



Research Article

Studies on Sono-Chemical Biodiesel Production Using Smoke Deposited Nano MgO Catalyst

P. Sivakumar¹, S. Sankaranarayanan¹, S. Renganathan¹, P. Sivakumar^{2*}

¹Department of Chemical Engineering, Anna University, Chennai-600 025, Tamilnadu, India

²Department of Petroleum Engineering and Technology, JCT College of Engineering and Technology, Coimbatore-641 105, Tamilnadu, India

Received: 18th March 2013; Revised: 20th August 2013; Accepted: 9th September 2013

Abstract

The comprehensive study of smoke deposited nano-sized MgO as a catalyst for biodiesel production was investigated. The transesterification reaction was studied under constant ultrasonic mixing for different parameters like catalyst quantity, methanol oil molar ratio, reaction temperature and reaction time. An excellent result of conversion was obtained at 1.5 wt% catalyst; 5:1 methanol oil molar ratio at 55 °C, a conversion of 98.7% was achieved after 45 min. The conversion was three to five times higher than those are reported for laboratory MgO in literature. This was mainly due to the enhancement of surface area of the catalyst and the activity of ultrasonic waves. Catalyst is easily recovered and reused up to eight times with easy regeneration steps. © 2013 BCREC UNDIP. All rights reserved

Keywords: Nano MgO; Transesterification; Sonication; Recovery; Regeneration

How to Cite: Sivakumar, P., Sankaranarayanan, S., Renganathan, S., Sivakumar, P. (2013). Studies on Sono-Chemical Biodiesel Production Using Smoke Deposited Nano MgO Catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 8 (2): 89-96. (doi:10.9767/bcrec.8.2.4628.89-96)

Permalink/DOI: <http://dx.doi.org/10.9767/bcrec.8.2.4628.89-96>

1. Introduction

Biodiesel is a renewable and potentially inexhaustible energy source for diesel engines, which can be synthesized by transesterification of vegetable oil or animal fat [1]. This reaction was catalyzed by both acids as well as alkali catalysts [2-4]. Acid-catalyzed transesterification uses homogeneous non-green catalysts (sulfuric acid, phosphoric acid, hydrochloric acid etc.) and the reaction is much slower when compared to alkali catalysis. Whereas, in alkali catalyzed process the catalyst

removal is tedious [5] and its remains in the biodiesel generated concern from the automotive producers. A solution to the problems associated with the homogeneous catalysis is to use heterogeneous catalysts, which can provide green, recyclable catalytic systems.

Current researchers concentrate more towards the development of industrial processes for biodiesel production using solid catalysts. The key benefits of using heterogeneous catalysts are that non-polluting and the catalysts do not mix with biodiesel that can be recovered and reused. Heterocatalytic process allows the production of biodiesel in continuous reactors instead batch reactors used with homogeneous catalysis. In addition to lower separation costs and less maintenance these catalysts are non-corrosive [6]. A number of recent

* Corresponding Author.

E-mail: sivakumarhap@rediffmail.com (P. Sivakumar), Tel: +91-9994-584588, Fax: +91-422- 2636901

studies highlight the current interest in heterogeneous catalysis for transesterification [7-11]. Magnesium oxide (MgO) is a solid and basic material. It does not dissolve in the reaction medium and hence it takes the role of heterogeneous catalyst in transesterification reaction. Commercial MgO is usually less active catalyst when compared to other metal oxides of the same group [12]. But the reduced size and ultrasonication induces high catalytic activity.

MgO possess basic active surface site, which makes them highly efficient in some catalytic processes. Smoke deposited catalyst have restructured metal oxide sites leading to an increase in defects which are electron donating O²⁻ centers, postulated as super basic sites in solid base catalysis. In this report, we founded this catalyst have higher conversion in biodiesel production. This is due to the higher surface area, which intern results in higher active sites.

No work has been established so far on the production of biodiesel using smoke deposited MgO in the literature. This study was aimed at the conversion of vegetable oils to biodiesel via transesterification reaction with MgO as heterogeneous catalyst assisted by ultrasonic energy. The physical structure, composition of the smoke deposited MgO was studied in detail by means of Scanning Electron Microscopy (SEM), Energy Diffraction X-Ray Spectroscopy (EDS), X-Ray Diffraction (XRD). The variables affecting the methyl ester conversion such as catalyst quantity, methanol oil molar ratio, reaction temperature and reaction time were investigated. The conversion of the resulted biodiesel was analyzed by H¹ Nuclear Magnetic Resonance Spectroscopy (H¹NMR).

