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Research Article

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Biodiesel production by Base-catalyzed trans-esterification of sunflower and date seed oils using methanol: Optimization of parameters

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ABSTRACT

In this study, the optimized experimental conditions to obtain the partial trans- esterification of sunflower and palm kernel oil with methanol, using KOH and NaOH as an alkaline catalyst, for biodiesel producing (methyl esters) were performed. The effect of various parameters including reaction temperature (40-60ºC), reaction time (30-60 min), quantity of catalyst (0.5-1.25 %wt.), and methanol on oil ratio (1:3-1:6) on the efficiency of biodiesel production were tested. Maximum biodiesel (98.12%) was produced by KOH catalyst at reaction time of 60min, temperature 60 ºC and methanol to oil ratio of 4:1. The optimum conditions for biodiesel production and biodiesel properties for the both catalysts were determined based on 14214EN and ASTM D6751 methods. Results showed that the best amount of catalysts to produce the biodiesel using sunflower oil and palm kernel oil was obtained 0.75 wt. %. in both catalysts.

Keywords: Biodiesel, Sunflower oil, Palm oil, Trans-esterification, GC-FID

INTRODUCTION

The great portion of the world desires energy has fossil sources (oil, coal and natural gases) with some difficulties like their limited resources and type of pollutions [1]. Biodiesels can produce from renewable sources such as vegetable oils, animal fats and waste oils [2]. In comparison to fuel oil, they are typically non-toxic, non-flammable, domestic, and biodegradable with high fat, low sulfur and aromatics contents, as well as very low exhaust gas emissions and energy equivalent to the energy range [3-6]. Biodiesel in pure form or as a mixture with diesel fuel can be used to reduce air pollutants [7].

Biodiesel fuel from renewable sources such as vegetable oils and animal fats are produced in the presence of alcohol and catalyst. It can be produced from primary sources (oil and fats) such as soybean [8, 9], crude palm, cotton seed [10], jatropha [11], sesame [12,13] oils, the fat goats [14], chicken fat or fat obtained from chicken feathers [15-17], and waste edible oils [18]. Most biodiesels are produced during the process of methyl ester (trans- esterification). The biodiesel is a chemical reaction between vegetable oil methyl esters (mainly tri glycerides) and short-chain alcohols (methanol and ethanol) [19]. Methyl esters process for the production of biodiesel is performed in the presence of various catalysts. The catalyst used in the esterification process can be base-catalysts (KOH and NaOH) [19, 20], acid-catalysts (H_2SO_4, HCl) [21, 22], and enzymes [23-26]. Amongst, the time and cost of the alkaline and acid catalyst esterification reaction are less than the enzyme catalyst [27]. Several studies have been showed the biodiesel production process affected by same parameters such as type and amount of catalyst, temperature and reaction time as well as the ratio of methanol to oil [28, 29]. In current study, the production of biodiesel from palm kernel and sunflower oils with a mix ratio of 1:1 by using base-catalyst and methanol esterification process was carried out. Furthermore, the effect of various variables on the production of biodiesel, such as the type and amount of catalyst, temperature and reaction time, and the ratio of methanol to oil were considered.

EXPERIMENTAL SECTION

Chemicals
All chemicals and solvents and the standards used for extraction and analysis of plant were analytical grade and purchased from Sigma (MO, USA) and Merck (Germany) Chemical Companies, USA.

Sample collection and oil extraction
Date palm fruit was purchased from farmers from Bushehr province in southern Iran. Sunflower oil was obtained from local markets. The date seed was initially separated from 1 kg date palm fruit and then washed with distilled water to remove any adhering flesh. Palm kernels were sun dried under ambient air during 12 hours. The dried masses were powdered after grinding, and kept in polyethylene bags and stored at 4ºC until analysis. The extraction using a Suxhelet apparatus and FAME of oil was performed according to Akbari et al., [30]. The extracted oil was putted into the evaporator rotating at 80ºC for 30 min until n-hexane possible within it evaporates and then oil into polyethylene bottles, stored at room temperature for biodiesel production.

Methods
The biodiesel characteristics including density (specific gravity), kinematic viscosity, acid value, cetane number, cloud point, pour point, and flame point as well as distillation temperature were determined using *EN14214* and *ASTM D6751* standards. Gas chromatography (GC-FID (Varian, CP- 3800) was used for measurement of fatty acids in oils.

