ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 12, No. 1 & 2 (2011) 95-101

Production of Biodiesel from Chicken Frying Oil

Emaad T. Bakir [1] and Abdelrahman B. Fadhil[2*]

[1]Department of Chemistry, College of Science, Tikrit University, Salahalddin, Iraq.
[2]Department of Chemistry, College of Science, Mosul University, Mosul, Iraq.

Received 01 July 2011, Revised 27 October 2011, Accepted 03 November 2011

Abstract

Chicken fried oil was converted into different biodiesels through single step transesterification and two step transesterification, namely acid-base and base–base catalyzed transesterification. Hydrochloric acid and potassium hydroxide with methanol were used for this purpose. The results showed that two step base catalyzed transesterification was better compared to other methods. It resulted in higher yield and better fuel properties. Transesterification of fried chicken oil was monitored by TLC technique and compared with that of the parent oil. Fuel properties of the products have been measured and found markedly enhanced compared to those of the parent oil. Also, the values satisfied the standard limits according to the ASTM standards. Blending of the better biodiesel sample with petro diesel was made using three volume percentages (10, 30 and 50% v/v). The results disclosed that blending had slight effect on the original properties of petro d*iesel.*

Keywords: Fried chicken oil; Single Step Transesterification; Two Step Transesterification; Fuel Properties; Blending Evaluation.

Introduction

Biodiesel is a nonpetroleum-based fuel defined as fatty acid methyl or ethyl esters derived from vegetable oils or animal fats and it is used in diesel engines and heating systems. Thus, this fuel could be regarded as mineral diesel substitute with the advantage of reducing greenhouse emissions because it is a renewable resource [1]. Biodiesel can be produced from vegetable oils or animal fats via transesterification. The transesterification is the reaction between oil or fat, with a short chain alcohol (methanol or ethanol), in the presence of a suitable catalyst, to produce biodiesel. Sodium or potassium hydroxide and sodium or potassium methoxide are used widely as catalysts in the transesterification reaction, as they give high production yield [1-2].

Oils of high free fatty acids content can be converted into biodiesel via dual step transesterification process. In the first step, the oil is treated by an acid dissolved in methanol to reduce FFA content, whereas in the second step the pretreated oil is transesterified with methanol in the presence of a base catalyst to form ester and glycerol [3]. Another dual step method has two successive base catalyzed transesterification. In the first step of this type of transesterification, oil is treated with the catalyst (KOH or NaOH in alcohol) at specific reaction conditions, then the glycerol layer is removed and another specified amount of the same catalyst is added [4].

Many studies investigated the availability of animal fats and waste oils for biodiesel production. Bhatti et.al [5] prepared biodiesel fuels from animal fats including beef tallow, mutton tallow and chicken fat. Ma et.al [6] used edible beef tallow as a feedstock for biodiesel preparation. Chung et.al [7] prepared biodiesel from duck tallow using methanol and potassium

---

*Corresponding Author Email: ***abdelrahmanbasil@yahoo.com***

hydroxide [7]. However, limited papers were reported about the use of chicken fat for biodiesel production. Awaluddin et.al [8] prepared biodiesel from waste chicken fat using CaO as heterogeneous base catalyst[8]. Alptekin and Canakci used chicken fat for biodiesel production. Chicken fat was pretreated with different acids to reduce the FFA content, then base catalyzed transesterification was conducted using potassium hydroxide and methanol [9].

The main objective of this paper was to study the possibility of biodiesel production from fried chicken oil through single step and two step transesterification. Two step transesterification included acid-baseand base-base transesterification. In both methods, hydrochloric acid and potassium hydroxide with methanol were utilized for this purpose. The work extended to include the assessment of the biofuel properties in comparison to the parent oil; monitoring the transesterification proceeding by TLC technique, and study the effect of blending of the biofuel with petro diesel on the fuel properties of the latter.