2. Materials and Methods

The transesterification reaction was carried out using the waste mixed vegetable oil purchased from local commercial source in Chennai, India. Magnesium ribbon of 99.9% pure purchased from Ranbaxy Chemicals (Mumbai, India) and methanol 99.9% pure was obtained from Merk (Mumbai, India). The chemicals were used without any further purification.

2.1. Catalyst Preparation

During the course of study, nanosized MgO was prepared by high temperature initiated, self-propagated gas producing combustion method. The process involves an exothermic combustion of Mg metal in air. The mechanism of combustion reaction is quite simple as shown in Equation (1).



Magnesium ribbon was accurately weighted and cut into small pieces. The contents were placed in a silica crucible on a clay triangle under the fume hood. Heat was supplied continuously using a Bunsen burner (moderate flame) until the magnesium starts to burn. Close the top of the crucible partially with a stain less steel (SS-316) metal plate. The gaseous entities formed absorb heat energy from subsequent combustion and acquire kinetic energy perpendicularly to the target to be deposited in a substrate to allow crystalline growth [13]. The escaping white vapors are particles of magnesium oxide. These particles deposited on the metal plate were scrapped off and stored in a nitrogen purged airtight containers, to avoid the attack of moisture and carbon dioxide.

2.2. Catalyst Characterization

The morphology and the structure of obtained powder were determined by SEM (S-3400N, HITACHI, Japan). Phase structure and the purity of the prepared samples were characterized by XRD (X'Pert PRO, PANalytical, Netherlands) with a diffractometer 2θ ranging from 10-80°, using Cu Kα (λ = 0.15141 nm) radiation operated at 45 kV and 30 mA. Quantitative analyses of elemental composition were investigated by EDS (Noran System Six, Thermo Electron Corporation, Japan).

2.3. Characterization of Oil

The important physical and chemical properties of the extracted oil were determined in the fuels and combustion laboratory according to AOCS Official Methods. Gas Chromatography (GC) analysis of the oil gives a qualitative and quantitative identification of fatty acids, which plays an important role in biodiesel production and its performance in diesel engine [14]. Fatty acids were initially transformed into their respective methyl esters following the methods as prescribed by Hartman and Lago [15]. The fatty acid composition of mixed oil was analyzed using GC, (CHEMITO GC 8610, India). The equipment was fitted with a BPX-70 column (50% Cyanopropyl, 50% Methyl siloxane). The peaks were identified by comparing with standards using Win-Chrome software.

2.4. Transesterification Mechanism

Transesterification is the displacement of alcohol from an ester by another alcohol [16]. Alcohol preferred here is methanol because of its low cost, polar nature and shortest chain [17]. Nano sized MgO, catalyses transesterification reaction as a basic heterogeneous catalyst. When Mg atoms located at corner or edge sites of MgO nano particles have

a relatively low coordination number and a positive charge that is substantially smaller than that in the bulk [18, 19]. These cations are expected to be the chemically active sites of the nanoparticles [20, 21]. The reaction occurs between the methanol molecules adsorbed on MgO free basic sites and the triglyceride from the liquid phase.

2.5. Transesterification Setup and Process

The batch experiments were performed in a hard glass reactor (300 ml, 7 cm internal diameter) with two neck grounded lid. One neck was connected with a titanium sonotrode S7 with a diameter of 7 mm and length of 100 mm. It can transmit constant ultrasound irradiation (amplitude 50% with 1 cycle per second) into the reaction mixture throughout the reaction time. An ultrasonic processor UP200S (Hielscher Ultrasonics) was used to operate the sonotrode with 200 W and 24 kHz frequency. The other neck was fitted with a customized, water-cooled, stainless steel condenser to reflux the evaporated methanol. The whole apparatus was placed in a constant temperature oil bath controlled by a proportional integral derivative temperature controller. The temperature can be raised up to 65 °C with an accuracy of ± 1 °C. All the experiments were carried in triplicates.

Accurately weighed oil along with catalyst and methanol were charged into the reactor. The different parameters like catalyst amount, methanol oil molar ratio, temperature and time were fixed as required. After the reaction was completed the product sample was collected, cooled and centrifuged at 10,000 rpm for 20 min. The upper layer was separated for which the ^1H NMR spectrums were recorded on a Bruker AV-III 500 MHz NMR, Switzerland. The peak differences in the ^1H NMR were used to find the conversion of biodiesel [22, 23].

