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Sono-synthesis of biodiesel from soybean oil by KF/γ-Al_2O_3 as a nano-solid-base catalyst

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ABSTRACT

In this work, biodiesel has successfully prepared via ultrasonic method in a short time and low temperature by nano-solid-base catalyst (KF/γ-Al_2O_3). The catalyst was obtained by calcination of a mixture of KF and γ-Al_2O_3 ($m_{KF}/m_{\gamma\text{-}Al_2O_3} = 70\%$) at 500 °C for 3 h. Nano-solid-base catalyst was characterized with scanning electron microscopy (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR), thermal gravimetry (TG) and the Hammett indicator methods. The TEM image depicted nanoparticles and uniform dispersion of active phase over alumina. The XRD analysis confirmed the formation of potassium aluminum fluoride (K_3AlF_6) and potassium oxide, active catalyst for transesterification. The transesterification of soybean oil with methanol was performed by using both low frequency ultrasonic reactor (20 kHz) and mechanical stirring in the presence of KF/γ-Al_2O_3. The influence of various parameters such as ultrasonic power, oil/methanol molar ratio, catalyst concentration, time, and temperature were studied on the biodiesel formation. The maximum yield (95%) was achieved by applying 45 W acoustic power, molar ratio of alcohol to oil at 12:1, catalyst concentration of 2.0 wt%, 40 min sonication, and temperature of 50 °C. The transesterification was performed in 360 min using mechanical stirring with 76% yield. The results confirm that ultrasound significantly accelerates the transesterification reaction in comparison with the mechanical stirring.

1. Introduction

The use of alternative fuels has increased recently due to several factors. Biodiesel is as clean fuel produced from renewable resources. Biodiesel is the major substitute for fossil diesel. The advantages of biodiesel (fatty acid methyl esters, FAMEs) include renewability, biodegradability, non-toxicity, low emission profiles, high flashpoint, and excellent lubrication of the system [1]. In addition, as an alternative fuel, biodiesel is virtually compatible with commercial diesel engines and practically there are no modifications required for the engine [2].

The viscosity of vegetable oils is 10–20 times higher than petroleum fuel. Therefore, using vegetable oils directly as a fuel can cause engine problems like injector fouling and particle agglomeration [3,4]. These effects can be reduced or eliminated through transesterification of the vegetable oils to form alkyl esters [4]. This process decreases the viscosity of vegetable oils but maintains their properties similar to the diesel fuel. Biodiesel synthesis is chemically described as the transesterification of triglycerides (oil sources) into alkyl esters using an alcohol [4]. The resulting alkyl esters (i.e., fatty acid alkyl esters) with various alkyl groups have been utilized as biodiesel in industry [5].

The transesterification reactions can be performed using acid catalysts such as sulfuric, sulfonic, phosphoric, or hydrochloric acid [6,7] or base catalysts such as metal hydroxides [8], metal alkoxides [9], alkaline-earth oxides [10], or hydrotalcites [11]. Base catalysts are usually preferred to acid catalysts because the higher reaction rates and the lower process temperatures are required as compared with acid catalyzed transesterification [11].

Some industrial processes have performed in batch or continuous stirred tank reactors at temperatures ranging from 60 to 200 °C using homogeneous base catalysts such as alkaline hydroxides or metal alkoxides [12]. Heterogeneous catalysts are promising candidates for biodiesel production from vegetable oils. Different types of heterogeneous catalysts and their activity for transesterification have been studied more than a decade [13].

A number of articles on the development of heterogeneous catalysts for biodiesel production have been published [14–17]. Alumina-supported catalysts were shown to give high activity in

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the transesterification reactions. For example KI/Al_2O_3 [15], and KOH/Al_2O_3 [16] have been developed to promote the transesterification of vegetable oils.

Up to now, researchers have proposed several methods such as supercritical alcohol process [18], Biox co-solvent process [19], in situ biodiesel process [20], and microwave-assisted method [21,22] to synthesize biodiesel.

The slow reaction rates are due to low diffusion since the heterogeneous media behave as a three-phase system. The reaction between these species can occur only in the interfacial region between the phases. Vigorous mixing is required to increase the area of contact between the phases. Hence, low-frequency sonication is a useful tool for emulsification of immiscible phases [23]. In general, sonochemical reactors can favor the reaction chemistry by enhancing the mass transfer and interface mixing between the phases and also can lower the requirement of the harshness of the operating conditions in terms of temperature and pressure [24].

Some papers have reported the enhancement effect of ultrasound on biodiesel synthesis [25–29]. Ji et al. [28] studied the investigation of the effects of mechanical stirring, sonication, and hydrodynamic cavitation on methyl ester yields in the alkaline (KOH) transesterification of soybean oil. They reported that sonication gave the shortest reaction time and highest yield compared with the mechanical stirring. Stavarache et al. [29] studied the alkaline (KOH and NaOH) transesterification of a series of vegetable oils using both mechanical stirring and sonication. They obtained identical yields in both cases but a significantly shorter reaction time in the case of sonication [29]. Current researchers concentrate more towards the development of industrial processes for biodiesel production using solid catalysts [27,30–32]. Kumar et al. [30] studied transesterification of non-edible vegetable oil using solid catalyst, Na/SiO_2 [30]. Takase et al. [31] investigated the modified TiO_2 doped with $C_4H_4O_6HK$ as heterogeneous solid base catalyst for transesterification of non-edible oil to biodiesel using methanol under ultrasound. Although heterogeneous catalysts have many advantages, the application of solid catalysts in transesterification reaction has been limited because of their low active sites available for catalytic reaction. As the tremendous surface area of nano materials increase the reaction area, we focused on the use of nanoparticle-based catalysts for the transesterification of the triglycerides into biodiesel. In this work, we have studied the use of ultrasonic waves (20 kHz) to promote the transesterification reaction of soybean oil by using heterogeneous catalyst (KF/γ-Al_2O_3). It seems that KF/γ-Al_2O_3 as a heterogeneous catalyst under ultrasonic irradiation could make a valuable contribution to the existing processes in the field of biodiesel synthesis. In addition, the use of heterogeneous catalyst instead of homogeneous one leading to safer, cheaper and more environment friendly operations.

2. Experimental

2.1. Materials

Powder Alumina (γ-Al_2O_3) 99.998% with trace metals basis, potassium fluoride, and methanol (purity 99.5 vol.%) were obtained from Merck. The soybean oil was purchased from a local food store. The soybean oil used in the transesterification reaction was of commercial edible grade with the characteristics reported in Table 1.

Table 1
Analysis of soybean oil.

