

## Suitable Condition of Biodiesel Production from Waste Cooking Oil–Al-Baha City – KSA

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Accepted 20 May April 2015, Available online 26 May 2015, Vol.3 (May/June 2015 issue)

### Abstract

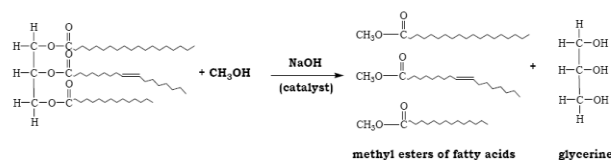
In this study biodiesel was synthesized from waste cooking oil from Al-Baha city – KSA by alkali catalyzed transesterification. Optimization of reaction conditions: catalyst amount, reaction temperature, reaction time and oil to methanol molar ratio have been studied. The best conversion value (96.33%) was obtained from 0.35 wt% NaOH catalyst amount, 30 min reaction time, 55°C reaction temperature and 1:6 oil to methanol molar ratio. Biodiesel viscosity, specific gravity, pour point, cloud point, acid value and cetane number were measured and compared with ASTM D 6571 standard for biodiesel. The fatty acid methyl esters have been analyzed by gas chromatography – mass spectrometry.

**Keywords:** Biodiesel, waste cooking oil, fatty acid methyl esters

### 1. Introduction

Concern for the environment become necessity especially with the increasing emission of toxic chemicals from various industries. Waste cooking oil (WCO) is one of the environmental pollutants in different areas around the world. Thus consuming it in the biodiesel production is one of the economical solutions to preserve the environment. One of the major advantage of using biodiesel as an alternative fuel is reducing air contaminants (NO<sub>x</sub>, So<sub>x</sub>, CO, particulate matter and volatile organic compounds) emitted from the use of petroleum diesel. Biodiesel offer a very promising alternative to diesel oil since they are renewable and have similar properties [1]. Biodiesel (monoalkyl esters) is obtained by transesterification of triglyceride oil with alcohol in the presence of catalyst under suitable reaction condition. Transesterification is the process of transforming one type of ester into another type of ester. The reaction is catalyzed by the presence of the strong base, NaOH.

In the first step of the reaction, the NaOH reacts with methanol in an acid base reaction. The products of this first step of the reaction are a very strong base, sodium methoxide, and water. In the second step, the sodium methoxide breaks the glycerine section from the fatty acid section. The separation of the glycerine portion leads to the formation of three methyl esters (the biodiesel) and glycerol (fig. 1). The biodiesel and glycerol are immiscible and will separate to form two layers.



**Figure 1:** Transesterification reaction

Different factors affecting the percentage yield and quality of biodiesel produced and those include: alcohol to oil molar ratio, weight of catalyst loaded, reaction temperature and time. Alcohols such as methanol, ethanol, propanol and butanol can be used in transesterification reaction. Methanol is widely applied among other alcohols due to its low cost and preferable chemical and physical properties [2, 3]. In overall results it has been found that increase of methanol ratio, improve the yield of biodiesel [2, 4]. Largest molar ratio of 1:74 has been used by Zheng *et al.* [5] in acid catalyzed transesterification of WCO which increase the cost of biodiesel production and separation.

Catalyst amount is one of the important factors that affect transesterification reaction. Both homogeneous and heterogeneous catalysts have been used. Among homogeneous basic catalysts that are commonly used are potassium hydroxide, sodium hydroxide and sodium alkoxides. Higher acid value of used oil is consuming catalyst and the highest conversion was obtained at 0.5wt% of catalyst amount [6, 7]. Acid catalyzed transesterification reaction was studied with different

molar ratios [8]. The maximum biodiesel yield for WCO was found at 6:1 molar ratio in acid esterification in comparison with 9:1 molar ratio in alkali esterification [9]. In other hand, the conversion of WCO increased with increment amount of sulfur acid within 4% and the conversion didn't increase with the exceeded amount of sulfur acid above 4% [10]. Heterogeneous catalysts were also well used in transesterification reaction for their easy separation at the end of the reaction and may also be reused [11-13].

Reaction temperature can influence the reaction rate and biodiesel yield because the intrinsic rate constants are strongly dependent on temperature [14]. The yield obtained at 90 and 80°C were higher than one obtained at 35°C [15]. Optimizing esterification conditions for higher yield of biodiesel were investigated by different authors [16, 17]. WCO was easy to collect and cheaper than other refined oils. Hence by using these oils as raw materials we can reduce the cost of biodiesel production. This work investigate the optimum conditions of biodiesel production from waste cooking oil collected from different seven restaurants in Al-Baha city. The characterization of biodiesel produced was also carried out to determine the quality of biodiesel produced according to ASTM D6751 standard. GCMS analysis of the product was performed.