Experimental

Feedstock preparation

Chicken meal is one of the most favorite meals which is served at the local restaurants in Iraq. About 400 liters of fried chicken oil are generated per day within Mosul and Tikrit cities. Large amounts of fried chicken oil (FCO) is produced, accumulated and most often discarded into the drains which could be a serious threat for water resources. This oil could be an attractive and novel feedstock for biodiesel production. Prior to use, the oil was washed by warm distilled water with gentle stirring to remove vinegar and spices which are added as flavors to improve chicken taste. Then the oil was transferred into a separating funnel, and left for a day to remove the settled water. Afterwards, it was mixed with freshly activated $MgSO_4$ and filtered by a cloth filter to remove solid impurities and $MgSO_4$ particles. Finally, it was placed in a dark bottle and sealed to be used later for biodiesel production. The average molecular weight of this oil was calculated according to the following formula: $MW = 56.1 \times 1000 \times \frac{3}{SV - AV}$ [10], where SV is the saponification value and AV is the acid value.

Single step transesterification (SSTE)

Transesterification (TE) was conducted using a batch reactor which is a three neck round bottom flask connected with a condenser and was placed in a water bath to perform the reaction at the desired temperature. A known quantity of the oil and freshly prepared catalyst (KOH = 0.50 % w/w of oil dissolved in specified ratio of 6:1 MeOH: oil) were introduced into the reactor. The mixture was refluxed for 1h at (60°C) with stirring. After the reaction was over, the mixture was transferred into a separating funnel and allowed to settle for 24h. Two layers were obtained, the upper layer was the methyl ester (ME) and the lower was the glycerol. Glycerol layer was withdrawn, whereas the methyl esters layer was distilled under vacuum to recover the excess of methanol. Soon after distillation, it was washed by distilled water (DW) three times and was dried by distillation under vacuum, and was kept for further assessment and identification.

Two step base catalyzed transesterification (TSBCT)

The first step of this process is same as described in the one step operation. However, the second step is performed after separation glycerol and allowing methyl ester to settle for 2h. The same used quantity of methoxy reagent was added and the reaction was carried out under the same conditions as in the first step. Finally, the desired product was obtained as explained above.

Acid-base catalyzed transesterification (ABCT)

A known quantity of FCO was transferred into a three neck round bottom flask placed in water bath, and equipped with mechanical stirrer, thermometer, and condenser. The catalyst (1% HCl w/w, dissolved in methanol with a molar ratio of 6:1) was added into the flask. The mixture was heated to the specified temperature (60 °C) for 1h with stirring. After the TE was over, the mixture was cooled down and transferred into a separating funnel and left over night to separate into two layers. The glycerol layer (lower Layer) was withdrawn, whereas the biodiesel layer (upper layer) was distilled under vacuum to recover the unreacted methanol, then it washed with distilled water and finally purified by distillation under vacuum. The second step was conducted under similar conditions of that of SSTE. The yield of the produced biodiesel from both methods was calculated using following formula [11-13].

$$\text{Yield}\,\% = \frac{\text{Wt of the refined methyl ester produced}}{\text{Wt of oil used in the TE}}$$

Monitoring the transesterification

The FCO or BD was dissolved in n-hexane, and spotted on thin layer chromatography (TLC) silica gel plates (3X10cm glass). The plates were developed (eluted) with hexane/ethyl ether/acetic acid (80:20:1, vol/vol/vol) mixture. Then, the solvent was evaporated (dried) and the spots on the TLC plate were visualized by iodine vapor [13-14].

Measurement of fuel properties

Most of the fuel properties of the parent oil and the produced biodiesels were measured according to the ASTM standards and were listed in (Table 1). Iodine number (IN) was measured according to Hanus method [15].

Table 1. **Physicochemical properties of CFO.**

Property	Test Procedure	CFO
Density @ 16 °C (D)	ASTM D4052-91	0.9222
KV @ 40 °C cSt	ASTM D445	50.0
Flash Point °C (T_F)	ASTM D93	210
Pour Point (PP) °C	ASTM D 2500	6
Cloud Point (CP) °C	ASTM D2500	2
AV mg KOH / g (AV)	ASTM D664	2.80
(IN) mg I_2 / 100 oil	[Paquot,1979]	61
Refractive Index (RI)	D1747 – 09	1.467
Sapo. value (SV) mg KOH / g oil	ASTM D5555-95	191
Cetane Index (CI)	[Krisnangkura,1986]	61.15
HHV MJ/Kg	[Demirbas, 2008]	39.60
Distillation I_{BP}/ F_{BP}	ASTM D1160	270/350

Higher heating value (HHV) was determined depending on equations proposed by Demirbas [16]. Calculation of cetane index (CCI) is based on Krisnagkura equation [17] who proposed an equation for estimation of cetane index (CI) depending on the saponification and iodine values, recommending that the equation is not to be used for the parent oils, but only for methyl esters.