Test	Results
Density at 15 °C (kg m^{-3})	910
Kinematic viscosity at 40 °C (cSt)	27
Average molecular weight (g mol^{-1})	877
Saponification value (mg_{KOH} g_{oil}^{-1})	192
Acid value (mg_{KOH} g_{oil}^{-1})	0.1
Unsaturated fatty acids (wt%)	79
Saturated fatty acids (wt%)	21

2.2. Equipment

The ultrasonic irradiation was carried out with equipment operating at 20 kHz (XL2020, Masonic). Ultrasonic waves were emitted from a titanium horn with a diameter of 13 mm. ^1H-NMR spectra were recorded on a Bruker-AC100 MHz spectrometer. Scanning electron microscope (S360, Cambridge Instrument) was employed for characterization of the prepared catalyst. The size and the shape of the samples were determined with transmission electron microscope (TEM, Philips CM120). The XRD of KF/γ-Al_2O_3 was recorded on Bruker, D8 advance model. Thermogravimetric analysis (TGA, Shimadzu TA-50) were carried out in air from room temperature to 950 °C at a heating rate of 10 °C min^{-1}. The KBr pellet technique was applied for determining IR spectra (IR spectrometer, Shimadzu-4300) of the samples. The temperature of the reaction mixture was controlled at the desired temperatures using a circulator.

2.3. Methods

2.3.1. Catalyst preparation and characterization

The Alumina was activated at 400 °C and then it was added into potassium fluoride saturated solution. The obtained mixture was aged for 16 h at room temperature and then drying at 120 °C for 12 h in the oven. The obtained catalyst was calcined at 500 °C in a furnace for 3 h. The structure and morphology of the as prepared nano catalyst were characterized by FT-IR, XRD, TEM and TGA. The SEM images of KF/γ-Al_2O_3 catalyst were taken before and after transesterification reaction. The titration by Hammett indicators was also used for the specification of the prepared catalyst.

2.3.2. Transesterification reaction

Methanol, soybean oil, and KF/γ-Al_2O_3 were fed into a 3-neck jacketed type glass reactor of 500 mL capacity with an internal diameter of 10 cm. The reaction temperature was controlled by passing water through the jacket. The reactor was also equipped with a condenser to reduce the loss of methanol due to evaporation. The amounts of methanol and soybean oil based on molar ratios were calculated for 70 mL of the reaction mixture. The horn of sonicator was placed at half depth of the mixture and sonication was started immediately. A laboratory-scale biodiesel production setup was shown in Fig. 1. After the transesterification reaction, the mixture was filtered and poured into a separatory funnel and it was kept for 1 h. The density of biodiesel and glycerol were 0.87 and 1.126 g/cm^3, respectively, and thus they separated easily from each other. The mixture was washed three times with a saturated aqueous NaCl solution. After separation of phases, the decantation was done. All experiments were done in duplicate at different times of sonication.

2.3.3. Purification of methyl esters

The methyl esters obtained from transesterification reaction were treated with a saturated aqueous NaCl solution. Then, it was washed by hot distilled water to remove the dissolved impurities such as catalysts, alcohol, etc. Finally, it was dried with sodium sulfate. After the purification step, different properties of the esters were measured.

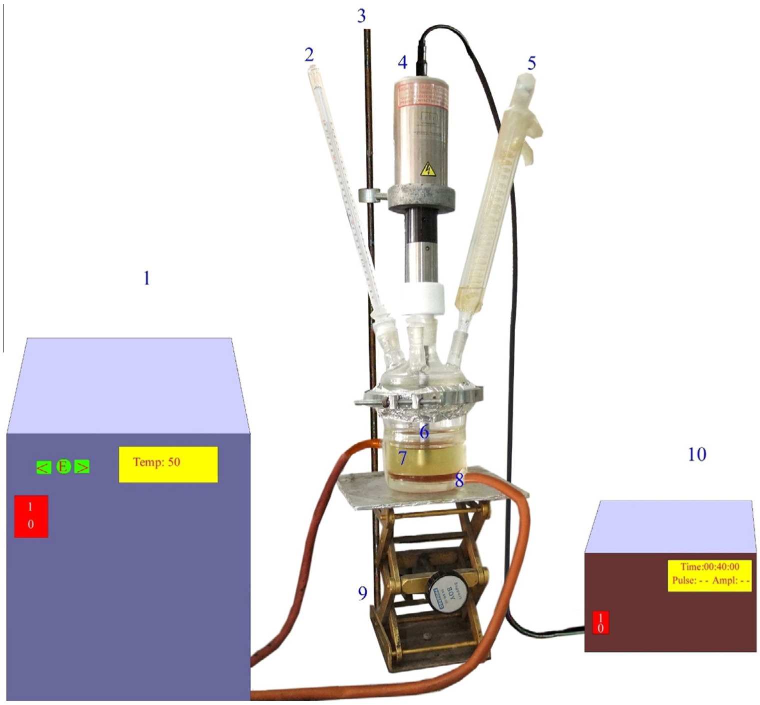

Fig. 1. Experimental setup used for the synthesis of biodiesel: 1. circulator 2. thermometer 3. laboratory stand 4. transducer 5. condenser 6. horn 7. biodiesel 8. glycerol 9. laboratory jack 10. ultrasonic generator.

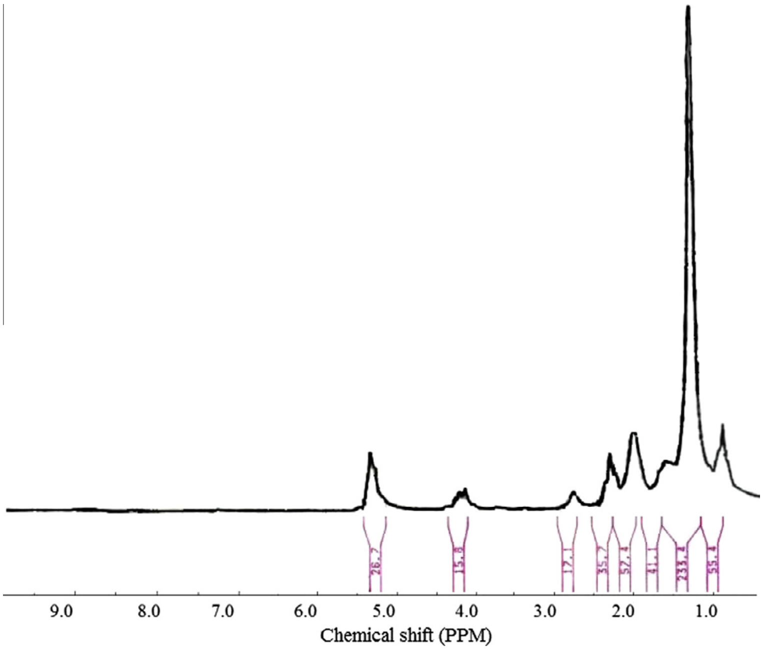

Fig. 2. ^{1}H-NMR spectrum of the soybean oil.