## 2. Experimental

### 2.1. Materials

The waste cooking oil (WCO) was obtained from seven different restaurants in Al-Baha city. The WCO was heated to 110 °C to remove water traces and then filtered under vacuum to remove any food particles. The methanol used (99% pure) is of analytical grade with boiling point of 78 °C; the NaOH, KOH and anhydrous calcium chloride were of analytical grade and purchased from Loba Chemie Pvt.Ltd. Hydrochloric acid and phenolphthalene used were also analytical grade product of Aldrich Chemical Co. Ltd. The magnetic stirrer with hot plate, two necks round bottom flask, beakers, measuring cylinder, separating funnel, burette, funnels, measuring flask and thermometers were used.

### 2.2 Transesterification Reaction

In a 250 ml two necked round bottom flask 100 ml of oil was introduced and heated to a temperature selected from 40°C, 45°C, 50°C, 55°C, 60°C and 65°C. The designed amount of NaOH catalyst: 0.15, 0.2, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55 and 0.6 wt% of oil was dissolved into designed amount of methanol and poured into the flask. The transesterification reaction performed at different molar ratio of oil to methanol, varying from 1:3, 1:4, 1:5, 1:6 and 1:7. The mixture was maintained under stirring at the reaction temperature for designed period of time (20, 30, 35, 40, 50, 60, 70 and 80 minutes). At the completion of

the reaction, the flask content was transferred to a separating funnel for glycerol and biodiesel separation for 12 h. The lower darker layer containing glycerol has been removed. The upper layer containing biodiesel was washed several times with water (to remove traces of glycerol), dried on anhydrous calcium chloride (CaCl<sub>2</sub>) to remove residual water. The percentage yield of biodiesel was calculated by the following equation:

$$\text{Yield \%} = \frac{\text{weight of produced biodiesel}}{\text{weight of WCO}} \times 100$$

### 2.3 Physico-chemical analysis

Different physic-chemical properties of WCO and biodiesel were determined: kinematic viscosity @40°C (ASTM D445), specific gravity @15°C (ASTM D97), cloud point (ASTM D2500), pour point (ASTM D97) and cetane index (ASTM D976). The average molecular weight was calculated by  $MW = 56.1 \times 1000 \times 3 / (SV - AV)$ , where AV ( $\text{mg}_{\text{KOH}}/\text{g}_{\text{oil}}$ ) and SV is the saponification value ( $\text{mg}_{\text{KOH}}/\text{g}_{\text{oil}}$ ) [15,18, 19].

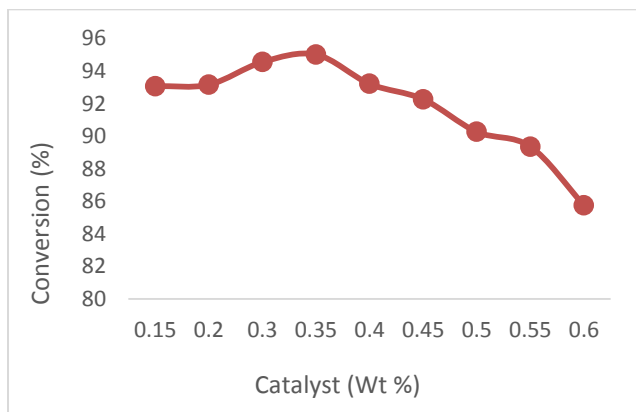
### 2.4 Gas chromatography – mass spectrometry (GC-MS)

To ensure the formation of fatty acid methyl ester (biodiesel), GC-MS analysis was accomplished using Varian CP3800 system incorporated with Varian 4000 mass-selective detector (MSD). A gas chromatograph equipped with a capillary column (VF-5MS, 30m x 0.25 mm ID). 1µL sample (dissolved in *n*-heptane) was injected into the GC (injector temperature 280°C). Helium was used as a carrier gas (flow rate: 1ml/min). The injection was performed in split ratio 100:1. Oven temperature program consist of: start at 80°C hold for 5 min, up to 280°C with 5°C/min interval hold for 10 min and up to 300°C with 10°C/min interval hold for 5min. total run time was 62 min. For MS parameters: scan type: SIS mode, ionization source EI, electron energy 70ev, source temperature 200°C, transfer line temperature 250°C and scan range 35-450 m/z.