Blending evaluation

Blending of the better biodiesel sample with petro diesel (PD) was performed using three volume percentages (10, 30 and 50 % vol/vol). Afterward, some properties of the blends such as density, kinematic viscosity, flash point and pour point were measured.

Results and Discussion

Feedstock properties

The major physiochemical properties of FCO used in this study are given in (Table 2). Each value represents the result of at least two trials and the mean average was recorded.

Table 2. **Fuel properties of the produced biodiesels.**

Property	OSTE	TSBCT	ABCT	CFBD*
Yield%	87	92	90	87.40
D@ 16°C g/ml	0.8890	0.8822	0.8829	0.8830
KV@ 40°C mm^2/s	5.5	3.86	4.24	4.49
PP °C	3	2	2	2
T_F °C	190	158	162	171.8
AV mg KOH / g oil	0.40	0.09	0.13	0.22
IN mg I_2/ 100 oil	57	60	60	
RI	1.456	1.445	1.447	
SV mg KOH / g oil	193	195	195	
CCI	61.75	60.78	60.78	
HHV MJ/KG	41.99	41.23	41.41	40.17

****Chicken fat biodiesel from the Ref.[Alptekin and Canakci,2010]***

The average molecular weight of FCO was found to be 878. Acid value of CFO was 2.80 mg KOH/g oil. This value was lower than that reported by Alptekin and Canakci for chicken fat which was 26.89 mg KOH/g of fat. Density and KV of FCO were 0.9222 g/mL and 50 mm^2S^{-1} respectively. These values were also lower than those reported for chicken fat 0.932 g/mL and 59.20 $mm^2\ S^{-1}$ [9]. The IN and PP values of FCO were 61 mgI_2 /100 g oil and 6 respectively, where as CCI was 61.15. This indicates that FCO contains higher unsaturated fatty acid content compared to the other animal fats like beef tallow [18].

Transesterification of the raw oil

Base catalyzed transesterification is not recommended for feed stock of high FFA content (higher than 2 mg KOH/ g oil) for it deactivates the catalyst and causes to soap formation. As a result, yield decreases [9]. Thus, if the feedstock had an acid value higher than the recommended limits, this value must be reduced to 2 mg KOH/g oil if base catalyzed transesterification is intended to be used for BD production. One of the method used for the reduction of the FFA content of the feed stock is pretreatment of the feedstock with an acid (hydrolysis) followed by treatment with the base (transesterification) [19]. Another possible method for increasing the yield of the produced biodiesel is conducting the TE through two step base catalyzed transesterification. Gökhan and Selim produced BD from used cooking oil through TSBCT and found that TSBCT gave higher yield compared to SSTE [4]. Ali and Fadhil produced biodiesels from spent frying oil of fish through SSTE and TSBCT. They also found that TSBCT gave higher yield compared to SSTE [13].

It can be seen from (Fig. 1), that TSBCT gave higher yield than those obtained through SSTE and ABTE. In comparison to SSTE, higher free fatty acid content of the feed stock deactivates the catalyst through the formation of soaps or /and the concentration of the base was not sufficient to conduct the TE completely. As a result, the yield decreases. As regard ABTE, two washing steps by DW were used. Therefore, the possibility of soap formation is higher. Consequently, the yield decreases. Alptekin and Canakci prepared BD from chicken fat through acid-base transesterification. The maximum yield obtained by them was 87.40% [9], whereas that prepared by us through ABTE was 90%.