The bottom catalyst layer was carefully removed and regenerated. The catalyst was regenerated by washing three times with n-hexane by simultaneous sonication and centrifugation. This was performed in between each cycle. The regenerated catalyst was then investigated for successive uses. The biodiesel properties were determined according to ASTM standard test methods and compared accordance with ASTM D 6751 standard for biodiesel.

3. Results and Discussion

3.1. Characterization of Oil

Physicochemical properties of mixed oil were determined and shown in Table 1. The fatty acids compositions illustrate the presence of high-level of unsaturated fatty acid content (87.75 wt%) and

low-level of saturated fatty acid (11.81 wt%) indicates that the oil is more of unsaturated fatty acids (Table 2). This makes the oil a clear liquid at room temperature.

The result shows that the raw material contains 18.91 wt% of mono unsaturated fatty acid, 68.76 wt% of poly unsaturated fatty acids and 0.44 wt% of undetected materials may be due to the presence of substances like sterols, hydrocarbons, aliphatic alcohols etc.

3.2. Characterization of Catalyst

Magnesium oxide (periclase) crystallizes in cubic symmetry (NaCl structure) were observed in SEM micrograph (Figure 1.) The MgO has a three-dimensional cubic shape and its edges were sharp and uniform. Most of MgO particles were of a similar shape. It was also found that the side length of MgO nano-cubic was approximately 60 nm.

From the Figure 2., X-ray diffraction pattern of the prepared powder shows the diffraction peaks that are indexed to cubic MgO. No characteristic peaks of other impurities were detected in the pattern. The sharp diffraction peaks indicate the good crystallinity of the prepared MgO powder. The crystallite size of MgO nano-cube was calculated

Table 1. Physical and chemical properties of mixed oil

Properties of mixed vegetable oil	
Specific gravity	0.912
Acid value	0.02 mg KOH g ⁻¹ of oil
Water content	0.01 vol%
Average molecular weight	873 g mol ⁻¹
Saponification value	199
Iodine value	141

Table 2. Fatty acid profile of sunflower oil

Fatty acid	Composition (wt%)
Palmitic	6.47
Palmitoleic	0.08
Stearic	4.73
Oleic	18.91
Linoleic	68.04
Linolenic	0.65
Arachidic	0.19
Eicosadieonic	0.07
Behenic	0.42

from the full width half maximum of all peaks. Average crystal size was found to be 50 ± 5 nm using Debye-Scherrer equation [24]. This value is close to the crystallite size 40-60 nm obtained from the SEM image. The XRD pattern is also compared with that of literature [25, 26].

EDX spectra in Figure 3., show that the nano particles were composed of magnesium and oxygen. The molar ratio of Mg:O calculated from EDX and stoichiometric data were close to each other. Except the two elements magnesium and oxygen, no other peak for any other element has been found in the spectrum, which confirms again that the grown nano particles are pure MgO.

3.3. Effect of Catalyst Loading

Nano magnesium oxides possess mostly basic surface sites, which make them highly efficient in catalytic processes [27]. The transesterification re-

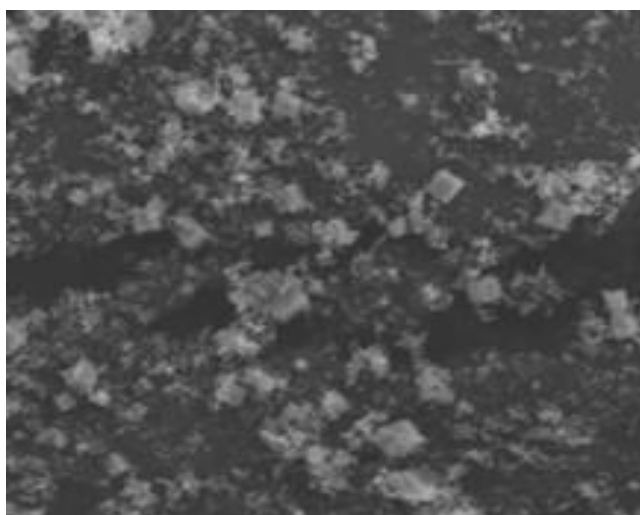


Figure 1. Typical surface-section SEM micrograph of the obtained smoke deposited MgO powder with 5μm resolution

