ISSN-1996-918X

Pak. J. Anal. Environ. Chem. Vol. 13, No. 1 (2012) 09-15

Biodiesel Production from Spent Fish Frying Oil Through Acid-Base Catalyzed Transesterification

Abdalrahman B. Fadhil* Mohammed M. Dheyab, Kareem M. Ahmed
and Marwa H. Yahya[a]

Department of Chemistry, College of Science, Mosul University, Mosul, Iraq

Received 30 November 2011, Revised 06 June 2012, Accepted 12 June 2012

Abstract

Biodiesel fuels were prepared from a special type of frying oil namely spent fish frying oil through two step transesterification viz. acid-base catalyzed transesterification. Hydrochloric acid and potassium hydroxide with methanol were used for this purpose. The oil was pre-treated with (1.0 wt% HCl) and methanol to reduce free fatty acids content of the oil. Then, conditions of the base catalyzed step such as base concentration, reaction temperature, methanol to oil molar ratio and reaction time were optimized. The study raveled that, 0.50% KOH w/w of oil; a 6:1 methanol to oil molar ratio; a reaction temperature of 60°C and a duration of 1h were the optimal conditions because they resulted in high biodiesel yield. Fuel properties of the products were assessed and found better than those of the parent oil. Furthermore, they met the specified limits according to the ASTM standards. Thin layer chromatography was used as a simple technique to monitor the transesterification of the oil. Blending of the optimal biodiesel sample with petro diesel using specified volume percentages was done as well. The results indicated that biodiesel had slight effect on the values of the assessed properties.

Keywords: Spent fish frying oil; Two step catalyzed transesterification; Acid-base catalyzed transesterification (ABCE); Biodiesel.

Introduction

Biodiesel can be defined as the alkyl monoesters of fatty acids from vegetable or animal fats. It can be used as an alternative for petro diesel for it is renewable, non toxic and biodegradable fuel [1]. Biodiesel have been produced from many vegetable oils [2-6]. However, production of biodiesel from edible oils competes with the use of those oils as food resource for human being. Thus, finding cheaper and non edible oils for biodiesel production is an important target. Therefore, some non edible oils and frying oils have been gained more attention as feedstocks for biodiesel production [7-10]. However, oils of higher free fatty acid (FFA) content cannot be transesterified in the presence of an alkaline base catalyst for it leads to catalyst deactivation and soap formation. As a result, the FFA content should be reduced [11]. A dual step transesterification namely acid-base transesterification (ABTE) was used to reduce the high FFA contents of oils or fats. The oil is pretreated with an acid dissolved in methanol, whereas the second step is base catalyzed transesterification in which oil reacts with methanol in the presence of an alkaline catalyst to form ester and glycerol [12].

The present study investigated the possibility of using a special type of frying oil, namely spent fish frying oil as a feedstock for biodiesel production via two step transesterification, namely acid-base catalyzed transesterification using hydrochloric acid and potassium hydroxide with methanol. Acid step was used to reduce fatty acid content of the oil, and the

---

*Corresponding Author Email: abdelrahmanbasil@yahoo.com conditions of the base catalyzed step were then optimized. The properties of the produced fuels were assessed. Furthermore, blending of the optimum biodiesel sample was made on volume basis with petro diesel.

Experimental

Feedstock Preparation and materials

Spent fish frying oil (SFFO) was used as a precursor for biodiesel (BD) production. At first, the oil was mixed with freshly activated magnesium sulphate ($MgSO_4$) and left for a day to remove any moisture. Then it was filtered under vacuum to remove any solid impurities and $MgSO_4$ particles. Finally, it was kept in sealed container for further use and assessment. Mean molecular weight of the SFFO was determined using the following formula [13]:

$$MW = 56.1 \times 1000 \times 3/(SV–AV) \ldots\ldots\ldots\ldots\ldots (1)$$

Where SV is the saponification value and AV is the acid value. Methanol (reagent grade) was purchased from BDH. Potassium and sodium hydroxides (KOH, NaOH) were supplied from Merck, while hydrochloric acid was supplied from Fluka. Chemicals were used without any further purification.