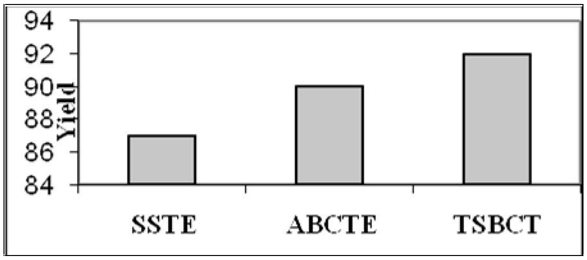

Figure 1. **Yields of the produced biodiesels.**

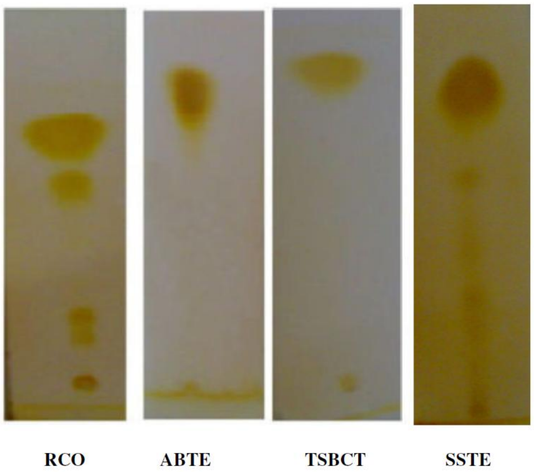

Figure 2. **TLC photographs of RCO and its biodiesels.**

Fuel properties of the produced fuels

To use the biodiesel as a fuel in the internal combustion engines, it must meet some specification according to the ASTM or European standards. Thus, some important properties for the produced biodiesels were measured and listed in (Table 2).

Density (D) is an important property that determines the quality of biodiesel. It is the weight of a unit volume of fluid. Fuel injection equipment operates on volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel [16]. Density of the produced fuels were lower than that of their respective oil. The values ranged from (0.8822 to 0.8890 g/ml). The viscosity of fuel is important for its flow through pipelines, injector nozzles and for atomization of fuel in cylinder [20]. These values were much lower than that of the parent FCO. The KV values ranged from 3.86 to 5.5 mm^2/s. An important disadvantage of BD is its poor low temperature flow properties. The pour point (PP) is the lowest temperature for movement of the sample under the prescribed conditions [20]. Pour points of the produced fuels were better in comparison to those of the parent oil. A temperature at which a fuel can produces sufficient vapor for spontaneous production of the hydrocarbon with the air in the presence of a spark is called flash point (T_F) [21]. Flash points for our samples were lower than that of their respective oil. The acid value can be used for monitoring the fuel quality. It can also be used to measure the FFA content in the biodiesel. The values were found much lower than those of the parent oil. It can be seen that BD samples produced through two step transesterification gave lower values than that produced through SSTE. This may mean that SSTE was not sufficient to reduce the FFA content of the oil. The property that can be used for measuring the unsaturation degree of fuel is defined as Iodine number (IN). This property greatly influences fuel oxidation and the deposits formed in the injector of the diesel engines [22]. Iodine numbers for the produced fuels ranged from 57 to 61 mg I_2/100 oil. Refractive Index (RI) at some reference condition i.e 20°C and 1 atm is another useful characterization parameter to estimate the composition and quality of petroleum fractions. RI is also used to estimate other physical properties such as molecular weight [21]. The RI values for the fraction were lower than that of the parent oil and ranged from (1.445 to 1.456). Saponification value SV represents milligram of potassium hydroxide required to saponify one gram of fat or oil. Saponification value for the feedstock FCO was 191 mg KOH/g oil, while those for the produced fuel ranged from 192 to 195 mg KOH/g oil. This indicate that the ester has lower molecular weight than the parent oil, since the higher the SV, the lower is the molecular weight [23]. The cetane index(CCI) was calculated through a simpler and more convenient experimental procedure by utilizing a cetane engine [17]. CCI for FCO was 61.15, whereas those of its BD fuels were between 60.78 and 61.75. The higher the CN, the more efficient is the ignition, and the higher is the engine performance. Higher heating value (HHV) is a measure of the energy produced when the fuel is burned completely [12]. The HHV values of the produced fuel were better than that of the parent oil and were between 41.23 and 41.99 million joules/kg.