GC analysis of sunflower and palm kernel oils
Fatty acid composition of palm kernel oil and sunflower oil was determined by using Gas Chromatography equipped with a FID (Varian CP-3800) with 30m capillary column. Helium (as the carrier gas), nitrogen (as a make-up gas), hydrogen and air flows, were 30, 30 and 300 ml/min, respectively. Initially, the column temperature after 60 sec was raised from 150ºC to 220ºC at a rate of 10 ºC/min and remained at this temperature for 2 min, then the temperature was reached to 235ºC at a rate of 7ºC/min and remained 2 min at this temperature. After that, it was reached to 255°C with the same speed and remained 1 min at this temperature. At the end it was reached to 268ºC at the rate of 10 ºC/min and maintained at this temperature for 30 min [30].

Biodiesel production
The palm oil extraction was placed on the heater at 85ºC to evaporate water of the oil. Then palm oil and sunflower oil were mixed with ratio of 1:1 and transferred into the flask and then located on a heater to reach the desired temperature. The mixture of methanol and catalyst was added to the blend of date seed and sunflower oil and the esterification reaction was carried out at the desired temperature (60 °C). After the compellation of reaction, the resulting solution was poured into a separating funnel and remained at room temperature for 24h until to be biphasic. Biodiesel in the up phase (supernatant), and glycerol, excess methanol and catalyst were observed in the bottom phase.

Filtration and washing of biodiesel
After separation of glycerol, biodiesel was washed several times with 70ºC-distilled water to remove residual catalyst and methanol. Then, about 15gr sodium sulfate was added and stirred for 20 min. As a final point, the biodiesel was filtered by Whatman filter under vacuum conditions and kept in plastic bottle caps for further analysis.

Determination of optimal conditions for biodiesel production
Temperature and time of the reaction, type and dose of the catalyst and methanol to oil ratio are important parameters in biodiesel production. Many studies have been conducted on the revealed parameters [22, 29]. In this study, temperature of 60ºC, time 60 min, amount of catalyst 1% wt. for both catalysts of sodium hydroxide and potassium hydroxide (base oil), and the ratio of methanol to oil (m/o) (1:3, 1:4, 1:5 and 1:6) was performed. After determining the optimal m/o and catalyst KOH and NaOH, the reaction towards optimum temperature of 60ºC, time of 60 min and different amounts of catalyst (0.5, 0.75, 1 and 1.25wt. %) for both catalyst was carried out. correspondingly, the optimum temperature (40, 50, 60 and 70ºC) and time (30, 40, 50 and 60 min) were also determined. In current work, all reactions at atmospheric pressure and heat and stirring the solution of the heater were equipped with a stirrer, mechanical model (yellow MAG HS 7) in stirring around 1500 rpm. all experiments were done duplicate.

RESULTS AND DISCUSSION

Fatty acid composition of date seed and sunflower oils

The fatty acid compositions of date seed and sunflower oils were analyzed by GC method and their related results was shown in table (1).

Table1: Fatty acid compositions of date seed and sunflower oils (%), as primary materials for production of biodiesel

Fatty acid composition	Date seed oil (%)	Sunflower oil (%)
Palmitic acid (C16:0)	37.71±0.17	8.30±0.2
Stearic acid (C18:0)	4.30±0.3	3.95±0.1
Oleic acid (C18:1)	42.44±0.75	34.33±0.85
Linoleic acid (C18:2)	13.71±0.15	57.86±1.13
Linolenic acid (C18:3)	-	0.11±0.68
Myristic acid (C14:0)	0.95±0.04	0.07±0.04

The optimum composition for the production of biodiesel from sunflower and palm oils

The Parameters of reaction time, reaction temperature, dose and type of catalyst and the ratio of methanol to oil were optimized and examined for production of biodiesel in the presence of the both catalysts KOH and NaOH (Table 2).