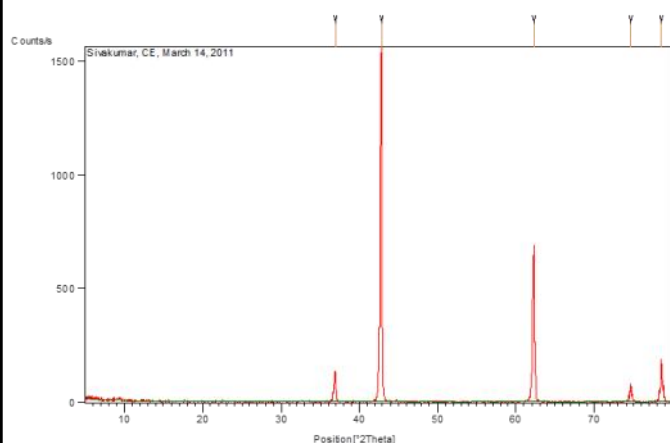


Figure 2. X-ray diffraction pattern of the obtained smoke deposited MgO powder

action was strongly affected by catalyst concentration. The biodiesel conversion was investigated with 6:1 molar ratio of methanol oil and a temperature of 55 °C for 30 min. When the catalyst concentration was increased from 0.5 wt% to 1.5 wt% the conversion was increased from 45% to 88% respectively as shown in Figure 4. However when the catalyst concentration was increased beyond 1.5 wt%, the conversion remained unchanged. This may be due to the presence of excess catalyst that may tend to the reverse the equilibrium.

3.4. Effect of Methanol to Oil Molar Ratio

Another important factor affecting the biodiesel conversion is methanol oil molar ratio. The stoichiometry of the transesterification reaction requires only three moles of methanol to yield one mole of glycerol and three moles of fatty esters [28]. Transesterification reaction being a reversible reaction excess methanol is used to shift the reaction to the right. The reaction was carried out by varying molar ratios of methanol from 3:1 to 6:1 under the conditions of 1.5 wt% catalyst, reaction

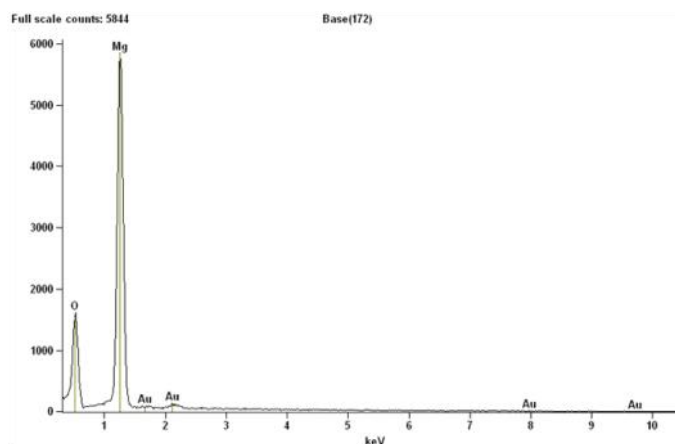


Figure 3. EDX pattern of the obtained smoke deposited MgO powder are composed of Mg and oxygen

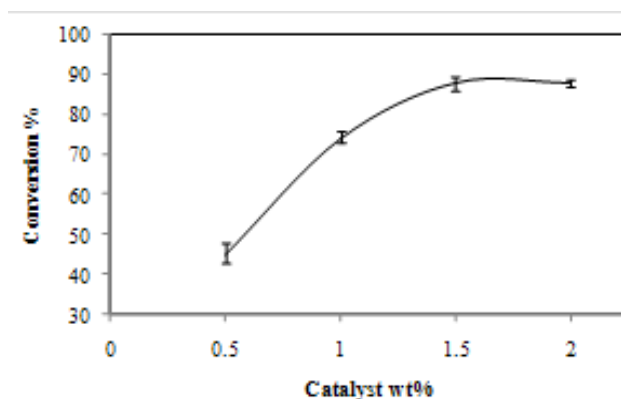


Figure 4. Effect of catalyst loading

temperature of 55 °C in 30 min. From Figure 5., conversion of biodiesel increased from 47 to 90% as the molar ratio increased up to a value from 3:1 to 5:1. The conversion dropped from 90 to 88% when the molar ratio was 6:1 due to the formation of methanol cloud on the liquid surface due to high power ultra sonic energy.

3.5. Effect of Reaction Temperature

Reaction temperature is another important factor that will affect the yield of biodiesel. Each experiment was run for 30 min with 1 wt% catalyst and 6:1 methanol oil molar ratio. The reaction temperature was varied from 35 to 65 °C as shown in Figure 6. The result indicates that the biodiesel conversion was low at lower temperature with only 30% at 35 °C, biodiesel conversion increased sharply and reached 94% at 55 °C. The conversion decreased on further increase in temperature 90% at 65 °C. When the temperature was higher methanol vapourizes and most part of the methanol in vapour phase in reactor head and condenser. Therefore the optimum temperature was 55 °C.

