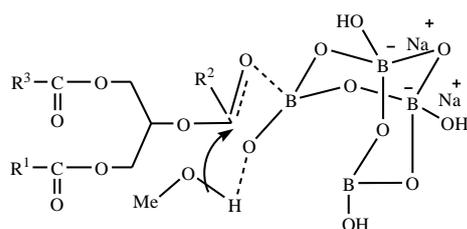
Property	Scale	Content
Fe	ppm	1.4
Cu	ppm	0.1
Pb	ppb	3.76
As	ppb	1.78
Moisture (105 °C)	-	0.08
saponification value	mg KOH/g	192.25
Acidic number	mg KOH	5.5
Iodine number	-	108.75

3.2. Transesterification of WSO with methanol

In order to optimize the reaction conditions for biodiesel synthesis, transesterification of WSO was carried out under different catalyst loading, reaction temperatures, methanol to oil molar ratios, and reaction times.

3.2.1. Catalyst nature

Borax can catalyze the transesterification reaction associated with KOH with low consumption of KOH. This is due to the pH control of borax solution in methanol and its duality as either Lewis acid for activation of carbonyl group or buffered Bronsted base to prevent the saponification (Scheme 1).



Scheme 1. Postulated catalytic role for $\text{Na}_2\text{B}_4\text{O}_7$ catalyzed transesterification of triglyceride in waste sesame oil.

3.2.2. Effect of catalyst loading

To study the effect of catalyst loading on the conversion of oil to methyl ester of fatty acids, transesterification of WSO with methanol (1:10 ratio) was carried out with various KOH and borax ratios under reflux conditions. The best yield was obtained with 0.4 wt. % KOH and 10 wt. % borax. Figure 1 shows the effect of KOH/10 wt. % borax loading as mixed catalyst.

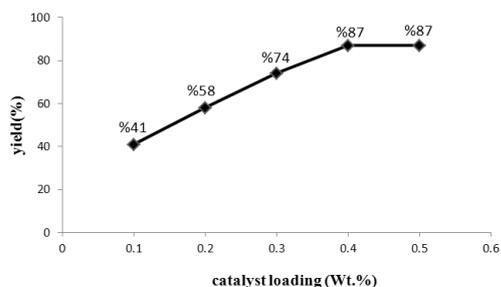


Fig 1. Effect of KOH/10 wt. % borax loadings on biodiesel yield. Reaction conditions: methanol to oil molar ratio = 10:1, reaction temperature = 65°C , reaction time = 2.5 h.

Figure 1 clearly explains the efficient role of KOH/borax as mixed catalyst in the transesterification of waste sesame oil to biodiesel with no saponification of oil. It can be observed that conversion continuously increased along with the increase in the catalyst loading of KOH from 0.1 to 0.4 wt. % and at 0.4 wt. % of KOH, the conversion was in its maximum range. By further increasing in the catalyst loading of KOH for example 0.5 wt. %, the yield did not change profoundly.

3.2.3. Effect of methanol to oil molar ratio

To reach the improved molar ratio, the reaction of sesame oil was studied with various amounts of MeOH using the optimized quantity of catalyst (0.4 wt. % KOH and 10 wt. % borax) for 2.5h under reflux conditions. The stoichiometric molar ratio of alcohol to oil is 3:1 and therefore, more than 3 mmol of alcohol is necessary for the complete transesterification of oil which includes three consecutive reversible reactions. The effect of MeOH to waste sesame oil molar ratios from the range of 3:1 to 12:1 on the conversion yield of biodiesel over 0.4 wt. % KOH and 10 wt. % borax is shown in Figure 2.

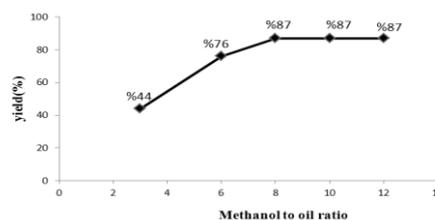


Fig 2. Effect of methanol to oil molar ratio on biodiesel yield. Reaction conditions: catalyst loading = 0.4 wt. % KOH and 10 wt. % borax, reaction temperature = 65°C , reaction time = 2.5 h.

The figure obviously shows that by increasing the methanol to oil molar ratio from 3:1 to 8:1, the biodiesel conversion increases considerably from 44% to 87% for the catalyst loading 0.4 wt. % KOH and 10 wt.% borax and reflux conditions of 2.5 h. Performing the reaction with higher molar ratios did not change the conversion yield of biodiesel. As a result, it can be concluded that the optimum range of methanol to oil molar ratio is 8:1 for the maximum transesterification of waste sesame oil to biodiesel by 0.4 wt. % KOH and 10 wt. % of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ catalyst.

3.2.4. Effect of reaction time

In order to verify the effect of reaction time on the biodiesel yield catalyzed by KOH/borax as mixed catalyst, the transesterification of waste sesame oil with optimized amount of KOH/borax and MeOH was investigated from 0.5 to 3h. Figure 3 shows the effect of reaction time on biodiesel yield.

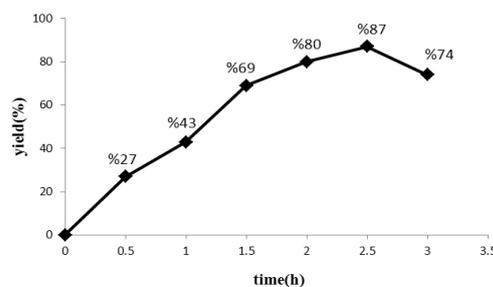


Fig 3. Effect of reaction time on biodiesel yield. Reaction conditions: catalyst loading = 0.4 wt. % KOH and 10 wt. % borax, methanol to oil molar ratio = 1:8, reaction temperature = 65°C .

As could be noticed from this figure, the conversion is sharply increased and reached to its maxima within 2.5 h. Further increase in the reaction time led to the decrease in yield, probably due to the side reaction of saponification.

3.2.5. Effect of reaction temperature

To study the effect of temperature on the conversion of waste sesame oil to biodiesel, a number of experiments were carried out at different temperatures over the range of $45\text{--}85^\circ\text{C}$ (Figure 4).

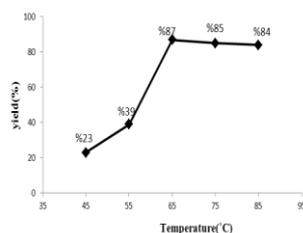


Fig 4. Effect of temperature on biodiesel yield. Reaction conditions: catalyst loading = 0.4 wt. % KOH and 10 wt. % borax, methanol to oil molar ratio = 1:8, reaction time = 2.5h.

As figure 4 obviously demonstrates, the percentage of conversion increased gradually in temperatures less than 65 °C and after passing this temperature the reaction reached to equilibrium. While the superior yield of biodiesel was obtained at 65 °C, further increase in the reaction temperature led to the decreasing in the conversion yield. Therefore, the temperature of 65 °C was chosen as the appropriate reaction temperature for the transesterification of sesame oil to biodiesel.

4. Conclusion

In this study, we have developed a new homogeneous mixed catalytic system for production of biodiesel that can be used as solid base mixed catalyst for biodiesel production via transesterification of waste sesame oil. The optimum conditions for KOH/borax was 0.4 wt.% KOH and 10 wt.% borax, 8:1 methanol to oil molar ratio, 2.5 h reaction time, and 60 °C. The results showed that the highest biodiesel yield of 87% was obtained at the optimum conditions. Waste sesame oil used in this study obtained from waste sesame seeds and WSO cannot be extracted by traditional methods.

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