Short Communication

Efficient Synthesis of Biodiesel From Waste Cooking Oil Catalysed by Al_2O_3 Impregnated with NaOH

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(Received 08 April 2014, Accepted 08 December 2015)

Abstract

Due to the high price of virgin vegetable oils and the drawbacks of the homogeneous catalytic transesterification, in this work an economically profitable alternative process was proposed for biodiesel synthesis in which transesterification of the low-cost waste cooking oil (WCO) with methanol in a heterogeneous system was done. Alumina impregnated with sodium hydroxide was utilized as a solid base catalyst along with a high yield and less waste streams. The optimum combination for transesterification reaction was determined as methanol-to-oil molar ratio 7:1, catalyst amount 1.5%, reaction time 4 hr and reaction temperature 70^{o}C. At this optimum condition, the fatty acid methyl ester (FAME) yield was over 92%. Fourier Transform Infrared spectroscopy (FT-IR) was the assessing technique for detection of biodiesel and glycerol in this work and biodiesel's physical properties including flash point, fire point, density, kinematic viscosity, cloud point, pour point and acid value have also been measured which satisfied the requirement of the international standards.

Keywords: Biodiesel, Heterogeneous catalyst, Transesterification reaction, Waste cooking oil.

1. Introduction

The increase of energy demand, as well as rising greenhouse gas emissions, along with environmental concerns have given rise to considerable attention to applying alternative and renewable sources of energy [1]. In this regard, the best substitute for conventional petro-based diesel fuel has so far been thought to be "biodiesel", which is also known as fatty acid alkyl ester. This fuel, which is friendly to environment, is prepared via a catalytic reaction between triglycerides and methanol. The by-product of the reaction is glycerol [2].

According to previous works, the operational cost of biodiesel production is associated with the raw material price which is deduced to a great extent. Hence, the price of feedstock is a key component when the economic feasibility of the process is evaluated [3]. In other words, waste cooking oil (WCO) has been attractive as a feedstock for biodiesel production in recent times due to its low-cost as well as recent concerns about sustainability and environment [4]. Likewise this end-use for WCOs eliminates not only their environmental impacts caused by the harmful disposal of these oils into drains [5-9], but also the oil extraction and refining steps from the biodiesel production process.

Yet, compared to homogeneous catalysts, heterogeneous catalytic processes are able to produce biodiesel more cost-effectively while greatly reduces formation of soap by-products [10] and increases the quality of FAME and glycerol. In fact, the development of heterogeneous catalyst systems can minimize the costs of catalyst and product separation and purification which make biodiesel economically viable and capable for competing with commercial petroleum-based diesel fuel [11, 12]. To date, many solid heterogeneous catalysts have been employed for biodiesel production, such as metal oxide catalysts (CaO, MgO, ZnO_2, TiO_2, SnO_2, and ZrO_2), zeolites, carbon group catalysts and waste material based catalysts [13-16].

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This paper was organized as follows: initially, a screening of the influencing parameters on biodiesel yield was carried out during transesterification reaction of WCO with methanol using $NaOH/Al_2O_3$ as a solid catalyst. Next, FT-IR spectroscopy was used to monitor biodiesel and glycerol quality. Finally, the biodiesel was characterised by measuring some of its physical properties including the flash point, the fire point, the cloud point, the pour point, the acid value, the kinematic viscosity and the density, according to the standard test methods.

2. Materials and Methods

In this research, WCO was collected from local domestic consumers and filtered to remove any solid residues. Methanol, Isopropanol, alumina (Al_2O_3), sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium sulphate (Na_2SO_4) and orthophosphoric acid were obtained from Merck, Germany.

2.1. Pre-treatment of the cooking oil

Prior to each reaction, the WCO sample was dried over sodium sulphate substrate, filtered under vacuum and then heated up to remove any water content. This particular oil was then characterized as a reagent for transesterification reaction and presented the following features (Table 1).