The density of soybean oil is in the range of 880–890 kg m^{-3} [33] and the conventional diesel is in 825–835 kg m^{-3} [33]. The density of the biodiesel obtained after dry washing was 870 kg m^{-3}.

Biodiesel is much less viscous than the oil. In the present study, the kinematic viscosity was determined using viscosimeter at 40 °C. The viscosity of the biodiesel after dry washing was 5.88 cSt.

2.3.4. Yield calculation

The conversion of fatty acids present in soybean oil to its esters was determined by ^{1}H NMR spectroscopy. Figs. 2 and 3 show ^{1}H NMR spectra of soybean oil and the biodiesel prepared by soybean oil with KF/γ-Al_2O_3 as the heterogeneous catalyst, respectively.

The conversion of the soybean oil to methyl ester (MEs) was determined by the ratio of the signals at 3.6 ppm, hydrogen of methoxy groups in the methyl esters, and 2.3 ppm, hydrogen of CH_2 group of all fatty acid derivatives, (Fig. 3). The following equation, given by Knothe [34] was used to calculate the conversion percentage:

$$C = 100 \times \frac{2A_{\mathrm{ME}}}{3A_{\alpha-\mathrm{CH_2}}} \tag{1}$$

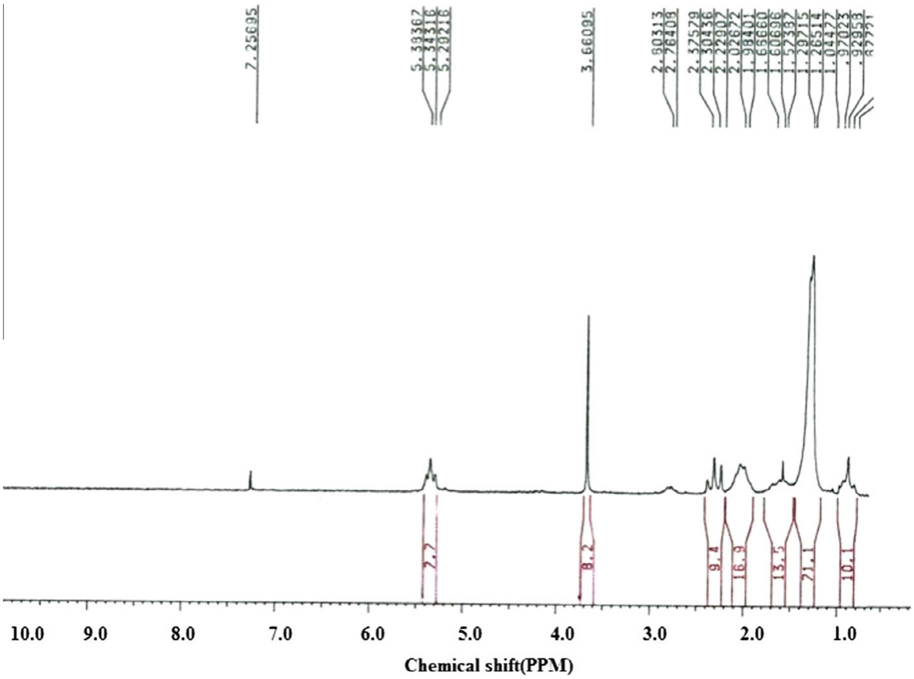

Fig. 3. ^{1}H-NMR spectrum of the biodiesel synthesized with 2.0 wt% catalyst in 40 min.

where C is the conversion percentage of triglycerides present in the feedstock to their respective MEs, A_{ME} is the integration value of the protons of the MEs, and $A_{\alpha\text{-}CH_2}$ is the integration value of the methylene protons. The yield of biodiesel can also be determined by the following equation given by Leung and Guo [35].

$$\text{Yield } (\%) = 100 \times \frac{\text{weight of biodiesel}}{\text{weight of oil}} \tag{2}$$

3. Results and discussion

3.1. Catalyst characterization

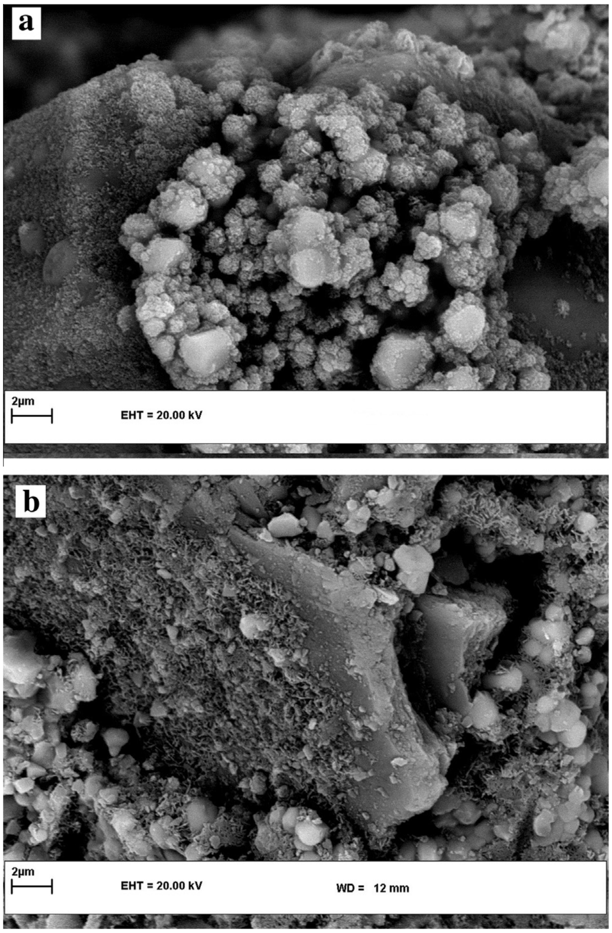

Fig. 4. The SEM images of KF/γ-Al_2O_3 catalyst (a) before reaction, (b) after reaction under ultrasound.