Table 2: Optimum conditions for the production of biodiesel using two catalysts of KOH and NaOH

Parameters	Catalysts	
	KOH	NaOH
methanol to oil ratio	1:4	1:4
reaction temperature (ºC)	60	60
reaction time (min)	60	60
amount of catalyst (%)	0.75	0.75
yield (%)	98.12	97.3

The effect of methanol to oil ratio (m/o)

One of the imperative parameters in the production of biodiesel is the ratio of methanol to oil. In this study, the different m/o of 3:1, 4:1, 5:1 and 6:1 for both catalysts (KOH and NaOH) as well as the optimum value were measured. To evaluation of the optimum m/o, the parameters of reaction temperature, amount of catalyst and reaction time were 60 ^{0}C, 1wt. % and 60 min, respectively. Maximum production of biodiesel was attained at ratio of 1:4 for both types of catalysts (Figure 1).

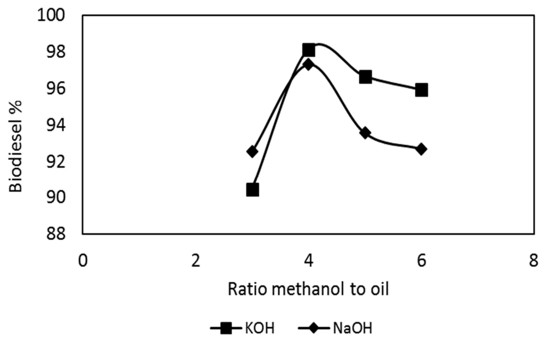

Fig. 1: the effect of methanol to oil ratio on biodiesel yield (T = 60 ºC, t = 60 min, the volume of catalyst=0.75% wt.)

The effect of the catalyst

two important factors on producing biodiesel yield are the amount and type of catalyst, due to alteration in the reaction rate by hydrolysis and saponification mechanisms [31].

For attaining the optimal amount of catalyst, the 0.5-1.25 wt. % values, were used. As defined in Figure 2, the production of the biodiesel was improved with increasing the catalyst amount; conversely, for the amount of catalyst higher than 0.75 wt. %, the biodiesel production was decreased with increasing catalyst percent. Therefore, the best amount of catalysts to produce the biodiesel using sunflower oil and date seed oil was obtained 0.75 wt. % (Figure 2).

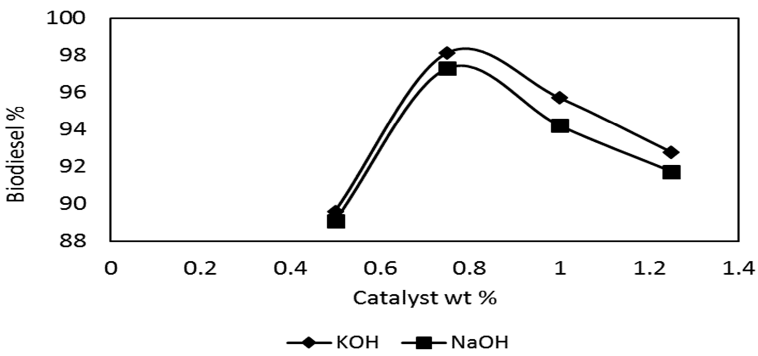

Fig. 2: Effect of type and amount of catalyst on the production of biodiesel (m/o= 4:1, T = 60 ºC, t = 60 min)

The effect of temperature and time

Esterification process can be affected by reaction time, temperature and the rate of esterification reaction to produce biodiesel [32]. The effects of temperature, reaction time on the production of biodiesel were shown in Figures (3) and (4), respectively. The temperature and time of reaction were studied in the range of 40-70ºC and 30-60 min. Biodiesel production was low at 40ºC and greater than before with increasing the temperature. Maximum biodiesel production was obtain in 60ºC, which amount for KOH and NaOH catalysts were 98.12% and 97.3%, respectively.

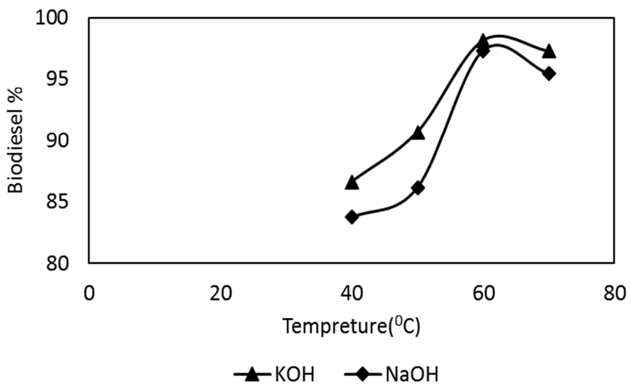

Fig.3: The effect of temperature on biodiesel yield (m/o= 4:1, t = 60 min, the catalyst: o.75% wt.)