Fuel properties of the biodiesels produced from FCO were lower than BD prepared from chicken fat. This is due to the higher methyl ester content of our fuels compared to that prepared from chicken fat. Encinar et.al reported that BD of the higher methyl ester content has better fuel properties such as D and KV[24]. Our findings were in accordance with that conclusion. Thus, it can be concluded that TSCBT is a practical method to produce biodiesel from FCO residue compared to other methods. However, the fuel properties of produced biodiesels were within the required limits specified by the ASTM standards.

Monitoring the transesterification reaction by TLC

Thin layer chromatography (TLC) was used for monitoring the progress of the TE using silica gel plates. It is fast and effective analytical technique. Therefore, many researchers have used this technique for monitoring the TE of oils or fats [25-29]. It is obvious from these plates which are depicted in Fig. 2 that the BD produced through SSTE showed many spots, indicating the presence of some impurities, whereas biodiesels produced through TSTE gave one spot indicating complete conversion into the corresponding methyl ester.

Distillation curve

Characterization of the volatility of fuel and its tendency to form soot and smoke is considered as an important indicator for long-term analysis of fuel performance relating to optimization and design engines and can be specified by a distillation curve. It is essential for biodiesel and its blends since biodiesel is oxygenated fuel which has the distinct difference to conventional diesel [30]. Distillation curves of the produced fuels as well as the parent oil are depicted in (Fig. 3) which show that the produced biodiesels had lower initial boiling point (IBP) than its respective parent oil. This can also be used as an extra evidence for the TE of the parent oil into its corresponding methyl esters. Petro diesel has lower molecular mass than BD, thus it is more volatile. The initial boiling point of our fuels were lower than those reported for BD fuel from waste cooking oil [30].

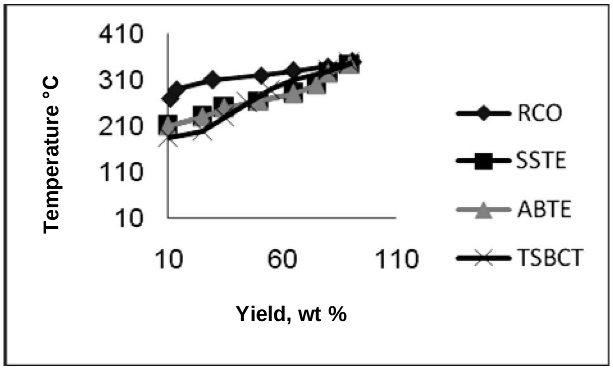

Figure 3. **Distillation curves of RCF and its biodiesels.**

Blending Evaluation

Biodiesel has some defects such as higher density, viscosity, flash point, and pour point. On the other hand, one of the most important disadvantages of PD is its high sulphur content which participates in environmental pollution. Thus, blending of petro diesel with specified percentages of BD decreases their disadvantages. It can be observed from (Table 3) that the values of D, KV, T_F and pp of PD increased with the increment of BD content in the blends. This is for the high molecular mass of BD compared to PD. Similar results were observed in our previous studies using biodiesels from spent frying oil of fish[13]. Similar results were also reported in the literature [31].

Table 3. **Fuel properties of PD+ BD blends.**

Property	PD	BD produced via TSBCT		
		10%	*30%*	*%50*
D @ 16 °C g/ml	0.8300	0.8332	0.8449	0.8501
KV @ 40°C mm^2/s	2.04	2.85	3.27	4.11
T_F °C	64	65	66	69
PP	-16	-14	-13	-11

Conclusions

Large amount of fried chicken oil from restaurants leftovers are thrown into the drains, that it could be a serious threat for the water sources. Therefore such waste could be an attractive and novel feedstock for biodiesel production. Thus, it was converted into biodiesel fuels through single step transesterification and two step transesterification (acid-base and base-base catalyzed transesterification). The results disclosed that the fuel properties of FCO have been markedly enhanced due to these processes. Also, it was found that TSBCT was more reliable than other methods. It resulted in higher yield and better fuel properties. In addition, blending of the better biodiesel sample in specified volume percentages with petro diesel had limited effects on the studied properties of the latter.