The basic strength of the catalyst was calculated by Hammett indicators. For this purpose, 25 mg of sample was added to 1 cm^3 of Hammett indicator and it was diluted by methanol and then left to reach equilibrium for 2 h. If the indicator exhibits a color change then the catalyst is labeled as stronger than the indicator, in otherwise catalyst was said to be weaker than the indicator [36]. The catalyst changed the color of both phenolphthalein ($H\_ = 8.2$) from colorless to pink and of 2, 4-dinitroaniline ($H\_ = 15$) from yellow to mauve but failed to change the color of 4-nitro aniline ($H\_ = 18.4$). Therefore, the catalyst basic strength were assigned as $15 < H\_ < 18.4$, and regarded as a strong base for transesterification reaction. The SEM images of KF/γ-Al_2O_3 catalyst before and after transesterification reaction were shown in Fig. 4. These graphs show a good dispersion of KF on the surface of γ-Al_2O_3. Particle diameter of the catalyst changed during the transesterification reaction period since the sonication granulated the catalyst particles. In order to obtain the structure and morphology of nano-solid-base catalyst prepared under optimal conditions, we focused on the TEM observation. The TEM image of the sample (Fig. 5) depicted nanoparticles in the sizes of about 50 nm and uniform dispersion of active phase over alumina. The XRD patterns of support material γ-Al_2O_3, KF and synthesized catalyst are shown in Fig. 6. The XRD was performed in a wide range angle ($2\theta = 10–80°$). In the XRD patterns of the catalyst, potassium aluminum fluoride (K_3AlF_6) and potassium oxide have been observed. Therefore, it was determined that the catalysis effect of KF/γ-Al_2O_3 was due to K_3AlF_6 and K_2O formed in the process of calcination. The TGA profile for KF/γ-Al_2O_3 nanoparticles is shown in Fig. 7. This figure showed

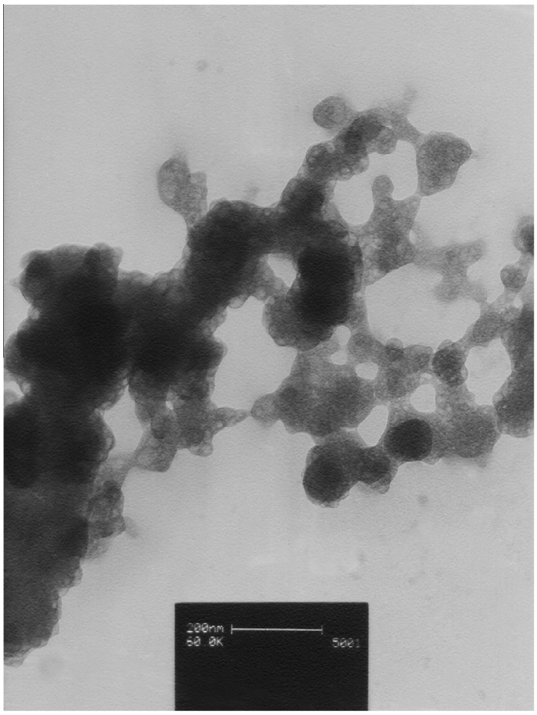

Fig. 5. TEM image of KF/γ-Al_2O_3 nano-solid-base catalyst.

the weight losses in the range of 80–940 °C which are attributed to the interaction of support and KF in the process of calcination. The FT-IR analysis was performed and the spectra were presented in Fig. 8. Specifically, all samples showed a very intense broad band at approximately 3480 cm^{-1}. The vibration frequency at 3480 cm^{-1} could be ascribed to the stretching vibration of Al–O–K groups. K^+ ions could replace the protons of isolated hydroxyl groups attached to γ-Al_2O_3 to form Al–O–K groups in the activation process [15]

3.2. Progress of the conversion

The gross conversion of triglycerides in oil was assessed by the ^1H-NMR [37]. The strong singlet at 3.6 ppm in the ^1H-NMR spectrum (Fig. 3) indicates methyl ester ($-CO_2CH_3$) formation. The signal at 2.3 ppm is related to the protons on the CH_2 groups adjacent to the methyl or glycerol ester moieties ($-CH_2CO_2CH_3$ for methyl esters). According to the Figs. 2 and 3, the disappearance of the resonance signal between 4.22 and 4.42 ppm and also the emergence of new signal at 3.67 ppm is a sign of biodiesel formation. For the identification of various peaks, the spectrum of Fig. 3 was compared with that of reported by Gelbard et al. [37]. For maximum yield of the transesterification process, an overall optimization is necessary. Different parameters affect the conversion and were itemized as follows.

3.2.1. Effect of ultrasound on the reaction system

The reaction mixture is triphasic system comprising of oil, alcohol and catalyst as a solid phase. Generally, the reaction between different reactants in different phases is slow and difficult. For enhancing these kinds of reactions, it is necessary to increase the interfacial area between different phases. In addition, the enhance of mass transfer is crucial in this triphasic system. Ultrasound facilitates the contact of reactants by overcoming the limitations of multiphasic system. Since the KF/γ-Al_2O_3 catalyst being hydrophilic in nature, it preferably likes to contact more with alcohol phase. The yield of the transesterification reaction depends on the concentration of the methoxide anions and interfacial area between phases. The methoxy ions are generated as a result of the adsorption of methanol molecule on the Al–O–K active sites surface. Ultrasound can increase the rate of adsorption. Also, sonication of reaction mixture induces intense mixing that significantly boosts the conversion of triglycerides. To study the effect of