The further operative parameter in the biodiesel production is the reaction time, but, with slighter influence than the other parameters. Correspondingly, several reaction times in the range of 30 to 60 minutes were used to determine the optimum time. To do so, the m/o, temperature and the amount of catalyst were 4:1, 60 °C and 0.75 wt. %, respectively as a condition to produce biodiesel. The increasing of biodiesel production was a direct relation with the reaction time (Figure 4).

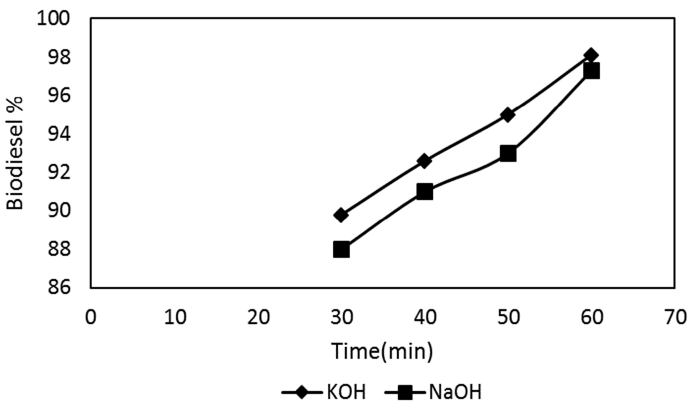

Fig. 4: Effect of reaction time on biodiesel yield (m/o= 4:1, T= 60 min, the catalyst =0.75% wt.)

Measurement and characterization of biodiesel

Subsequently, biodiesel properties such as density, kinematic viscosity, acid value, cetane number, distillation temperature, pour point, cloud point, and flame point were performed. Density is one of the most important characteristics of the fuel, the injection system, the pumps are ideal for burning the ideal amount of fuel ready to release [33]. Density is the ratio of the mass of a certain volume of liquid at a temperature of 15ºC (60^{o}F) to equivalent mass volume of pure water at the same temperature. Hydrometer was used to measure the density according to standard *EN14214*. The density of the produced biodiesel was obtained 874 Kg/m^3. Several studies have been reported the biodiesel densities about 860-900 Kg/m^3 [34, 35]. Kinematic viscosity was determined by Oswald viscometer according to *ASTM-D445*. Kinematic viscosity measurement is the time in seconds to cross a certain volume of the sample in the capillary viscometer calibrated weights on the pressure at the top of the column specimens.

Acid value was measured according to *ASTM-D664* and *EN*. The potentiometric method to test the reaction of acetic acid and toluene solvent ratio of 1:1 with KOH 1 N and a specific weight of sample was done. Endpoint of reaction indicated acid value that according of indicated standard is 0.5 (mg KOH/g). Several studies have been reported the acid number of less than 0.5 [36]. *EN14214* and *ASTM-D6751* standards were used for measure of cetane number. Equation (1) was used to measure the cetane number [37].

$$CN = \sum X\text{me(wt\%)}.\text{CNme} \qquad \text{(Equation 1)}$$

Where CN, is the cetane number of the biodiesel; X_{ME} is the weight percentage of each methyl ester and CN_{ME} is the cetane number of individual methyl ester.

To measure cloud point of the sample, the analysis was performed according to *ASTM-D2500*. First, a certain volume of the sample is cooled with a certain speed and studied at a certain temperature interval. The temperature in which a cloud is observed at the bottom of the container for the first time recorded as the point cloud. According to *ASTM-D2500*, minimum and maximum values of the Cloud point have not been reported, but in many studies that have been used to produce biodiesel from various sources Cloud point value reported about 15-21.6 [38-42]. Pour point *ASTM-D6751* and *EN14214* biodiesel standard values have been reported in some studies based on *ISO 3016* [42]. In this study the *ASTM-D6751* and *EN14214* methods were used for measure the flame and the distillation temperature. Tables (3) and (4) show the properties of the produced biodiesel using KOH and NaOH.