Acknowledgements

The authors express their sincere thanks for Chemistry Department, College of Science, Mosul University, Mosul, Iraq for providing facilities that made this work successful.

References

1. J. P. Zlatica, *Fuel*, 87 (2008) 3522.
2. P. Felizardo, M. J. Neiva Correia, I. Raposo, J. F. Mendes, R. Berkemeier and J. M. Bordado, *Waste Manage*, 26 (2004) 87.
3. H. M. El-Mashad, R. Zhang and J. A. Roberto, *Biomass Engineering*, 99 (2008) 220.
4. Ç. Gökhan and K. Selim, *Fuel Processing Technology*, 89 (2008) 118.
5. H. N. Bhatti, M. A. Hanif, M. Qasim and A. Rehman, *Fuel*, 87 (2008) 2961.
6. F. Ma, L. D. Clements and M. A. Hanna, *Ind. Eng. Chem. Res.* 37 (1998) 3768.
7. K. H. Chung, J. Kim and K. Y. Lee, *Biomass Bioenergy*, 33 (2009) 155.
8. A. Awaluddin, Saryono, A. Prayitno and T. A. Amri, International Conference on Energy and Sustainable Development: Issues and Strategies, (2010) 1.
9. E. Alptekin and M. Canakci, *Fuel*, 89 (2010) 4036.
10. A. George, Z. Ypatia, S. Stamoulis and K. Stamatis, *Energies*, 2 (2009) 365.
11. U. Rashed and F. Anwar, *Energy Fuels*, 22 (2008) 1307, 1310.
12. U. Rashed and F. Anwar, *Fuel*, 87 (2008) 266.
13. L. H, Ali and A. B. Badhil, *Accepted Energy Sources, Part A*, (2010).

14. S. Hawash N. Kamal F. Zaher O. Kenawi, and G. El Diwani, *Fuel*, 88 (2009) 580.
15. C. Paquot, 6th edition, Pergomon press: (1979) 1.
16. A. Demirbas, *Fuel*, 87 (2008) 1744.
17. K. Krisnangkura, *JAOCS*, 3 (1986) 55.
18. A. B. Fadhil, *Arabian Journal for Science and Engineering*, (2011).
19. A. S. Ramadhas, S. Jayaraj and C. Muraleedharan, *Fuel*, 84 (2005) 335.
20. U. Faizan, N. Asia, H. Ishtiaq and B. Asghari, *African Journal of Biotechnology*, 8 (2009) 3289.
21. M. R. Riazi, ASTM, 100 Barr Harbor, West conshohoken, P.A, (2005) 1948, USA,1-421.
22. J. M. Encinar, J. F. González and A. Rodríguez-Reinares, *Fuel Processing Technology,* 88 (2007) 513.
23. A. H. Molla, C. Saha, M. S. Ahsan, S. M. Talukder and M. T. Alam, *Univ. J. Zool. Rajshahi*, 26 (2007) 21.
24. J. M. Encinar, J. F. Gonzalez and A. Rodrıguez-Reinares, *Ind. Eng. Chem. Res*., 44 (2005) 5495.
25. K. Vinod, J. Babu, W. R. Pramod, M. Abin and J. Firdaus, *J. Chem. Pharm. Res*., 3 (2011) 226.
26. N. Dalvi 1, P. E. Funde, R. D. Pokharkar and K. C. Mohite, International Conference on Renewable Energies and Power Quality (ICREPQ'09) Valencia (Spain), 15th to 17th April, (2009).
27. S. Yuji, W. Yomi, S. Akio and T. Yoshio, *Journal of Molecular Catalysis B: Enzymati*, 17 (2002) 133.
28. F. Francisco, P. Santosa, Sueli Rodriguesb, and A. N. F. Fabiano, *Fuel Processing Technology*, 90 (2009) 312.
29. K. Pankaj, M. R. Suseela and T. Kiran, *Asian J. Exp. Biol. Sci.*, 2 (2011) 493.
30. N. Phan and T. M. Phan, *Fuel*, 87 (2008) 3490.
31. M. J. Colaco, C. V. Teixeira and L. M. Dutra, *Fuel*, 89 (2010) 3745.