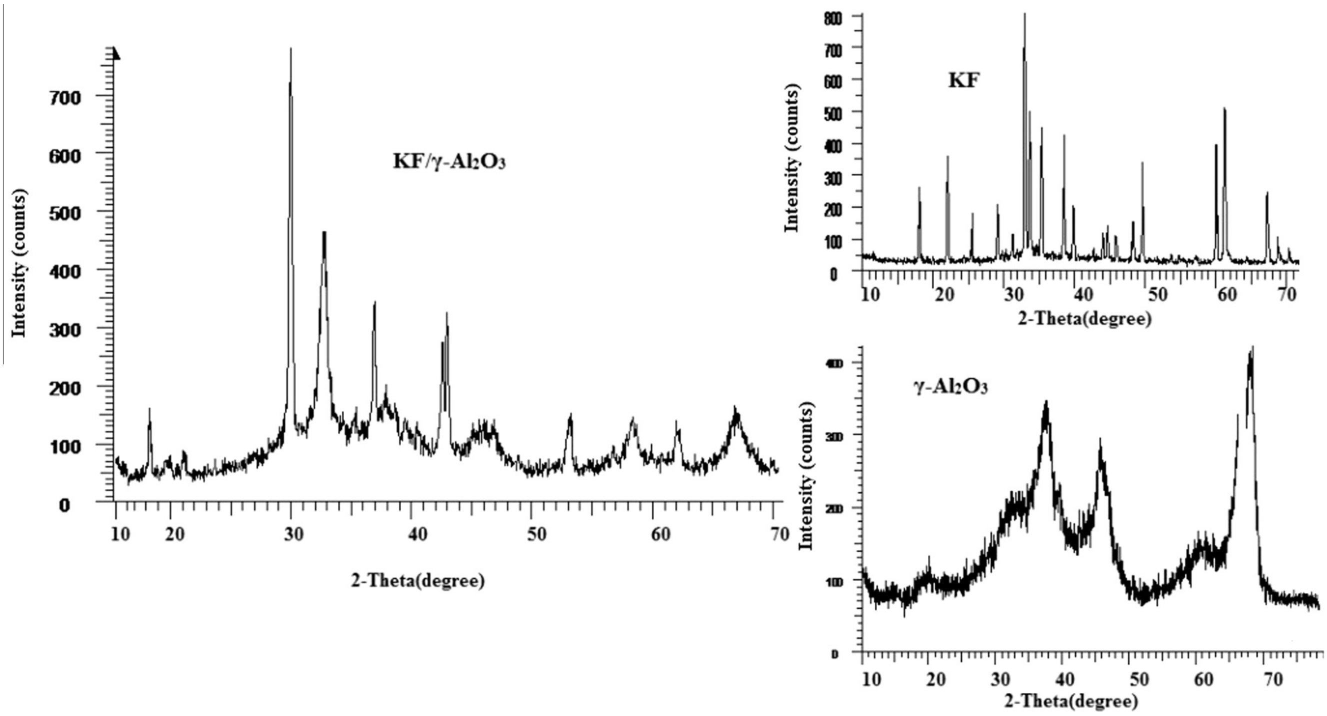

Fig. 6. XRD patterns for samples: γ-Al_2O_3, KF and KF/γ-Al_2O_3.

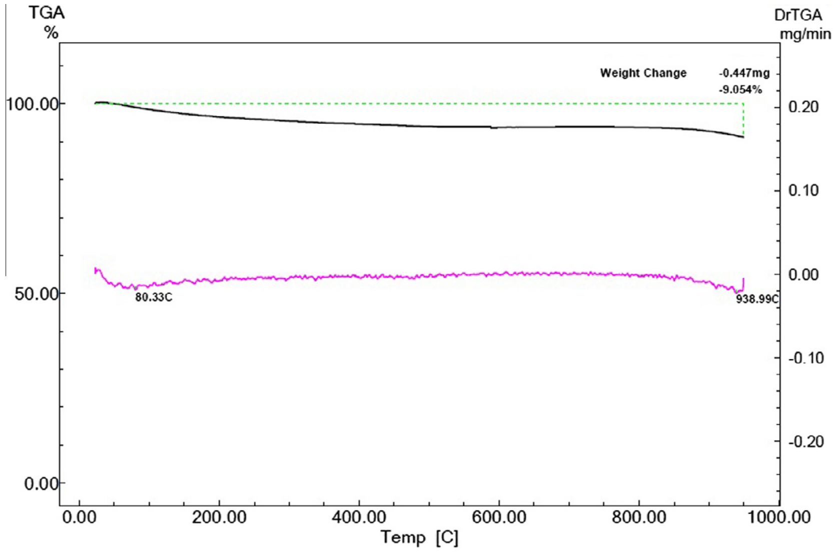

Fig. 7. TGA plot for KF/γ-Al_2O_3 nano-solid-base catalyst.

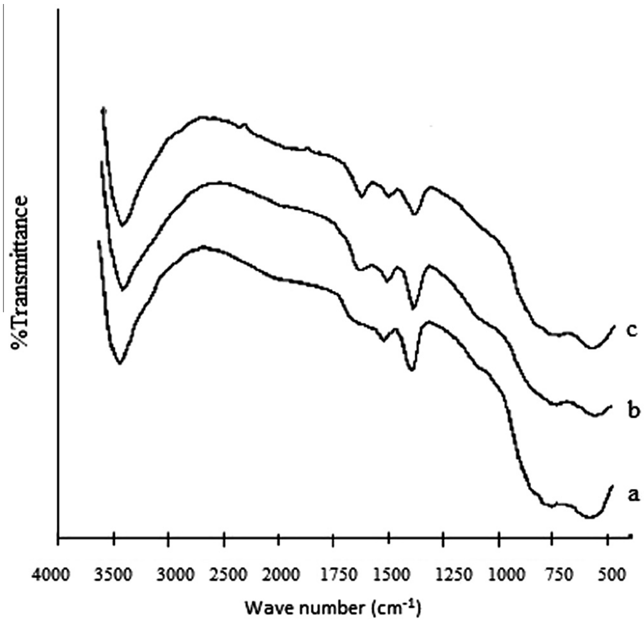

Fig. 8. FT-IR spectra of sample KF/γ-Al_2O_3 calcined at different temperatures for 3 h: (a) 873 K, (b) 773 K, (c) 673 K.

sonication in the transesterification reaction, we studied the effects of horn position and ultrasonic power. Higher yield was observed when the horn of sonicator was placed at half depth of the mixture.

In general, an increase in power will provide an increase in the sonochemical effects. In this heterogeneous system, the phases would be practically unsolvable in each other. Thus, the reaction will only occur at the interfacial region between the phases. Vigorous mixing is required to increase the area of contact between the phases. Experiments were carried out in four different powers. The intensity of mixing increases with increasing the ultrasonic power due to the acoustic streaming generated by cavitation process. The ultrasonic powers were 25, 33, 39, and 45 W which were measured by calorimetric method [38]. Higher power input leads to the generation of higher number of cavities with stronger collapsing. The harsher the collapse of the cavitation bubble leads to the higher micro-mixing and jet velocity at the phase boundary between the oil and methanol phases. This results to the finer emulsion formation, a higher mass-transfer coefficient, and thus higher yield (Fig. 9). The best yield was obtained at 45.1 W.

3.2.2. Molar ratio (oil to alcohol)

The influence of different molar ratios of methanol to oil (9:1, 12:1, 15:1, and 18:1) on the conversion process was studied. Fig. 10 shows that the less conversion was obtained for the ratios of 9:1 and 18:1. The reason may be explained based on the viscosity. The viscosity reduces from 9:1 to 18:1. By decreasing the viscosity, the cavity can be formed easily but, the collapse is not harsh enough. The amount of catalyst is the same for all ratios. Therefore, at low ratio (9:1), the concentration of oil is high as a positive impact and the viscosity is also high as a negative impact, has influenced the reach of the species to the active sites of the catalyst.