Table 3: Properties of biodiesel production using KOH

Properties	Biodiesel production (value)	EN-14214	ASTM-D6751
Density at 15 °C (Kg/m^3)	874	860-900	-
Viscosity at 40 °C (mm^2/s)	4.3	3.5-5	1.9-6
Acid value (mg KOH/g)	0.14	0.50 max	0.50 max
Cetane number	56	51min	47 min
Cloud point (ºC)	8	-	-
Poure point	4	-	-
Flash point (ºC)	171	101min	93.0 min
Distillation temperature (ºC)	345	-	360 max

The properties of biodiesel production using NaOH catalyst were very similar to the catalyst KOH.

Table 4: Properties of biodiesel production using NaOH

Property	Biodiesel production	EN-14214	ASTM-D6751
Density at 15 °C (Kg/m^3)	877	860-900	-
Viscosity at 40 °C (mm^2/s)	4.7	3.5-5	1.9-6
Acid value (mg KOH/g)	0.15	0.50 max	0.50 max
Cetane number	58	51min	47 min
Cloud point (ºC)	7	-	-
Poure point	5	-	-
Flash point (ºC)	178	101min	93.0 min
Distillation temperature (ºC)	350	-	360 max

Eman and his colleagues [38] in their similar study, were conducted the optimum conditions for the production of biodiesel from palm oil; they found that the optimal ratio of methanol to oil 6:1, reaction temperature 60 ºC, time of reaction 60 min, the catalyst used is KOH 1% and optimum conditions for biodiesel production were 88%; while the yield of biodiesel production from palm oil and sunflower oil blend in optimal condition using KOH and catalyst NaOH were 98.12 and 97.3%, respectively.

According to Saleh et al., [43] to produce biodiesel from sunflower oil using a catalyst concentration of 1% of KOH the maximum efficiency was of 96% that this yield, was lower than concurrent study.

CONCLUSION

Due to the limited and non-renewable petroleum resources, the production of biodiesel from renewable resources such as vegetable oils and animal fats are taken into consideration. Date seed and sunflower oils used to produce biodiesel, which are abundant in southern Iran. In this survey, biodiesel was produced from the composition of the sunflower oil and date seed oil with the ratio of 1:1, KOH and NaOH as catalyst and methanol. The study found that the combination of date seed oil and sunflower oil for biodiesel production is more efficient than either of them alone. In conclusion, Analysis of biodiesel according to *ASTM-D6751* and *EN14214* can be used as a desirable fuel source in its pure form or mixed with other fuels.