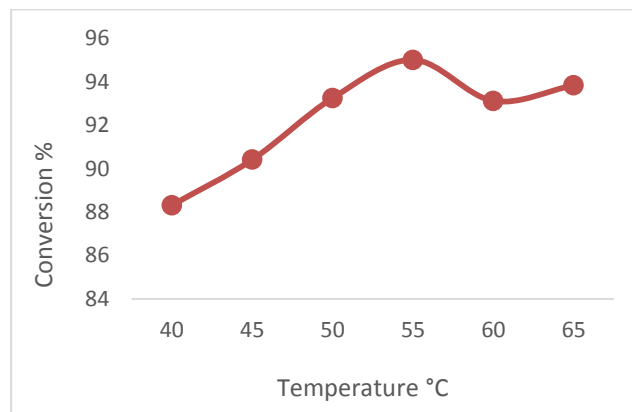
## 3. Results and Discussion

### 3.1 Optimization of catalyst amount

Fig.2 shows the influence of catalyst amount on methyl esters yield. Oil to methanol molar ratio, reaction time and temperature were fixed at 1:3, 30min and 55°C respectively. As results from Fig. 2, increase of catalyst amount from 0.15 to 0.35% (weight of NaOH / weight of oil) resulted in increase of biodiesel yield from 93.08 to 95.02%. The biodiesel yield decreased as the catalyst amount increase above 0.35% (85.76% yield for 0.6% catalyst amount).



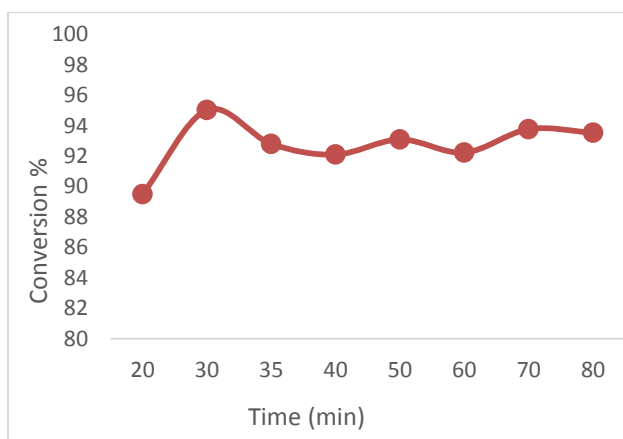
**Figure 2** Effect of catalyst amount on reaction conversion



**Figure 4** Effect of reaction temperature on reaction conversion

**3.2 Optimization of Reaction Time:**

Fig.3 shows the influence of reaction time on methyl esters yield. Oil to methanol molar ratio, catalyst amount and reaction temperature were fixed at 1:3, 0.35 wt% and 55°C respectively. The optimal conversion for WCO biodiesel was obtained at 30 min reaction time which gave a maximum yield of 95.02% (fig. 3). We observed that if the reaction time exceeded 30 min, the conversion value decreased and for higher reaction time the conversion remained stable. This fact can be explained by possibility of the reverse reaction [6].



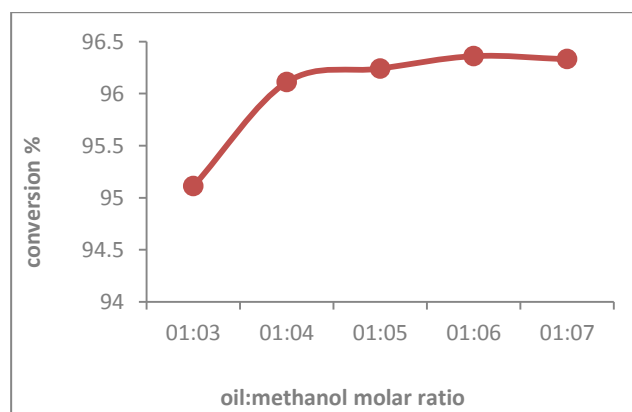
**Figure 3** Effect of reaction time on reaction conversion

**3.3 Optimization of Reaction Temperature**

Fig.4 shows the influence of reaction temperature on methyl esters yield. Oil to methanol molar ratio, catalyst amount and reaction time were fixed at 1:3, 0.35 wt% and 30 min respectively. The reaction was carried out at 40, 45, 50, 55, 60 and 65°C to evaluate the influence of reaction temperature. The optimal conversion for WCO biodiesel was obtained at 55°C, which gave a maximum yield of 95.02%. The conversion value decreased if the reaction temperature exceeded 55°C.