At high ratio (18:1), the concentration of oil is low (negative effect) and the viscosity is also low (positive effect). Under this condition, the contact of the species on the catalyst is not proper too. The yield for the ratio of 12:1 is highest. This means that under optimum ratio, the contact is highest and the sonication is more effective than other cases. In addition, the optimum amount of methanol provides additional cavitation events in the reactor which leading to the formation of emulsion with smaller droplet size.

In this situation, the increased surface area related to the smaller sizes of the emulsion is providing additional interface for the reaction and hence the yield increases. Stavarache et al. [29] reported the excess of methanol leading to a higher number of cavitation events that facilitates the conversion of vegetable oil in transesterification process. In ratios beyond 15:1, the yield of biodiesel formation decreases. This may be related to the high concentration of methanol which is volatile and causes a reduction of the intensity of cavitation collapse by more entering methanol into the cavity. Hence, the optimum operating ratio for conversion is 1:12.

3.2.3. Temperature

Another important variable was the temperature of the transesterification process. The biodiesel was prepared at 30, 40 and 50 °C, under optimized conditions (molar ratio of oil/methanol:

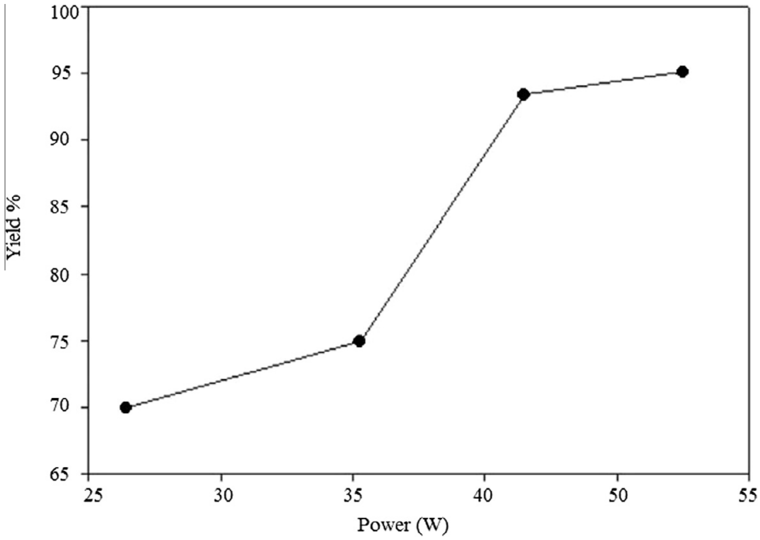

Fig. 9. Effect of ultrasonic intensity on the yield of biodiesel (methanol/oil molar ratio: 12:1; catalyst concentration: 2.0 wt%; temperature: 50 °C; time of sonication: 40 min).

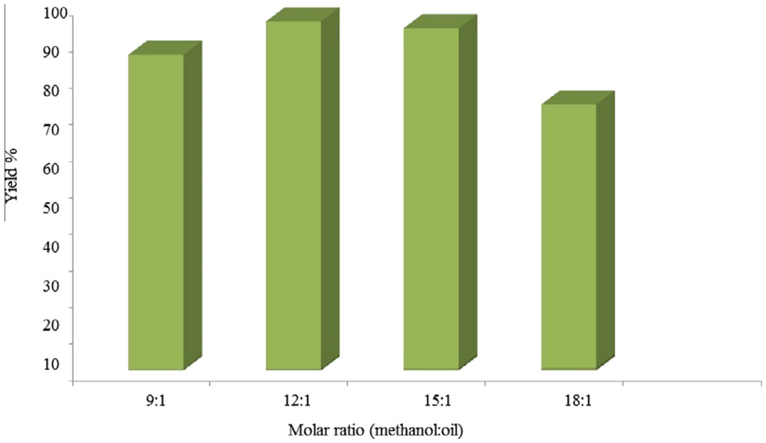

Fig. 10. Effect of molar ratio of methanol to oil on the yield of biodiesel (catalyst concentration: 2.0 wt%; temperature: 50 °C; ultrasonic power: 45 W: time of sonication: 40 min).

1:12, catalyst: 2% (wt), and ultrasonic power: 45 W) to study the influence of temperature on the yield (Table 2). By increasing temperature, the viscosity of the soybean oil decreases and the miscibility of oil-methanol and activity of the cavitation events increases. Also, the rate of reaction increases with raising the temperature. Both of the effects facilitate the biodiesel formation.

The reaction cannot be proceeded at temperatures greater than 50 °C. At temperatures near or above the boiling point of methanol, the effects of sonication are diminished. Under this condition, the bubble contents at the collapse are dominated by methanol vapor. This vapor cushions the collapse of the bubble, at the same time increases the heat capacity of the bubble contents. Due to these two effects, the temperature and pressure peaks reached at the collapse of cavitation bubble are rather moderate. The species generated from dissociation of methanol vapor are essentially of molecular type (CH_4, H_2O, and CO_2). Thus, there is no sonochemical effect involved. In addition, most of the methanol as a reactant can be evaporated at high temperatures and hence yield and rate of the reaction decrease. The maximum rate and yield of biodiesel formation were obtained at 50 °C. At temperatures less than 30 °C, the formation of the biodiesel by ultrasound was very long.

Table 2
Effect of temperature on the yield of biodiesel in 40 min sonication.

Temperature (°C)	30	40	50
Yield of ME (%)	80	90	95

3.2.4. Amount of the catalyst

The catalyst obtained by calcining a mixture of KF and γ-Al_2O_3 ($m_{KF}/m_{\gamma\text{-}Al_2O_3} = 70\%$) at 500 °C for 3 h, was found to be the optimum one and gave the highest catalytic activity in the reaction. The very high activity and surface reactivity were related to the high surface/volume ratio of nano-sized catalyst particles. The amount of the catalyst (KF/γ-Al_2O_3) on the transesterification of soybean oil in the range of 0.5–3.0 wt% (based on the oil weight) was investigated (Fig. 11). When the dose of catalyst increased from 0.5% to 2%, the yield of biodiesel was increased from 89% to 95%. It seems the number of active sites at 2%, are relatively much more than that of 0.5%. However, when the concentration increased from 2% to 3%, the yield of the reaction was approximately remained constant. In the absence of the catalyst, even by applying ultrasound, no transesterification was observed. The maximum yield (95%) was obtained when the amount of KF/γ-Al_2O_3 base catalyst was