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REFERENCES

[1] MJ Ramos; CM Fernández; A Casas; L Rodríguez; Á Pérez. *Biores. Tech*., **2009**, 100(1), 261-268.
[2] HJ Cho; S H Kim; SW Hong; Y-K Yeo. *Fuel.*, **2012**, 93, 373-380.
[3] BR Moser. *Fuel.*, **2012**, 99, 254-261.
[4] E Alptekin; M Canakci; H Sanli. *World Renewable Energy Congress- Sweden.*, **2011**, May 8-13.
[5] E Alptekin; M Canakci. *Fuel.*, **2011**, (8), 2630-38.
[6] K Jacobson; R Gopinath; LC Meher; AK Dalai. *Appl. Cat. B: Env.*, **2008**, 85(1–2), 86-91.
[7] X Zhang; W Huang. *Procedia Env. Sci Part B*., **2011**, 11, 757-762.
[8]- W Xie; D Yang. *Bioresource Tech*., **2012**; 119, 60-65.
[9]- Y Li; F Qiu; Yang; P Sun; X Li. *Food Bioprod. Proces*., **2012**, 90(2), 135-140
[10] S Yusup; M Ali Khan. *Biomass Bioenerg*., **2010**, 34(10), 1500-4.
[11] JC Juan; DA Kartika; TY Wu; TYY Hin. *Biores. Tech.*, **2011**, 102(2), 452-460.
[12] MN Varma; PA Deshpande; G Madras. *Fuel.*, **2010**, 89 (7), 1641-46
[13] K Ferdous; M Rakib-Uddin; MR Khan; MA Islam. *Int. J. Eng. Tech*., **2012**, 1 (4): 420-431
[14] R Chakraborty; H. Sahu. *Appl. Energy*, **2014**, 114,827-836.
[15] VF Marulanda; G Anitescu; LL Tavlarides. *J.Supercrit. Flu*., **2010**, 54(1), 53-60.
[16] W Shi; J Li; B He; F Yan; Z Cui; K Wu; L Lin; X Qian; Y Cheng. *Biores. Tech*., **2013**, 139, 316-322.
[17] D Nivedita; V Kulkarni; M Lokhande. *I.J.P.E.E.*, **2013**, 4(2), 2314 – 7318.
[18] M Agarwal, G Chauhan; SP Chaurasia; K Singh. *J. Tai. Inst. Chem. Eng*., 2012, 43(1), 89-94.
[19] Z Al-Hamamre; J Yamin. *Energy Conv.Manag.*, **2014**, 79, 246-254.
[20] K Tahvildari; N Davari; MA Ghasri; M Behrourzinavid. *World Academy of Science, Engineering and Technology*. **2011**, 55.
[21] K Ramezani; S Rowshanzamir; MH Eikani. *Energy.*, **2010**, 35(10), 4142-48.
[22] AK Tiwari; A Kumar; H Raheman. *Biomass Bioenerg*., 2007, 31(8), 569-575.
[23]- JH Lee; DH Lee; JS Li; BH Um; C Park; SW Kang; SW Kim. J.*Microb. Biotech*., 2008,18 (12),1927-1931.
[24] S Shweta; S Sharma; MN Gupta. *Energy. Fuels.*, 2004, 18 (1), 154-159.
[25] S Tamalampudi; M R Talukder; S Hama; T Numata; A Kondo; H Fukuda. *Biochem.Eng. J*., 2008, 39(1), 185-189.
[26] PD Patil; VG Gude; HK Reddy; T Muppaneni; S Deng. *J. Env. Protec.*, **2012**, 3, 107-113.
[27] JV Gerpen; F. *Proces. Tech.*, **2005**. 86(10), 1097-1107
[28] K Ramezani; S Rowshanzamir; MH. Eikani. *Energy*., **2010**. 35(10), 4142-48.
[29] M Kılıç; BB Uzun; E Pütün; AE Pütün. *Fuel Proces. Tech*., **2013**, 111, 105-110.
[30] M Akbari; R Razavizadeh; GH Mohebbi; A Barmak. *Afr. Jour. Biotech.*, **2012**, 11(57), 12088-93.
[31]- Y Li; Fn Qiu; D Yang; P Sun; X Li. *Food. Bioprod. Proces*., 2012, 90(2), 135-140.
[32] LYihuai; Q Fengxian; D Yang; X Li; P Sun. *Biomas. Bioenerg.*, **2011**, 35 (7), 2787-95.
[33] JM Encinar; JF González; A Pardal. *Fuel Process.Tech.*, **2012**, 103, 9-15.
[34]- B Eriola; TF Adepoju. *Int. J. Energ. Env. Eng*., **2013**, 4, 1.
[35] LSG Teixeira; MB Couto; GS Souza; MA Filho; JCR Assis; PRB Guimarães; LAM Pontes; SQAlmeida; JSR Teixeira. *Biomas. Bioenerg.*, **2010,** 34(4), 438-41.
[36] DYC Leung; XW; MKH Leung. *Appl. Energ*., **2010**, 87 (4), 1083-95.
[37] MJ Ramos; CM Fernández; ACL Rodríguez; Á Pérez. *Bioresource Tech.*, **2009**, 100(1), 261-268.
[38] Eman NA; IT Cadence. *Procedia Eng*., **2013**, 53, 7–12.

[39] C Swaminathan; J Sarangan. *Biomass. Bioenerg.* **2012**, 39, 168-174.
[40] BH Diya'uddeen; AR Abdul Aziz; WMAW Daud; MH Chakrabarti. *Proc. Safe. Env. Protec.*, **2012**, 90(3), 164-179.
[41] FX Yang; YQ Su; XH Li; Q Zhang; RC Sun. *Indust. Crop. Prod.*, **2009,** 29(2–3), 622-8.
[42] HN Bhatti; MA Hanif; M Qasim; Ata-ur-Rehman. *Fuel.*, **2008**, 87(13–14), 2961-66.
[43] S Soleimani; AP Azari; R Sharifi; SM Atyabi; D Norouzian. *J. Appl. Chem. Res.*, **2013**, 7(1), 50-56.