Table1: Physical properties of WCO & Diesel

Quality	Unit	WCO	Diesel
Flash point	^oC	> 300	88
Could point	^oC	4	3
Density	g/cm^3	0.91	0.83
Viscosity	mm^2/s	38.1	3.1
Acid value	mg KOH/g	1.01	0.11

The data of Table 1 show that WCO sample has 1.01 mg KOH/g of acid value which is a perfect match property for the alkali catalysed transesterification reaction. The sample also has a flash point of above 300^oC, a density of 0.91 g/cm^3, a cloud point of 4^oC and a viscosity of 38.1 cSt.

Although some literature is available regarding the application of unmodified vegetable oils in the diesel engines [17-19], high viscosity of WCO compared to diesel fuel ultimately leads to operational problems during its directly utilization as an alternative fuel in diesel engines. Hence to avoid this problem, biodiesel fuel with lower viscosity is produced by means of a transesterification reaction.

2.2. Heterogeneous Catalyst preparation

In this research, the catalyst was prepared based on the procedure described elsewhere [20] and by impregnation of alumina with an aqueous solution of sodium hydroxide. The impregnation method involved loading 15 ml of (50%) sodium hydroxide onto 10 g of alumina, followed by drying in atmospheric dryer. The catalyst was finally calcined in a muffle furnace (at 773 K) in air for 3 hours.

2.3. Transesterification procedure with $NaOH/Al_2O_3$

To optimize the reaction conditions, a series of parallel reactions were carried out using the same method to obtain the maximum yield of biodiesel. 50 g of the treated oil and an appropriate mixture of catalyst ranging from 1 wt.% to 5 wt.% of WCO in methanol was provided. The target composition is to reaching alcohol/oil molar ratios of 5:1, 6:1, 7:1, 9:1 or 12:1 were placed into a dry reaction flask equipped with a reflux condenser, a thermometer and magnetic stirrer. Reaction mixture was stirred at 600 rpm and heated simultaneously for 3, 4 and 5 hours up to a temperature of 70^oC. At the end of the reaction period, the catalyst was separated from the product mixture by hot vacuum filtration, washed with methanol, dried and enabled to be reused for future reaction. After being settled down in a decantation funnel, the crude biodiesel phase was separated from the glycerol phase due to the difference in their densities. The former phase was washed 3 times with 20 ml of distilled water at 60^oC to reach neutral pH, centrifuged, dried by anhydrous sodium sulphate and finally filtered.

2.4. Transesterification procedure with NaOH

The transesterification of WCO was carried out using homogeneous NaOH catalyst: 50 g of WCO was transferred to a two-neck flask equipped with a thermometer and a reflux condenser. A mixture of methanol and sodium hydroxide was added to the oil and the transesterification reaction began. The temperature was kept at around 70^{o}C for 3 hr. The study was carried out using a molar ratio of methanol/WCO of 6:1 and catalyst quantity equivalent to 1.5 % of oil. At the end of the reaction period, the glycerol rich-phase was separated from the methyl ester layer in a decantation funnel. The methyl ester layer was washed with water to provide a purified biodiesel and then dried over sodium sulphate and filtered under vacuum.

2.5. Analyses

FT-IR spectrometer (Perkin Elmer GX system with a horizontal ATR accessory and flow cell) was used to determine the FAME of the crude biodiesel phase after purification and analyse the purified methyl ester, as well as the crude glycerol quality according to the method described by Siatis et al. [21]. The biodiesel was also evaluated by a series of standard tests to determine if the product met the international specifications for biodiesel (ASTM D6751). Fuel density and viscosity were determined using ASTM D1298 and ASTM D445 standards, respectively. Flash point, fire point, cloud point & pour point were measured using ASTM D93, ASTM D93, ASTM D2500 and ASTM D97, respectively. Finally acid value of sample was obtained by titration (ASTM D664 standard).

3. Results & Discussion

3.1. Optimization of reaction parameters

3.1.1. Heterogeneous Catalyst/WCO mass ratio

As shown in Figure. 1, different catalyst amounts (*$NaOH/Al_2O_3$):* 1%, 1.5%, 2%, 2.5% and 5%, relative to the WCO weight (50 g) were employed and the maximum biodiesel yield obtained with 1.5%, optimum value of catalyst.