Biodiesel preparation

In this study, biodiesel fuels were prepared from SFFO via two routes, as follows:

Acid catalyzed transesterification

Transesterification (TE) of SFFO was carried out in a laboratory-scale setup. A 1000 g of SFFO was preheated to 60°C. Next freshly prepared catalyst solution (1% HCl by weight of oil dissolved in methanol at a molar ratio of 6:1 of oil) was poured into the reactor which was a three necks round bottomed flask provided with a mechanical stirrer, thermometer and a condenser, and was placed into a water bath. The TE was conducted at (32 or 60°C) for 1h with continuous stirring (600 rpm). After the reaction was over, the mixture was left to cool down, then the mixture was transferred into a separating funnel and left overnight to obtain two layers. Glycerol layer (lower layer) was withdrawn, and the higher layer (methyl ester layer) was distillated under vacuum to recover excess methanol, then it was washed by distillated water (DW). Finally, it was mixed with a freshly activated sodium sulphate (Na_2SO_4) and filtered to be used later in the next step [14].

Alkaline Catalyzed transesterification

For batches, 50g of the acid treated oil (ATO) was poured into a 250 mL three necks rounded bottom flask equipped with a mechanical stirrer, and a condenser, and was placed in a water bath. Next, freshly prepared catalyst solution (KOH % by w/w of oil dissolved in methanol at a ratio of 6:1 MeOH: oil) was introduced into the reactor. The mixture was refluxed for 1h with continuous stirring (600 rpm) at different temperatures namely 32°C or 60°C. After the reaction was over, the methyl ester layer was purified as explained above. The percent yield was calculated on a weight basis with respect to oil used in TE [15].

$$\text{Yield}\,\% \frac{\text{Wt of the refined methyl esters}}{\text{Wt of oil used}} \times 100$$

Biodiesel fuels assessment

Fuel properties of the parent oil and its biodiesels were determined according to the ASTM standards. These including density (D) at 16°C (ASTM D4052-91), Kinematic viscosity (KV) at 40°C (ASTM D445), flash point (T_F) (ASTM D93), cloud and pour points (CP and PP) (ASTM D 2500), refractive Index (RI) @ 20°C (D1747-09), Conradson carbon residue (CCR%) % (D 4530), and saponification value (SV)(ASTM D5555-95). Iodine Number (IN) was measured according to Hanus method [16]. Higher Heating Value (HHV) was determined depending on equations proposed by Demirbas [17]. The calculated cetane index (CCI) is based on Krisnagkura equation [18]:

$$CCI = 46.3 + (5458/SV) – (0.225\, IN) \ldots\ldots\ldots\ldots (1)$$

Where, SV is the saponification value and IN is the iodine number.

Blending evaluation

The optimum BD sample was blended with petro diesel in specified volume percentages (10, 30 and 50% vol/vol). The blends were referred to as (B_{10}, B_{30} and B_{50}) respectively. Some properties of these blends such as (density, kinematic viscosity, flash point and pour point) were assessed according to the ASTM protocols.

Monitoring the transesterification

The thin layer chromatography (TLC) was used as a rapid and simple technique for monitoring the TE of SFFO. Silica gel plates (3X 10 cm glass) were washed with methanol. The plates were then activated in an oven at 110°C for 2h. The oil or BD was dissolved in *n*- hexane, and spotted on the TLC silica gel plates. Then, the plates were developed (eluted) with a mixture of hexane/ethyl ether/ acetic acid (80:20:1, vol/vol/vol). After the fractionating, the solvent was evaporated and the spots on the TLC plates were visualized by iodine vapor [19].

Results and Discussions

Feedstock properties

Fried fish meal is one of the popular meals that served at local restaurants over all Iraq. As a result, large amounts of spent fish frying oil (SFFO) are left over. The fate of these oil finishes in the drains which comprises a serious contamination for the environment. This oil was used as a novel precursor for biodiesel preparation. The major physicochemical properties of SFFO are given in (Table1). Each property was measured in duplicate and only the mean was recorded. Mean molecular weight of SFFO was determined before the initiation of the TE reaction, and found 998. This higher value of molecular weight may be due to contamination from animal oil of the fried fish. Properties of SFFO indicate that this oil is good starting material for biodiesel production. The IN of SFFO was 106 mgI_2/100 g oil, whereas, pour point was -8. Thus, one can conclude that SFFO has high unsaturated fatty acid content. SV of SFFO is 174, whereas its AV is 5.41 mg KOH/g oil.