3.6. Effect of Reaction Time

The conversion increases with reaction time as shown in Figure 7. The effect reaction time on reaction conversion was conducted at optimized 5:1 molar ratio of methanol, reaction temperature 55 °C with 1.5 wt% catalyst. The conversion of biodiesel increased with the reaction time from 15 min as 53.1% and reached a maximum 98.7% at a reaction time of 45 min. The result indicates that an extension of reaction time from 45-60 min had no significant effect on the conversion of triglycerides but leads to a reduction in product yield. This is because longer reaction time enhances reverse reaction [29].

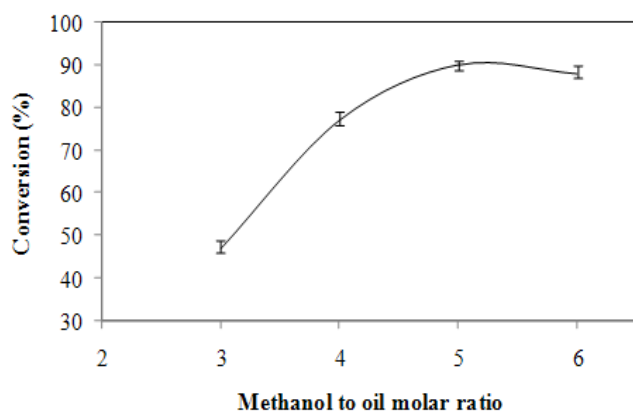


Figure 5. Effect of methanol oil molar ratio

3.7. Effect of Catalyst Deactivation

Figure 8 shows the effect of catalyst reusability on the biodiesel conversion percentage. Regeneration removes the substances that were adsorbed on the surface of the catalyst that would decrease the contact between the basic sites and reactants. Deactivation of the catalyst during recycle and reuse was observed. This is due to physical loss of catalyst up to 1 wt% due to action of emptying the reaction mass from the reactor, regeneration and also contributed by leaching. The biodiesel yield was decreased from 98.7% to 90.1% when the process was repeated for eighth time use. Biodiesel conversion was decreased below 90% is observed only after the eighth cycle. Therefore the service life of the catalyst to attain a conversion above 90% was 8 times.

3.8. Mechanism for Transesterification Reaction

Many reaction models were proposed for the mechanism of transesterification on catalyst surface based on the Eley-Rideal form of mechanism. These models proposed that solely methyl alcohol was adsorbed on the catalyst surface, which react with free triglyceride. But according to Yan et al. [30], a mechanism was proposed in Scheme 1. Initially, methanol and triglycerides were adsorbed on the two-neighboring free active sites. Then methanol was adsorbed on each Brönsted and Lewis base sites and where nucleophilic attack occurs to create a tetrahedral intermediate. Thus, the -C-O- bond breaks and forms two sorts of esters, methyl group ester and diglyceride. These transesterification mechanisms are often extended to di- and monoglyceride.

3.9. Kinetics of Transesterification Reaction

The proposed mechanism assumes homogeneous catalytic reaction. This reaction follows a first