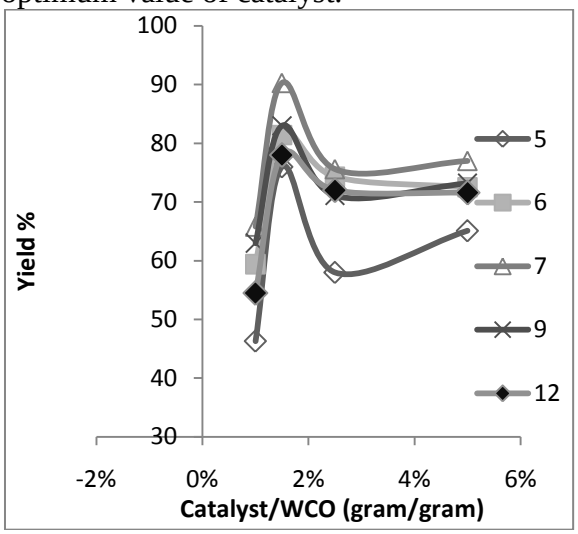

Figure 1: Biodiesel yield as a function of Catalyst/WCO mass ratio. Reaction time 3 hr, Reaction temperature 70^{o}C. Methanol/WCO molar ratio: ◇ , 5:1□ , 6:1△ , 7:1; × , 9:1; ◆, 12:1.

3.1.2. Methanol/oil molar ratio

As recognised by researchers comprehensively, the transesterification requires more methanol than the stoichiometric value (3:1) to enhance the reaction rate and this is even more important when solid catalysts are used due to its slower mass transfer in a three-phase reaction systems. Figure2 illustrates biodiesel yield as a function of different methanol/oil molar ratios ranging from 5:1 to 12:1 at a constant temperature of 70^{o}C and a rotation speed of 600 rpm in the presence of $NaOH/Al_2O_3$ as a solid base catalyst.

From the results presented, biodiesel yield maximized when a molar ratio of methanol/WCO of 7:1 was employed. Similarly, Arzemendi et al. [22] produced biodiesel from sunflower oil by using the same catalyst and methanol loading amount of 12:1 relative to oil. More recently, Yap et al. [23] obtained 99% biodiesel yield by using the same catalyst and methanol/Palm oil molar ratio of 15:1. All in all, these results are consistent with observations made by Zhang and his colleagues [13]; that the original oils' chemical characteristics

such as the initial acid value often determine the amount of methanol to be consumed for a high conversion production of biodiesel. Yet using a high methanol/oil molar ratio is useful to a certain extent, beyond that, extra methanol often leads to some technical problems associated with the phase separation (methyl ester phase from glycerol phase) and consequently extra steps plus additional costs will be required for recovering the excess methanol from biodiesel (or glycerol).

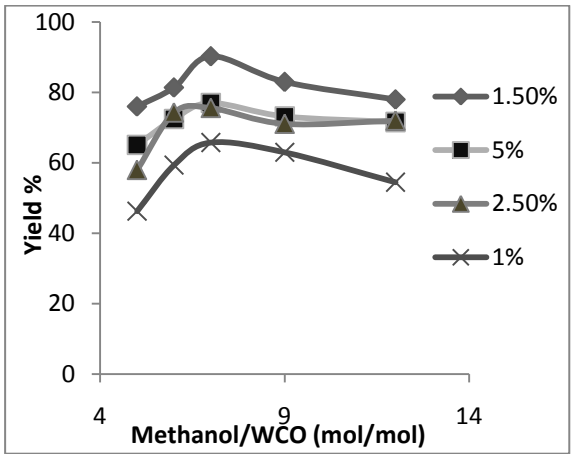

Figure 2: Biodiesel yield as a function of Methanol/WCO molar ratio. Reaction time 3 hr, Reaction temperature 70 °C. Catalyst/ WCO mass ratio: × , 1 %; ◆,1.5%; △, 2.5%; ■, 5%.