Table1. **Major physicochemical properties of SFFO.**

Property	Method	SFFO
Density @ 15.6 (D)	ASTM D4052-91	0.9291
Kinematic Viscosity @ 40 °C (KV)	ASTM D445	29.14
Flash Point (T_F)	ASTM D93	250
Acid Number mg / g (AV)	ASTM D664	5.41
Saponification value (SV)	ASTM D5555-95	172
Iodine Number mg I_2 / 100 (IN)	Hanus method	106
Cloud Point °C (CP)	ASTM D 2500	1
Pour Point °C (PP)	ASTM D 2500	-7
Distillation Curve (IBP/FBP)	ASTM D1160	175/350
Conradson Carbon Residue (CCR %)	ASTM D4530	0.60
Cetane Index (CI)	(Willard,1997)	32

Esterification of SFFO

Acid catalyzed step (ACS) was used to reduce free fatty acid content of the parent oil. The pre-esterification of SFFO was conducted at two different temperature namely room temperature (32°C and at 60°C) to find out the optimal temperature for the esterification. It was found that performing the esterification at 60°C resulted in higher yield and lower acid value. As a result, oil pre-esterified at 60°C was used as a precursor for the next step. The acid value of the parent oil was reduced to 1.97 mg KOH/g oil which corresponds to (0.985 %) FFA. This value is lower than that recommended for alkaline transesterification.

Alkaline transesterification of SFFO

Effect of base concentration and reaction temperature

Transesterification of SFFO was conducted using various concentrations of KOH (0.25, 0.50, 0.75 and 1.0% w/w of oil). In all experiments, a 6:1 methanol to oil molar ratio, 32 or 60 °C reaction temperature, 1h reaction duration and 600 rpm stirring rate were chosen. (Table 2) lists yields and the fuel properties of the produced BD samples using different concentrations of KOH. It was found that the highest BD yield

Table 2. **Effect of KOH concentration and temperature on the yield and properties of biodiesel.**

property	SFFO/32°C				SFFO /60°C			
	KOH%				KOH%			
	0.25	**0.50**	**0.75**	**1.0**	**0.25**	**0.50**	**0.75**	**1.0**
Yield %	70.22	88.80	91.83	90.11	81.84	94.0	91.08	90.98
D@ 16°C ASTM D4052-91	0.8977	0.8972	0.8888	0.8902	0.8927	0.8802	0.8827	0.8856
KV@40°C mm^{2}s^{-1} ASTM D445	4.61	4.12	4.00	4.10	3.15	2.78	3.23	3.27
(CP) °C ASTM D 2500	0.0	-1	-1	0.0	-1	-2	-2	-1
(PP) °C ASTM D 2500	-5	-5	-6	-5	-6	-7	-7	-7
T_F) °C ASTM D93(	170	158	165	160	160	157	160	165
AV mg KOH/g ASTM D664 l	0.52	0.45	0.41	0.42	0.51	0.44	0.45	0.45
SV ASTM D5555-95	185	187	185	186	187	191	187	188
IN mgI_2/100g oil	103	102	104	101	101	105	101	103

(94%) was obtained with a 0.50% KOH w/w of the oil. After this concentration, a decline in the yield was observed. This is for higher concentrations accompanied by soap formation. As a result yield decreases [11]. It can also be seen from (Table 2) that performing the reaction at (60°C) resulted in higher BD yield. This means that reaction rate increases with increasing reaction temperature. Our conclusion is in accordance with results reported by some investigators [15].

Effect of the molar ratio of methanol on the transesterification of SFFO

The TE of SFFO was conducted using different molar ratios of methanol (3:1, 6:1, 9:1 and 12:1), while other parameters were kept constant (0.50% KOH, 60°C,1h and a stirring rate of 600 rpm). (Fig. 1) displays the effect of methanol to oil molar ratio on the yield of the produced biodiesel samples. It was observed that maximum conversion (94%) was obtained at a molar ratio of 6:1. A significant reduction in the BD yield was observed (91.12%) at a ratio of 12:1. This is because high molar ratio of alcohol to oil interferes with the separation of glycerin because the solubility increases. Consequently, separation of the products becomes harder. As a result yield decreases [20].