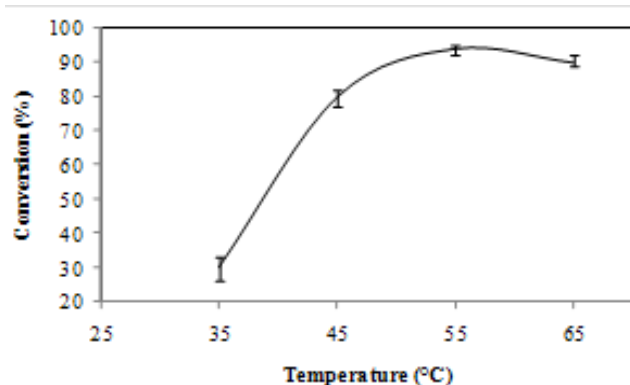


Figure 6. Effect of reaction temperature

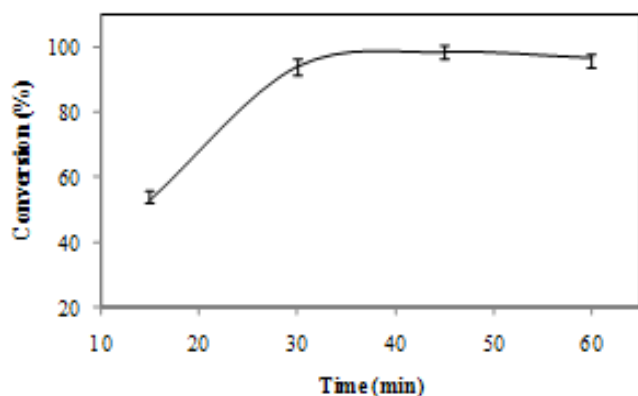


Figure 7. Effect of reaction time

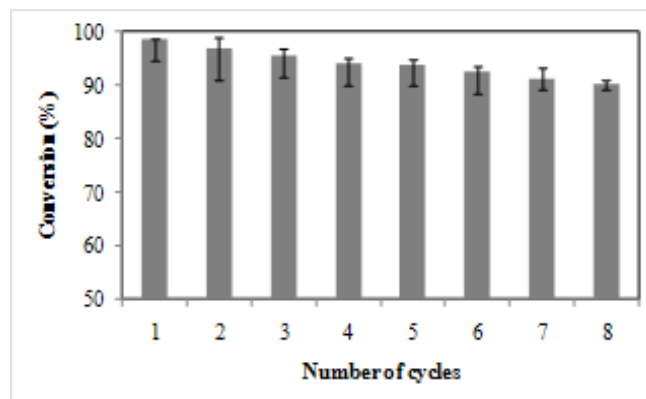
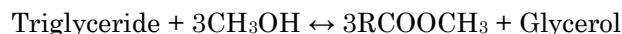


Figure 8. Effect of catalyst deactivation

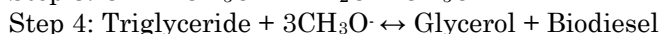
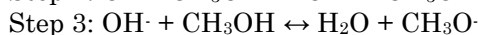
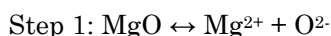
Table 3. Properties of biodiesel produced under optimal reaction conditions and ASTM 6751 limits

Properties	Units	ASTM Limits	Biodiesel
Specific gravity	-	-	0.870
Flash point	°C	130 min	159
Cloud point	°C	Report	1
Viscosity @40 °C	mm ² s ⁻¹	1.9-6	4.27
Acid value	mg KOH g ⁻¹	0.05 max	0.036
Carbon residue	wt%	0.05 max	0.042
Water & sediments	vol%	0.05 max	0.037
Cu strip corrosion	-	No. 3 max	1a
Na & K	ppm	5 max	0.2
Ca & Mg	ppm	5 max	5
Phosphorous	wt%	0.001 max	0.0009

order kinetics as a function of the concentration of oil (Triglyceride). Due to the high methanol concentration, methanol was not considered as a limiting reactant. This also shifts the equilibrium to the right; therefore the overall reaction was assumed to be a single step shunt reaction (neglecting the intermediate reaction). Here three ester groups were attacked by the methoxy ion at the same time. Kinetic rate constant (k) was established using this model, ignoring the intermediate step [31].



The rate constant for different temperatures was obtained at the optimum condition. Fitting the



Scheme 1. Possible mechanism for transesterification reaction catalyzed by MgO

different k values to Arrhenius equation, the apparent activation energy was calculated as 58.49 kJ mol⁻¹ was calculated. From the observations, it was found that the assumption of irreversible reaction was agreeable. Similarly the rate constants are found to be increasing with increase in temperature for the forward reactions.

3.10. Properties of Biodiesel

The NMR spectrum of the biodiesel showed (Figure 9) a conversion of 98.7%. The produced biodiesel was purified by phosphoric acid treatment method [32]. The specific gravity of the product biodiesel decreased sharply from 0.912 to 0.870. Lower value of the specific gravity of the final biodiesel is an indication of completion of reaction [33].

The acid values obtained after purification step was 0.036 mg KOH g⁻¹, which was slightly higher than the feedstock sunflower oil (0.02 mg KOH g⁻¹). This may be due to the hydrolysis of esters in contact with water during purification step. There is a high probability for the entry of Mg and phospho-