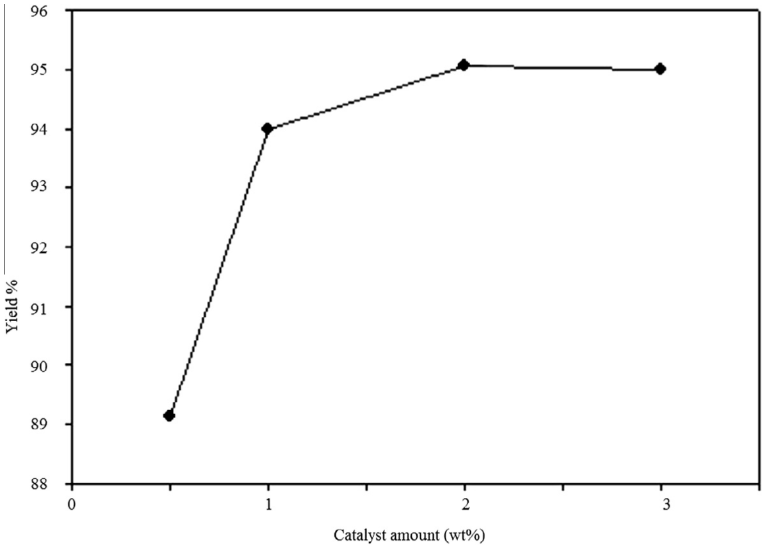

Fig. 11. Effect of amount of catalyst on the yield of biodiesel (methanol/oil molar ratio, 12:1; temperature: 50 °C; ultrasonic intensity: 45 W; time of sonication: 40 min).

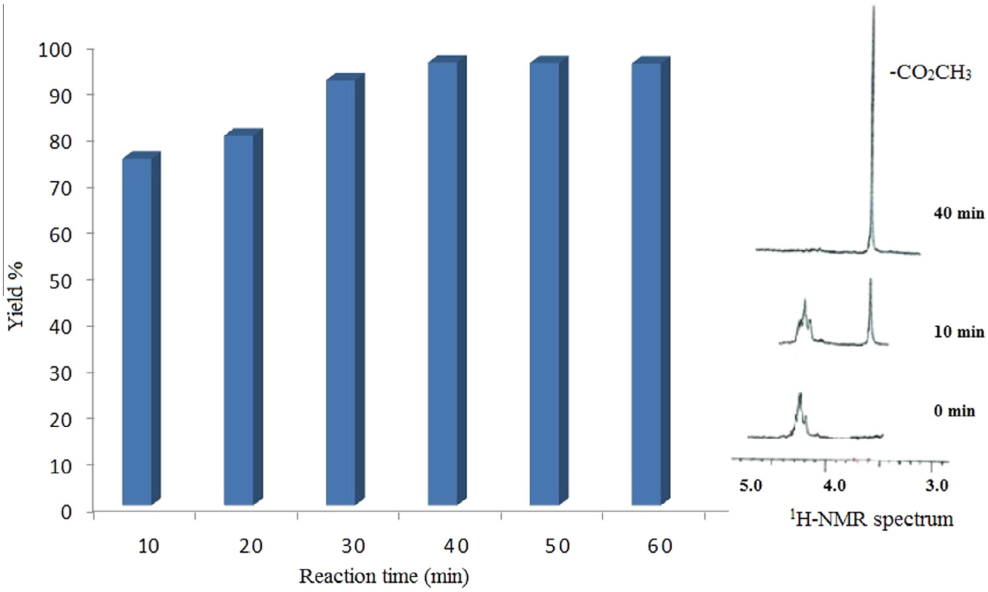

Fig. 12. Yield of biodiesel as a function of reaction time (methanol/oil molar ratio: 12:1; catalyst: 2.0 wt%; temperature: 50 °C; ultrasonic power: 45 W).

2%. This may be associated with the relatively high basicity and the high surface to volume ratio of the catalyst particles. Heterogeneous catalyst (KF/γ-Al_2O_3) has the potential to be recovered by a simple filtration.

3.2.5. Reaction time

Sonication increases the chemical reaction rate of transesterification of soybean oil.

The effect of sonication time on the yield of the biodiesel was studied at different interval times ranging from 10 to 60 min at constant temperature (50 °C) and the catalyst amount (2%). The yield of biodiesel was 76% in 10 min and 95% in 40 min of sonication (Fig. 12). Thus, it can be concluded that the suitable time for the sonication was 40 min. Table 3 summarizes optimal conditions of experiments with and without ultrasound. The conversion from about 76% in 6 h in stirring method was changed to about 95% in 40 min under sonication. Thus, the use of ultrasonic irradiations is beneficial in both the enhancement of the rate of reaction as well as the yield of the reaction. This is due to the intense turbulence and micro-scale liquid circulation currents produced by cavitation process which help in uniform mixing at micro-level and hence in the reduction of the mass transfer resistances.

Table 3
Optimal conditions of experiments with and without ultrasound.

Method	Molar ratio	Temp. (°C)	Catalyst (wt%)	Reaction time (min)	Yield (%)
Ultrasound	12:1	50	2	40	95
Stirring	15:1	65	3	360	76

4. Conclusions

In this work, KF/γ-Al_2O_3 nanoparticles have been successfully synthesized as an effective solid-base catalyst for the transesterification reaction of vegetable oils. We studied the transesterification reaction of soybean oil with synthesized solid base catalyst using both mechanical stirring and sonication. It was shown that ultrasonic irradiation can be an effective method for the preparation of biodiesel from soybean oil. The results confirmed that the transesterification under ultrasonic waves leads to a higher yield (95%) in a shorter time (40 min). Ultrasonic mixing results in the formation of very small emulsion droplets that allow an excellent contact between the reactants and catalyst. The synthesized catalyst has recovered by a simple filtration. The important chemical properties such as density and viscosity of the synthesized biodiesel have also been investigated.

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References

[1] E. Stauffer, D. Byron, Alternative fuels in fire debris analysis: biodiesel basics, J. Forensic Sci. 52 (2007) 371–379.

[2] A.K. Agarwal, Biofuels (alcohol and biodiesel) applications as fuels for internal combustion engines, Prog. Energy Combust. 33 (2007) 233–271.

[3] L.G. Dodge, T.J. Callahan, The effects of vegetable oil properties on injection and combustion in two different diesel engines, J. Am. Oil Chem. Soc. 61 (1984) 1610–1619.

[4] G. Knothe, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, Fuel Process. Technol. 86 (2005) 1059–1070.