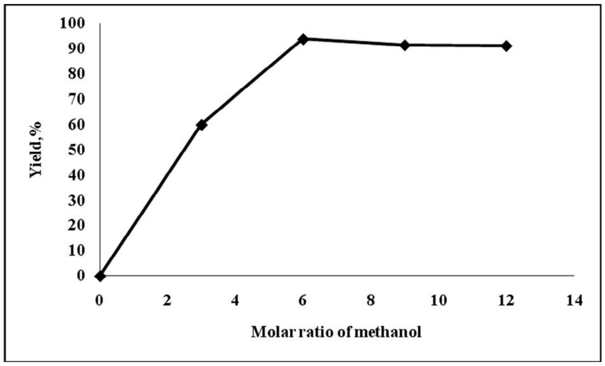

Figure1. **Effect of the molar ratio of methanol.**

Influence of the reaction time

Transesterification of SFFO was performed using various durations (30,60,90 and 120 min.) as depicted in (Fig. 2), keeping other parameters constant (0.50% KOH, a 6:1 methanol ratio, 60°C and a stirring rate of 600 rpm). It is clear from (Fig.2) that the highest conversion (94%) was obtained at 60 minutes. A dropping was observed after 60 minutes. The probable reason could be that, longer reaction time may lead to hydrolyze of some of the produced esters (reverse reaction of transesterification or/and increases soap formation at the expense of the TE; consequently, the yield decreases [21].

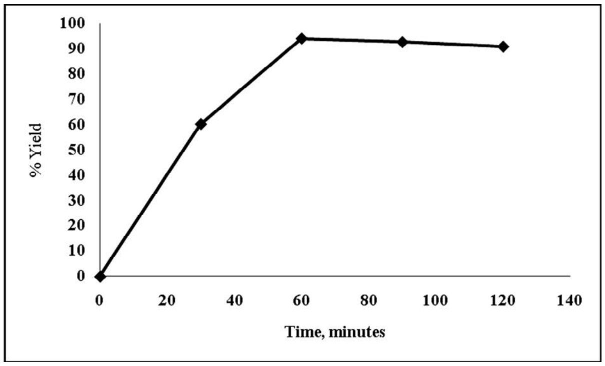

Figure 2. **Effect of the reaction time.**

Fuel properties

Biodiesel properties must meet certain specifications to be used as a fuel in the internal combustion engines. In this study, the fuel properties were measured according to the ASTM protocols. It can be seen from (Table 2) that fuel properties of SFFO have been markedly enhanced due to ABCT. Density values ranged between (0.8802 to 0.8977 g/mL). Kinematic viscosity values of the produced samples ranged from (2.78 to 4.61 mm^2s^{-1}). Our values were lower than some reported BD fuels prepared from used cooking oil (4.77, 4.80 and 4.89 mm^2s^{-1}) [22-24]. Flash point can be used as a measure of the volatility of a fuel. Flash point values of the produced fuels were higher than that of the parent oil. The values ranged from (157 to 170). Our value were also lower than some BD fuels reported in the literature (176 and 188)[23,25].The higher the flash point, the safer is the fuel [15]. Flow properties including cloud point and pour points of the produced fuel were also enhanced due to the TE process, so that the values of cloud points ranged from (0 and -2), whereas those for pour points from (-5 to -7). Such values could be a good indicator that BD prepared by us is suitable for use in cold weather conditions prevailing in northern Iraq in winter. The IV is a measure of the average amount of unsaturation of fats and oils. The IN values for the produced fuels ranged from (101 to 105). Acid value of SFFO was (5.41 mg KOH/g oil). This value reduced to (1.97 mg KOH/g oil) after the esterification. However, after base catalyzed transesterification the values ranged from (0.41 to 0.52 mg KOH/ g). Higher heating vale (HHV) of the produced fuels ranged from (40.89 to 41.58 million joules/kg). Saponification values of the produced fuels ranged from (185-191 mg KOH/ g oil). However, the higher the SV, the lower the molecular weight is [26]. Cetane index of the produced fuels were determined according to equation proposed by Krisnagkura [18]. Cetane index of the produced fuels were between (51.25 and 52.91). However, these values were close to that reported for ASTM No. 2. Diesel (53.20) [27]. It can be seen from (Tables 2-4) that fuel properties of the produced biodiesels have been markedly enhanced compared to their parent oil after ABCT. Besides, the properties met the specified limits according to the ASTM standards. Thus one can conclude that biodiesels based on SFFO can be used as fuel in diesel engines without any modification of the engine.

Table 3. **Effect of the molar ratio of methanol.**

MeOH Ratio	D@ 16°C ASTM D4052-91	KV@40°C mm^2s^{-1} ASTM D445	T_F °C ASTM D93
1:3	0.8903	3.98	175
1:6	0.8802	2.78	157
1:9	0.8880	2.82	170
1:12	0.8888	2.84	158

Table 4. **Effect of the reaction time.**

T_F °C ASTM D93	KV@40°C mm^2s^{-1} ASTM D445	D@ 16°C ASTM D4052-91	Time minutes
175	3.60	0.8988	**30**
157	2.78	0.8802	**60**
170	3.55	0.8892	**90**
156	3.69	0.8921	**120**

Distillation Curves

Distillation curves of petro diesel, SFFO and its optimum BD fuel were depicted in (Fig. 3). It is evident from this figure that BD had lower initial boiling point (IBP) than its respective parent oil which is rather expected, and this may be used as an extra evidence for the TE reaction. IBP of our BD was lower than that of BD fuel prepared from used frying oil (213°C) [24]. However, higher IBP compared to PD was due to higher volatility and lower molecular weight of the former [28].