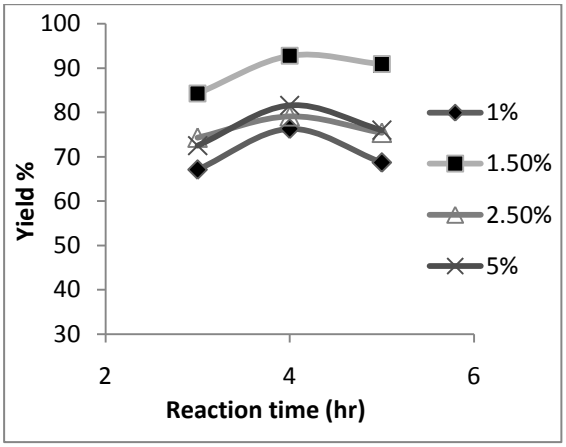

Figure3: Biodiesel yield as a function of Reaction Time, Methanol/WCO molar ratio fixed at 6:1, Reaction temperature fixed at 70 °C. Methanol/WCO mass ratio: ◆,1%; ■,1.5%; ▲,2.5%; × , 5%.

3.1.3. Reaction time

The relationship between the reaction time & biodiesel yield with different catalyst/WCO mass ratios is demonstrated in Figure3. When the transesterification equilibrium shifted to right for 4 hours in this three-phase reaction system, the optimum biodiesel yield reached 92.8%. However, further increase in reaction time resulted in slight reduction in biodiesel yield because of phase separation problems.

3.2. Investigation of biodiesel quality FT-IR spectra

FT-IR spectroscopy was the analytical technique employed in this work to identify the main functional groups presence at both the optimum produced biodiesel sample and its parent waste vegetable oil. As shown in Figure. 4, WCO (triglyceride) and biodiesel (methyl ester) have similar FT-IR spectra and little changes occur as a result of transesterification of triglyceride into methyl ester. Therefore, comparison of peaks inside the region from 1000 cm^{-1} to 1500 cm^{-1} shows the reaction process. The absorption peak appearing at 496 cm^{-1} is representative of -CH_2 rocking and the other one at 1750 cm^{-1} is representative of C=O ester stretch.

The sharp peak at 1750 cm^{-1} which appears in both WCO and biodiesel spectra, represents the C=O group of ester. The main difference between the two FTIR spectrums is related to the transformation of ester groups at the waste oil sample into methyl esters at the produced biodiesel.

The OH deformation peak appears in the region of 1238-1248 cm^{-1} in both spectra [21]. The WCO spectrum additionally revealed peaks of –CH_2 vibration at 1465 cm^{-1} and C-O ester vibration (bonded to –CH_2 group) at 1164 cm^{-1}, respectively. The C-O vibration of ester appears at a different region (1171 cm^{-1}) in biodiesel spectrum indicating –C-O-CH_3 group. Moreover, as can be seen in this figure, the CH_2-O-stretching vibration in oil was reduced to the CH_3-O- vibration in biodiesel. Other characterisation peaks observed in biodiesel spectrum are at 1197 cm^{-1} and 1436 cm^{-1} representing the bending stretching of –O-CH_3 group and the presence of CH_3 asymmetric stretching, respectively.

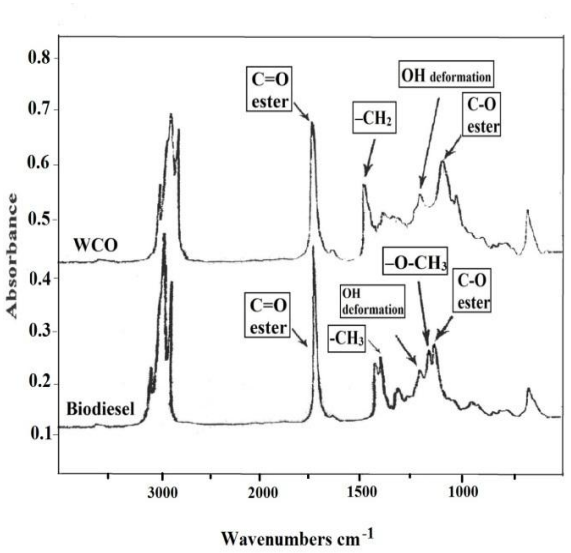

Figure4: FT-IR Spectra of Waste cooking oil & biodiesel by $NaOH/Al_2O_3$ catalyst.

3.3. Characterization of Biodiesel

After the methyl ester phase was purified, different physical properties of B100 including the flash point, the fire point, the cloud point, the pour point, the acid value, the kinematic viscosity and the density were measured to ensure these meet the international standards (ASTM D6751). Table 2 lists the results and also compares them with those of petroleum diesel fuel. It can be seen from this table that the biodiesel produced in this research has the required properties to be used in diesel engines.