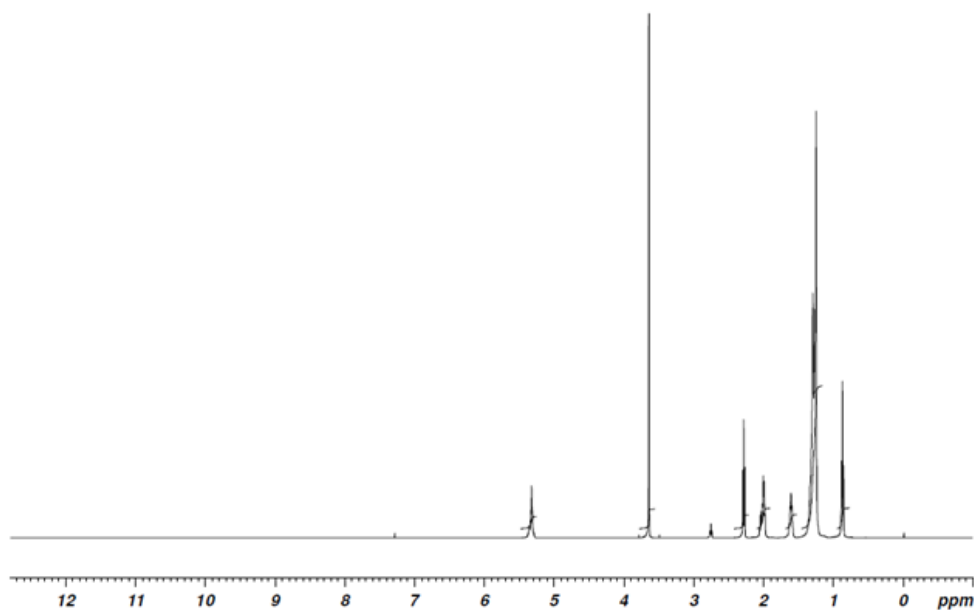


Figure 9. ^1H NMR spectrum of biodiesel

rous in to the biodiesel from the catalyst and during purification step. But the test results clearly indicate Mg and phosphorous are removed during washing and are in the range of fuel properties prescribed American standards. Other quality parameter in biodiesel is given in Table 3. The determination of biodiesel fuel quality is therefore an issue of great importance to the successful commercialization of this fuel. Accordingly, the analysis of biodiesel confirms the fuel qualities are according to ASTM 6751 standards.

4. Conclusion

A higher conversion of biodiesel (97.8%) was obtained which can be comparable with the homogeneous catalyst makes the former an upcoming catalyst for the future. The production of catalyst is quiet simple and catalytic conversion by these materials is good when compared to other MgO catalyst reported in the literature. Attempts to recover and reuse the catalyst were also made. The result reveals that it can be reused up to eight times with easy regeneration makes it economical and a preferable one. In this regard the use of these catalysts for continuous production of biodiesel at the industrial level can be the subject for further investigation.

References

- [1] Sharma, Y.C., Singh, B., Upadhyay, S.N. (2008). Advancements in development and characterization of biodiesel: a review. *Fuel*, 87: 2355-2373.
- [2] Meher, L.C., Vidya, S.D., Naik, S.N. (2006). Technical aspects of biodiesel production by transesterification: a review. *Renew. Sust. Energy Rev.*, 10: 248-268.
- [3] Nouredini, H., Zhu, D. (1997). Kinetics of transesterification of soybean oil. *J. Am. Oil Chem. Soc.*, 74: 1457-1463.
- [4] Freedman, B., Butterfield, R.O., Pryde, E.H., (1986). Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.*, 63: 1375-1380.
- [5] Singh, A.K., Fernando, S.D. (2008). Transesterification of soybean oil using heterogeneous catalysts. *Energy Fuel*, 22: 2067-2069.
- [6] Liu, X., He, H., Wang, Y., Zhu, S. (2007). Transesterification of soybean oil to biodiesel using SrO as a solid base catalyst. *Catal. Commun.*, 8: 1107-1111.
- [7] Dossin, T.F., Reyniers, M.F., Marin, G.B. (2006). Kinetics of heterogeneously MgO catalyzed transesterification. *Appl. Catal. B: Environ.*, 61: 35-45.
- [8] Kiss, A.A., Omota, F., Dimian, A.C., Rothenberg, G. (2006). The heterogeneous advantage: biodiesel by catalytic reactive distillation. *Topics in Catal.*, 40: 141-150.
- [9] Watkins, R.S., Lee, A.F., Wilson, K. (2004). Li-CaO catalyzed triglyceride transesterification for biodiesel applications, *Green Chem.*, 6: 335-340.
- [10] Kim, H., Kang, B., Kim, M.J., Park, Y.M., Kim, D., Lee, J., Lee, K. (2004). Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. *Catal. Today*, 93-95: 315-320.
- [11] Leclercq, E., Finniels, A., Moreau, C. (2001). Transesterification of rapeseed oil in the presence of basic zeolites and related solid catalysts. *J. Am.*

Oil Chem. Soc., 78: 1161-1167.