[5] A. Kalva, T. Sivasankar, V.S. Moholkar, Physical mechanism of ultrasoundassisted synthesis of biodiesel, Ind. Eng. Chem. Res. 48 (2009) 534–544.

[6] B. Davies, G.V. Jeffreys, Continuous transesterification of ethyl alcohol and butyl acetate in a sieve plate column: II. batch reaction kinetics studies, Trans. Inst. Chem. Eng. 51 (1973) 271–274.

[7] J. Otera, Transesterification, Chem. Rev. 93 (1993) 1449–1470.

[8] B. Freedman, R.O. Butterfield, E.H. Pryde, Transesterification kinetics of soybean oil, J. Am. Oil. Chem. Soc. 63 (1986) 1375–1380.

[9] J. Schmidt, D. Reusch, K. Elgeti, R. Schomacker, Kinetics of transesterification of ethanol and butyl acetate – a model system for reactive rectification, Chem. Ing. Tech. 71 (1999) 704–708.

[10] S. Gryglewicz, Alkaline-earth metal compounds as alcoholysis catalysts for ester oils synthesis, Appl. Catal. A 192 (2000) 23–28.

[11] A. Corma, S. Iborra, S. Miquel, J. Primo, Catalysts for the production of fine chemicals, J. Catal. 173 (1998) 315–321.

[12] D. Darnoko, M. Cheryon, Kinetics of palm oil transesterification in a batch reactor, J. Am. Oil Chem. Soc. 77 (2000) 1263–1267.

[13] Y. Zu, G. Liu, Z. Wang, J. Shi, M. Zhang, W. Zhang, M. Jia, CaO supported on porous carbon as highly efficient heterogeneous catalysts for transesterification of triacetin with methanol, Energy Fuels 24 (2010) 3810–3816.

[14] I. Lukic, J. Krstic, D. Jovanovic, D. Skala, Alumina/silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil, Bioresour. Technol. 100 (2009).

[15] W. Xie, H. Li, Alumina-supported potassium iodide as a heterogeneous catalyst for biodiesel production from soybean oil, J. Mol. Catal. A Chem. 255 (2006) 1–9.

[16] N. Krisada, I. Pisitpong, L. Apanee, J. Samai, A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil, Renewable Energy 34 (2009) 1145–1150.

[17] Y. Tang, M. Meng, J. Zhang, Y. Lu, Efficient preparation of biodiesel from rapeseed oil over modified CaO, Appl. Energy 88 (2011) 2735–2739.

[18] S. Saka, D. Kusdiana, Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, J. Fuel 80 (2001) 225–231.

[19] D.G.B. Boocock, S.K. Konar, V. Mao, H. Sidi, Fast one-phase oil-rich processes for the preparation of vegetable oil methyl esters, Biomass Bioenergy 11 (1996) 43–50.

[20] A. Mondala, K. Liang, H. Toghiani, R. Hernandez, T. French, Biodiesel production by in situ transesterification of municipal primary and secondary sludges, Bioresour. Technol. 100 (2009) 1203–1210.

[21] J. Hernando, P. Leton, M.P. Matia, J.L. Novella, J. Alvarez-Builla, Biodiesel and FAME synthesis assisted by microwaves: homogeneous batch and flow processes, J. Fuel 86 (2007) 1641–1644.

[22] N. Azcan, A. Danisman, Alkali catalyzed transesterification of cottonseed oil by microwave irradiation, J. Fuel 86 (2007) 2639–2644.

[23] J.L. Luche, Effect of ultrasound on heterogeneous systems, Ultrason. Sonochem. 1 (1994) 111–118.

[24] P.R. Gogate, Cavitational reactors for process intensification of chemical processing applications: a critical review, Chem. Eng. Process. 47 (2008) 515–527.

[25] J.A. Colucci, B.E. Ernesto, A. Fabio, Biodiesel from an alkaline transesterification reaction of soybean oil using ultrasonic mixing, J. Am. Oil Chem. Soc. 82 (2005) 525–530.

[26] P.A. Parkar, H.A. Choudhary, V.S. Moholkar, Mechanistic and kinetic investigations in ultrasound assisted acid catalyzed biodiesel synthesis, J. Chem. Eng. 187 (2012) 248–260.

[27] H.A. Choudhury, S. Chakma, V.S. Moholkar, Mechanistic insight into sonochemical biodiesel synthesis using heterogeneous base catalyst, Ultrason. Sonochem. 21 (2014) 169–181.

[28] J. Ji, J. Wang, Y. Li, Y. Yu, Z. Xu, Preparation of biodiesel with the help of ultrasonic and hydrodynamic cavitation, Ultrason. Sonochem. 44 (2006) 411–414.

[29] C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, Fatty acids methyl esters from vegetable oils by means of ultrasonic energy, Ultrason. Sonochem. 12 (2005) 367–372.

[30] D. Kumar, G. Kumar, G. Kumar, Poonam, C.P. Singh, Ultrasonic-assisted transesterification of Jatropha curcus oil using solid catalyst, Na/SiO_2, Ultrason. Sonochem. 17 (2010) 839–844.

[31] M. Takase, Y. Chen, H. Liu, T. Zhao, L. Yang, L. Yang, Xi Wu, Biodiesel production from non-edible *Silybum marianum* oil using heterogeneous solid base catalyst under ultrasonication, Ultrason. Sonochem. 21 (2014) 1752–1762.

[32] A.P.C. Teixeira, E.M. Santos, A.F.P. Vieira, R.M. Lago, Use of chrysotile to produce highly dispersed K-doped MgO catalyst for biodiesel synthesis, J. Chem. Eng. 232 (2013) 104–110.

[33] A. Srivastava, R. Prasad, Triglycerides-based diesel fuels, Renewable Sustainable Energy Rev. 4 (2000) 111–133.

[34] G. Knothe, Analytical methods used in the production and fuel quality assessment of biodiesel, Trans. ASAE 44 (2001) 193–200.

[35] G. Gelbard, O. Bres, R.M. Vargas, F. Vielfaure, U.F. Schuchardt, ^{1}H nuclear magnetic resonance determination of the yield of the transesterification of rapeseed oil with methanol, J. Am. Oil Chem. Soc. 72 (1995) 1239–1241.

[36] D.Y.C. Leung, Y. Guo, Transesterification of neat and used frying oil: optimization for biodiesel production, Fuel Process. Technol. 87 (2006) 883–890.

[37] W. Xie, X. Huang, Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst, Catal. Lett. 10 (2006) 53–59.

[38] M.H. Entezari, P. Kruus, Effect of frequency on sonochemical reactions II. Temperature and intensity effects, Ultrason. Sonochem. 3 (1996) 19–24.