The flash point of B100 (182^{o}C) was much higher than that of diesel (88^{o}C), and hence, shows that there is no alcohol residue in biodiesel structure. Consequently, transportation, storage and handling of this biodiesel are better than the conventional diesel in terms of safety.

The cloud point and pour point are greater than those obtained by other researchers, making this biodiesel less suitable for performance in cold conditions if used in pure form. However, biodiesel is frequently blended at different ratios with petroleum diesel to overcome these problems of the pure form.

Chemical conversion of WCO into biodiesel resulted in significant reduction of the viscosity from 38.1 mm^2/s for WCO to 4.6 mm^2/s for biodiesel. This fact shows that biodiesel viscosity is well consistent with the required value in ASTM standard. Therefore, by transesterification, engine problems associated with high viscosity of waste cooking oils such as incomplete combustion and ignition delay will be eliminated. The density of biodiesel, which influences the quality of atomization process of this fuel, and the acid value of biodiesel, which is a measure of free fatty acid content, also matched ASTM standards, as shown in table 2.

Table2: Characterization of biodiesel properties & comparison with Diesel & ASTM D6751 standards

Fuel property	Biodiesel (sample)	Biodiesel (Standard)	Method	Diesel
Flash point (^{o}C)	182	> 130	ASTM D93	88
Fire point (^{o}C)	202	-	ASTM D93	107
Pour point (^{o}C)	1	-	ASTM D97	-7
Cloud point (^{o}C)	5	-	ASTM D2500	3
Viscosity @ 40 ^{o}C (mm^2/s)	4.6	1.9 – 6.0	ASTM D445	3.1
Density (g/cm^3)	0.87	0.86 – 0.90	ASTM D1298	0.83
Acid value (mgKOH /g)	0.48	< 0.8	ASTM D664	0.11

3.4. Comparison of optimum experimental conditions & biodiesel yields when using different alumina-based heterogeneous catalysts and homogeneous NaOH catalyst

Table 3 presents different studies that developed alumina-based heterogeneous catalysts for the transesterification of various vegetable oils with methanol into biodiesel. The results indicate that all alumina-based heterogeneous catalysts listed within the table, except $LiNO_3/Al_2O_3$, are capable of catalyzing the transesterification reaction of different vegetable oils; resulting in high biodiesel yields and can accomplished with

homogeneous catalysts. As is shown, compared to different alumina-based heterogeneous catalysts, the yield of biodiesel from WCO catalysed by $NaOH/Al_2O_3$ is slightly lower.

Nevertheless, the transesterification reaction in this research required not only a lower amount of the solid catalyst, but also the lower molar ratio of methanol to oil and the lower reaction time than those found in most similar researches with alumina-based solid catalysts.

However, the reaction time of WCO with $NaOH/Al_2O_3$ is slightly longer than that of palm oil. Overall, biodiesel production from WCO catalysed by $NaOH/Al_2O_3$ is both economically efficient (using low-cost feedstock) and technically justifiable (lower methanol/oil molar ratio and reaction time). Also, by using homogeneous catalysts such as NaOH , reaction occurs at mild conditions.

However, when the free fatty acid content in the oil is more than 2% , the formation of soap will cause problems during water washing and purification steps and will decrease the biodiesel yield.

3.5. Investigation of Glycerol quality by FT-IR spectra

What is shown in Figure5 is the FT-IR spectra of the crude glycerol compared to the commercial glycerol. The common peaks in the two spectra include following absorption bands:

The broad peak at approximately 3300 cm^{-1} and the small peak at around 930 cm^{-1} are due to the O-H stretching and O-H bending, respectively. Moreover, the C-H stretching bands occur in the region of 2900-2935 cm^{-1} and the C-O stretching appears as a small peak at 2100 cm^{-1}. However, compared to the commercial glycerol, the crude glycerol spectrum additionally shows one peak at 1558 cm^{-1} which is due to some impurities including COO^- of soap [30].