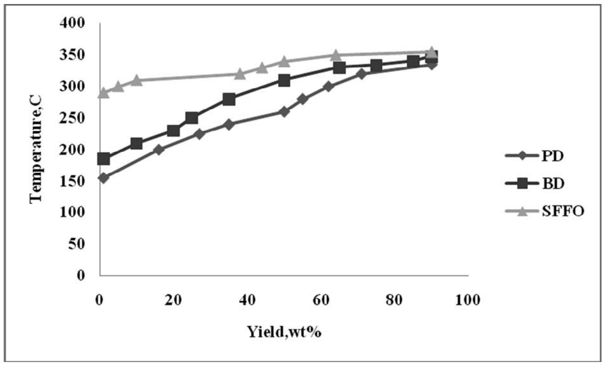

Figure 3. **Distillation curves (ASTM D1160) of SFFO and its BD fuel.**

Monitoring the transesterification

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 [29-33]. It is clear from TLC plate which is depicted in (Fig. 4) that the parent oil showed many spots, whereas BD sample showed one spot. The spot in the BD indicating that the triglycerides has completely disappeared after the TE of the parent oil. This means that our handling was successful to convert SFFO into its corresponding ester.

Blending of biodiesel and petro diesel

In this study, the optimum BD fuel was blended with PD in different volume percentages (10, 30 and 50 % v/v). Then some properties of the blends were assessed like density, kinematic viscosity, flash point and pour point. (Table 5) indicates that the fuel properties of PD increased with the further increase of BD ratio in the blends. This is because BD has higher molecular mass compared to PD. Similar results were observed in our previous studies [14, 34-35]. Furthermore, our results came in accordance with those reported by some authors [17, 21].

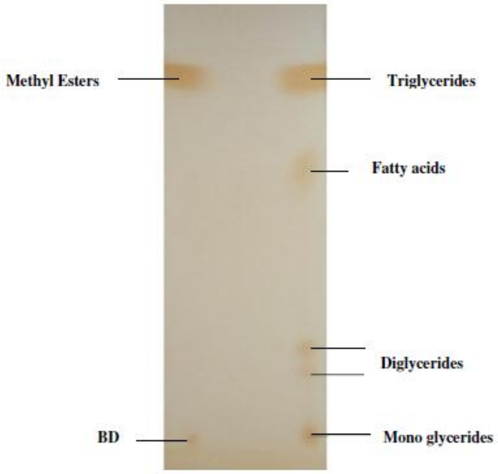

Figure 4. **TLC of SFFO and its BD fuel.**

Table 5. **Properties of (BD + PD) blends.**

PP °C ASTM D 2500	T_F °C ASTM D93	KV@40° C mm^2s^{-1} ASTM D445	D@ 16°C ASTM D4052-91	Property
-16	64	2.14	0.8300	PD
-16	66	2.78	0.8398	B_{10}
-14	68	3.55	0.8434	B_{30}
-11	70	3.69	0.8564	B_{50}

Conclusion

Large amounts of used frying oil are generated at restaurants. Discarding these oils into water drains comprise a serious threat to water resources. Consequently, a solution must be found to diminish the risks of such contaminates. In the present study, spent fish frying oil was chemically converted to biodiesel fuels via two step transesterification, namely acid-base catalyzed transesterification using hydrochloric acid and potassium hydroxide with methanol. After acid treatment of the oil, the conditions of the base catalyzed step were optimize. However, the results indicated that a (0.50% KOH by weight of oil) was the optimal base concentration, a 6 : 1 molar ratio of methanol was the best choice, 60°C was the optimal temperature and a duration of 1h was enough to give the highest conversion. Blending of the optimum biodiesel sample with petro diesel using specified volume percentages had slight effects on the assessed properties of the latter.