- [12] Arzamendi, G., Arguiñarena, E., Campo, I., Zabala, S., Gandia, L.M. (2008). Alkaline and alkaline-earth Metals compounds as catalysts for the methanolysis of sunflower oil. *Catal. Today*, 133-135: 305-313.
- [13] Ohring, J. ed. (1992). *The Material Science of Thin Films*. San Diego, Academic-Press.
- [14] Dorado, M.P., Ballesteros, E., Lopez, F.J., Mittelbach, M. (2004). Optimization of alkali-catalyzed transesterification of Brassica carinata oil for biodiesel production. *Energy Fuel*, 18: 77-83.
- [15] Hartman, L., Lago, R.O. (1973). Rapid preparation of fatty methyl esters from lipids. *Lab. Pract.*, 22: 475-6.
- [16] Srivastava, A., Prasad, R. (2000). Triglycerides-based diesel fuels. *Renew. Sust. Energy Rev.* 4: 111-133.
- [17] Fangruil, M.A., Hanna, M.A. (1999). Biodiesel production: a review. 70: 1-15.
- [18] Rodriguez, J.A., Maiti, A. (2000). Adsorption and decomposition of H₂S on MgO(100), NiMgO(100), and ZnO(0001) surfaces: a first-principles density functional study. *J. Phys. Chem. B.* 104: 3630-3638.
- [19] Rodriguez, J.A., Jirsak, T., Chaturvedi, S. (1999). Reaction of H₂S with MgO(100) and Cu/MgO (100) surfaces: Band-gap size and chemical reactivity. *J. Chem. Phys.* 111: 8077-8087.
- [20] Rodriguez, J.A., Jirsak, T., Kim, J.Y., Larese, J.Z., Maiti, A. Interaction of NO and NO₂ with MgO (100): photoemission and density-functional studies. *Chem. Phys. Lett.* 330: 475-483.
- [21] Soave, R., Pacchioni, G. (2000). New bonding mode of CO on stepped MgO surfaces from density functional cluster model calculations. *Chem. Phys. Lett.*, 320: 345-351.
- [22] Knothe, G., Kenar, J.A. (2004). Determination of fatty acid profile by H¹NMR spectroscopy. *Eur. J. Lipid Sci. Tech.*, 106: 88-96.
- [23] Gelbard, G., Bres, O., Vargas, R.M., Vielfaure, F., Schuchardt, U.F. (1995). H¹ Nuclear Magnetic Resonance determination of the yield of the transesterification of rapeseed oil with methanol. *J. Am. Oil Chem. Soc.* 72: 1239-1241.
- [24] Cullity, B.D. (1978). *Elements of X-ray diffraction*. Philippines Addison, Wesley Publishing Company Inc.
- [25] Rao, K.V., Sunandana, C.S. (2008). Structure and microstructure of combustion synthesized MgO nanoparticles and nanocrystalline MgO thin films synthesized by solution growth route. *J. Mater. Sci.* 43: 146-154.
- [26] Naoyuki, T. (2007). Simple and rapid synthesis of MgO with nano-cube shape by means of a domestic microwave oven. *Solid State Sci.*, 9: 722-724.
- [27] Aramendia, M.A., Borau, V., Jimenez, C., Marinas, J.M., Ruiz, J.R., Urbando, F.J. (2003). Influence of the preparation method on the structural and surface properties of various magnesium oxides and their catalytic activity in the Meerwein-Ponndorf-Verley reaction. *Appl. Catal. A* 244: 207-215.
- [28] Murugesan, A., Umarani, C., Chinnusamy, T.R., Krishnan, M., Subramanian, R., Neduzchezhain, N. (2009). Production and analysis of biodiesel from non edible oils-reviews. *Renew. Sustain. Energy Rev.* 13: 825-834.
- [29] Eevera, T., Rajendiran, K., Saradha, S. (2009). Biodiesel production process optimization and characterization to assess the suitability of the product for varied environmental condition. *Renew. Energy*, 34: 762-765.
- [30] Yan, S., Kim, M., Salley, S.O., Ng, K.Y.S. (2009). Oil transesterification over calcium oxides modified with lanthanum. *Appl. Catal. A: Gen.*, 360: 163-170.
- [31] Sivakumar, P., Sindhanaiselvan, S., Gandhi, N.N., Devi, S.S., Renganathan, S. (2013). Optimization and kinetic studies on biodiesel production from underutilized *Ceiba pentandra* oil. *Fuel*, 103: 693-698.
- [32] Predojevic, Z.J. (2008). The production of biodiesel from waste frying oils: A comparison of different purification steps. *Fuel*, 87: 3522-3528.
- [33] Miao, X., Wu, Q. (2006). Biodiesel production from heterotrophic microalgal oil. *Bioresour. Technol.*, 97: 841-846.