**3.4 Optimization of Oil: Methanol molar ratio**

Theoretically the transesterification reaction requires three moles of methanol and one mole of triglyceride in the presence of catalyst to yield three moles of biodiesel and one mole of glycerol. The transesterification is reversible and higher amounts of methanol to oil molar ratio can shift the equilibrium to the product side. Fig.5 shows the influence of reaction temperature on methyl esters yield. Catalyst amount, reaction temperature and reaction time were fixed at 0.35 wt%, 55°C and 30 min respectively. The reaction was carried out at 1:3, 1:4, 1:5, 1:6 and 1:7 (oil to methanol molar ratio). The conversion increased as the oil to methanol molar ratio increases and reaches 96.36% at 1:6 molar ratio. The conversion did not vary significantly above this molar ratio.



**Figure 5** Effect of oil to methanol molar ration on reaction conversion

**3.5 physico-chemical analysis**

The physicochemical properties of WCO are given in Table 1. It is clear that the biodiesel obtained from WCOs meets the standards specified by ASTM D6571. Among the various properties measured for biodiesel, cetane number is the indicator of the ignition quality of the

diesel fuel. Biodiesel has a higher cetane number compared to petroleum diesel because of higher oxygen content. Another important property is the acid value. Higher acid number could cause degradation of rubber parts in engines resulting in filter clogging [20]. Lower acid values for both WCO and biodiesel indicate the suitability of the oil for transesterification in biodiesel synthesis.

### 3.6 Fatty acid methyl ester composition

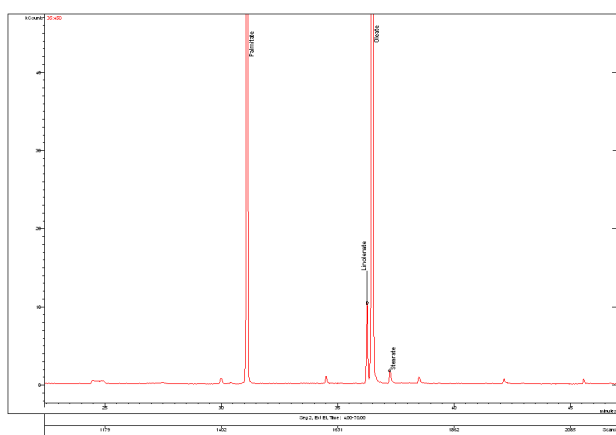
The synthesized biodiesel product was analyzed by GCMS to determine the composition of fatty acid methyl esters (fig. 6). Identification of individual fatty acid methyl esters was accomplished by NIST library. Table 2 presents the results for biodiesel obtained from WCOs. The main methyl esters are oleate and palmitate.

**Table 1:** Physicochemical properties of WCO and biodiesel

Properties	Raw WCO	ASTM D6571	Diesel	Biodiesel from WCO
Specific gravity (g/cm <sup>3</sup> , @15°C)	0.9185	0.86 – 0.89	0.85	0.87
Kinematic viscosity(cSt, @40°C)	43.39	1.9 – 6	2.049	5.82
Cloud point (°C)	15	-3 – 15	<10	13
Pour point (°C)	6	-5 – 10	-6	8
Cetane No	–	Min 45	47.73	48.7
Acid value (mg KOH/g)	1.4	≤ 0.5	0.72	0.22
Saponification value (mg KOH/g)	288.91	–	–	–
Average molecular weight (g/mol)	585.36 ± 8	–	–	–

**Table 2** Composition of biodiesel methyl esters

No	Name	Formula	RT	Area %
1	palmitate	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	31.12	29.69
2	Linoleate	C <sub>19</sub> H <sub>34</sub> O <sub>2</sub>	36.26	0.2782
3	oleate	C <sub>19</sub> H <sub>36</sub> O <sub>2</sub>	36.50	69.97
4	Stearate	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	37.26	0.0617



**Figure 6** GCMS of biodiesel

## Conclusion

This study revealed that the waste cooking oil from Al-Baha city could be a good source for biodiesel production by alkali catalyzed transesterification. Optimization of reaction conditions: catalyst amount, reaction temperature, reaction time and oil to methanol molar ratio have been studied. The best conversion value (96.33%) was obtained from 0.35 wt% NaOH catalyst amount, 30 min reaction time, 55°C reaction temperature and 1:6 oil to methanol molar ratio. Biodiesel viscosity, specific gravity, pour point, cloud point, acid value and cetane number were according to the ASTM D 6571 standard for biodiesel. The GCMS analysis confirms the structure and composition of fatty acid methyl esters produced.

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