References

1. M. Canakci, *Bioresource Technology*, 98 (2007) 183.
2. U. Rashid and F. Anwar, *Energy & Fuels*, 22 (2008) 1306.
3. O. J. Alamu, M. A. Waheed and S. O. Jekayinf, *Fuel*, 87 (2008) 1529.
4. J. M. Encinar, J. F. Gonzalez Rodriguez J. J. and A. Tejedor, *Energy Fuels*, 16(2002) 443.
5. M. Mittelbach and S. Gang, *JAOCS*, 78 (2001) 573.
6. Z. J. Predojevic, *Fuel*, 87 (2008) 3522.
7. A. V. Tomasevic and S. S. Marinkovic, *Fuel Process Technol*, 81 (2003) 1.
8. S. M. A. Sujana, S. Hiratab and T. Minowa, *Bangladesh J. Sci. Ind. Res.*, 44 (2009) 347.
9. L. C. Meher, S. S. Vidya and S. N. Naik, *Bioresource Technology*, 97 (2006) 1392.
10. N. Malaya, L. C. Meher, S. N. Naik and L. M. Das, *Biomass and Bioenergy*, 32 (2005) 354.

11 Y. C. Sharma, B. Singh, and S. N. Upadhyay, *Fuel*, 87 (2008) 2356.

12. H. M. El-Mashad, R. Zhang and J. A. Roberto, *Biomass Engineering*, 99 (2008) 221.
13. H. Zhu, Z. Wu, Y. Chen, P. Zhang, S. Duan, X. Liu and Z. Mao, *Chin. J. Catal*, 27 (2006) 392.
14. A. B. Fadhil, M. M. Dheyab, L. A. Saleh, Accepted for publication in Energy Sources, Part A: Recovery, Utilization and Environmental Effects, DOI: UESO- (2011). 2010.
15. U. Rashed and F. Anwar, *Fuel*, 87 (2008) 266.
16. C. Paquot, "Standard methods for the analysis of oils, fats and derivatives", 6th, edition, Pergomon press, (1979) 1.
17. A. Demirbas, *Fuel*, 87 (2008) 1744.
18. K. Krisnangkura, *JAOCS*, 3 (1986) 55.

19 S. Hawash, N. Kamal, F. Zaher, O. Kenawi, and G. El Diwani, *Fuel*, 88 (2009) 584.

20. J. M. Encinar, J. F. Gonzalez and A. Rodrı´guez-Reinares, *Ind. Eng. Chem. Res*, 44 (2005) 5495.
21. D. Y. C. Leung, Y. Guo Fuel Processing Technology, 87 (2006) 888.
22. B. Freedman, E. H. Pryde and T. L. Mounts, *JAOCS*, 61 (1984) 1640.
23. J. M. Encinar, J. F. González and A. Rodríguez-Reinares, *Fuel Processing Technology*, 88 (2007) 519.
24. A. N. Phan and T. M. Phan. *Fuel*, 87 (2008) 3494.
25. M. Cetinkaya and F. Karaosmanoglu, *Energy Fuels*, 18 (2004) 1890.
26. A. H. Molla, C. Saha, M. S. Ahsan, S. M., Talukder and M. T. Alam, *U iv. J. Zool. Rajshahi*, 26 (2007) 23.
27. C. Y. Lin and R. J. Li, *Fuel Processing Technology*, 90 (2009) 133.
28. R. A. Candeia, M. C. D. Silva, J. R. Carvalho Filho M. G. A. Brasilino, T. C. Bicudo, I. M. G. Santos and A. G. Souza, *Fuel*, 88 (2009) 742.
29. K. Vinod, J. Babu, W. R. Pramod, M. Abin and J. Firdaus, *J. Chem. Pharm. Res.*, 3 (2011) 226.
30. N. Dalvi, P. E. Funde, R. D. Pokharkar and K. C. Mohite, International Conference on Renewable Energies and Power Quality (ICREPQ. 09) Valencia (Spain) (2009) 15th to 17th April,
31. S. Yuji, W. Yomi, S. Akio and T. Yoshio, Journal of Molecular Catalysis B: Enzymatic, 17 (2002) 133.
32. F. Francisco, P. Santosa, S. Rodriguesb and A. N. F. Fabiano, Fuel Processing Technology, 90 (2009) 312.
33. P. Kumar, M. R. Suseela and K. Toppo, *Asian J. Exp. Biol. Sci.*, 2 (2011) 493.
34. L. H. Ali and A. B. Fadhil, Accepted for publication in Energy Sources, Part A: Recovery, Utilization and Environmental Effects (2011). DOI: UESO-2010-0235
35. A. B. Fadhil, Accepted for publication in The Arabian Journal for Science and Engineering, (2011). DOI: AJSE-D-10-00060R2.