Table3: Comparison of experimental conditions & biodiesel yields by using different alumina-based heterogeneous catalysts and homogeneous NaOH

Author	Raw materials	Catalysts	Methanol/oil molar ratio	Catalyst amount	Reaction temperature	Reaction time	Biodiesel Yield
Arzemendi et al.[22]	Sunflower Oil	$NaOH/Al_2O_3$	12:1	2.06 %	50 ^oC	24 hr	99 %
Li et al.[24]	Soybean Oil	Eu_2O_3/ Al_2O_3	6:1	10 %	70 ^oC	8 hr	63.2 %
Xie et al.[25]	Soybean Oil	KI/ Al_2O_3	15: 1	2.5%	60 ^oC	8 hr	96 %
Boz et al.[26]	Canola Oil	KF/ Al_2O_3	15:1	3 %	60 ^oC	8 hr	99.6 %
Zabeti et al.[27]	Palm Oil	CaO/ Al_2O_3	12:1	6 %	65 ^oC	5 hr	98.6 %
Istadi et al.[28]	Palm Oil	$LiNO_3/ Al_2O_3$	6:1	1 %	60 ^oC	5 hr	80 %
Yap et al.[23]	Palm Oil	$NaOH/Al_2O_3$	15:1	3 %	60 ^oC	3 hr	99 %
Evangelista et al.[29]	Rice bran Oil	KI/ Al_2O_3	15: 1	5 %	60 ^oC	8 hr	95.2 %
This work	Waste cooking Oil	$NaOH/Al_2O_3$	7:1	1.5 %	70 ^oC	4 hr	> 92 %
This work	Waste cooking Oil	NaOH	6:1	1.5%	70 ^oC	3 hr	81%

3.6. Catalyst solubility

Biodiesel catalysed under different conditions was subjected to AAS analysis to determine the catalyst content. The result indicated that only 10% of $NaOH/Al_2O_3$ dissolved after completion of the transesterification. Most of the catalyst was preserved after reaction and easily separated by centrifugation. The dissolution of the heterogeneous catalyst could be partly attributed to the existence of fatty acid methyl esters [31].

4. Conclusion

Combination of utilizing the WCO as a low-cost feedstock as well as $NaOH/Al_2O_3$ as a heterogeneous base catalyst overcomes problems associated with homogeneous acid and alkali-catalysed biodiesel production such as saponification and purification. Moreover, this method offers a less pollutant, more environmentally friendly and economically profitable process for biodiesel synthesis. The elimination of the harmful disposal of WCOs, the removal of oil extraction step and refining step for biodiesel production and the reduction of large volume consumption of water in the purification of the crude product are the most important benefits of this process. The results of this work are comparable to the previous researches as the transesterification of WCO with methanol by $NaOH/Al_2O_3$ required less solid catalyst, methanol/oil molar ratio and reaction time compared to similar researches. The synthesised biodiesel has properties close to the international biodiesel standards and the crude glycerol has a reasonable quality.

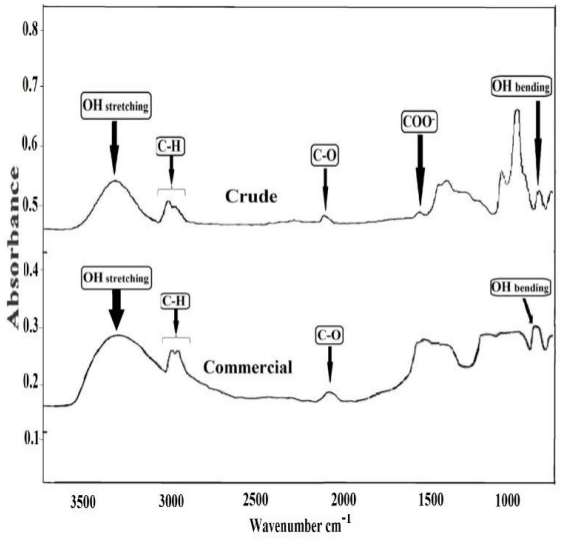

Figure5: Comparison of FT-IR Spectra of Crude glycerol and commercial glycerol

Acknowledgement

Tahereh Hajy Heidar would like to acknowledge the Department of Applied Chemistry, Islamic Azad University of North Tehran Branch for providing experimental facilities.

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