

Microwave assisted transesterification of waste cooking oil over modified forms of zirconia coated on honeycomb monolith

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Microwave assisted transesterification of waste cooking oil over honeycomb monoliths coated with zirconia based catalysts such as MgO/ZrO₂ and CaO/ZrO₂ to synthesize biodiesel is reported. For comparison, biodiesel synthesis via transesterification using conventional heating method has also been carried out. The solid acid Al₂O₃/ZrO₂ coated on a honeycomb has also been used as a catalyst to reduce the percentage of free fatty acid in waste cooking oil via esterification using conventional heating. The honeycomb monoliths have been coated with solid bases and characterized for their physico-chemical properties such as surface acidity, surface basicity, crystallinity and morphology using suitable techniques. The honeycomb monoliths coated with solid catalysts are found to be highly efficient and reusable in the process of synthesizing biodiesel from waste cooking oil. A maximum yield of biodiesel (98%) is obtained at 60 °C in 10 min by keeping the molar ratio of oil:methanol ratio at 1:6 under microwave irradiation.

Keywords: Catalysts, Modified catalysts, Biodiesel synthesis, Transesterification, Microwave, Waste cooking oil, Honeycomb monoliths, Zirconia catalysts, MgO/ZrO₂, CaO/ZrO₂

Due to increase in the energy demand and environmental hazards on the use of fossil fuels, it has become a necessity to develop alternative fuels. Among these, biodiesel is an interesting option because it is biodegradable, non-toxic and it is produced from renewable sources^{1,2}. Biodiesel is produced from edible vegetable oils such as canola, soybean, cotton seed, jatropha, etc^{3, 4}. However, a major hurdle in the industrial level production of biodiesel from edible vegetable oils is the high production cost. One way to reduce the cost of biodiesel is to use less expensive raw materials such as waste cooking oils (WCO) and non-edible vegetable oils⁵.

Waste cooking oil (WCO) has disposal problems, which can be turned into economical and environmental benefit by proper utilization and management as a fuel substitute. WCO can be converted into biodiesel by transesterification using alcohols such as methanol, ethanol, propanol, etc., in presence of suitable acidic or basic catalysts⁶⁻⁸. Since WCO is associated with high levels of free fatty acids (FFA), a two-step process (acid esterification followed by alkali transesterification) is employed to remove

high FFA content and to improve the biodiesel yield. However, the long reaction time and low recovery of catalyst are disadvantages of this two-step process.

An alternative method, i.e., microwave-assisted catalytic transesterification has been developed that gives high yield of biodiesel with high purity. Microwave-assisted transesterification is an energy-efficient and quick process to produce biodiesel from renewable sources^{9,10}. A single step direct transesterification of vegetable oil consisting of high levels of FFA using microwave irradiation is also reported¹⁰. Microwave-assisted synthesis of biodiesel from rapeseed oil, cotton seed oil, etc., via transesterification has been reported by several researchers^{9,11,12}.

Cordierite (Mg₂Al₄Si₅O₁₈) honeycomb monolith (HC) plays a vital role as catalyst carriers for heterogeneous catalysts. Honeycomb monoliths coated with catalysts are advantageous over powder catalysts with high active surface area. Moreover, less amount of catalyst loaded on the HC is highly efficient, easy separable and recoverable from the reaction mixture¹³. HCs coated with catalyst are mostly used in automotive applications involving gas

phase reactions such as combustion of VOCs, ozone abatement and reduction of NO_x , etc¹³. The use of HCs as catalyst carriers, especially for solid catalysts, would be a cost effective and eco-friendly process and also will be an interesting initiative step in the field of microwave assisted synthesis of biodiesel.

In the present article, an attempt has been made to synthesize biodiesel via transesterification of WCO using microwave irradiation over modified forms of zirconia (MgO/ZrO_2 , CaO/ZrO_2 consisting of 20% Mg or 5% Ca) coated on honeycomb monoliths. For comparison, biodiesel has also been synthesized by conventional heating method. Modified zirconia were coated on honeycomb monoliths by 'dip and dry' method and characterized for their physico-chemical properties. Reactivation and reusability studies of HC catalysts were also carried out.

Materials and Methods

Waste cooking oil (%FFA or acid value = 12.4 mg KOH/gm) was obtained from restaurants across Bengaluru, India. Zirconyl nitrate, calcium nitrate, magnesium nitrate, aluminum nitrate and methanol were supplied by Loba Chemie India Pvt Ltd. Honeycomb monoliths (HC) (height = 0.6 cm; diameter = 1.5 cm; hole size = 0.15 cm) were purchased from Shreya Ceramics, Baroda, India.

Preparation and characterization of HC catalysts

Honeycomb monoliths (HCs) were coated with MgO/ZrO_2 or CaO/ZrO_2 by 'dip and dry' method. In a typical method, known amount of zirconyl nitrate (3.0 g) with/without magnesium nitrate (1.8 g)/calcium nitrate (1.4 g) was taken in a 125 mL beaker to which 30 mL of deionized water was added. The resulting solution was coated on a bare honeycomb by 'dip and dry' method¹⁴ in a muffle furnace was preheated at 400 °C (kept for drying for 2-3 min). 'Dip and dry' steps were carried out 10-12 times until ~0.2 g of the solid base catalyst was coated on the HC. Finally, the HCs coated with ZrO_2 , MgO/ZrO_2 and CaO/ZrO_2 were calcined at 550 °C for 3 h. The thus calcined HC catalysts were designated as ZrO_2 (Z), MgO/ZrO_2 (MZ) and CaO/ZrO_2 (CZ) respectively.

Similarly, the HC was also coated with a solid acid such as 20% $\text{Al}_2\text{O}_3/\text{ZrO}_2$ using zirconyl nitrate (6.1 g) and aluminum nitrate (5.0 g), and abbreviated as AZ.

The HCs coated with Z or MZ or CZ or AZ were characterized by CO_2 -TPD/ NH_3 -TPD method for surface basicity/acidity using Mayura-TPD unit. XRD patterns were recorded on a X-ray diffractometer

(Philips X'pert) using Cu-K α ($\lambda = 1.5418 \text{ \AA}$) and SEM images were recorded on JEOL-2010 instrument.

Microwave assisted synthesis of biodiesel (using HC catalysts)

Honeycomb monoliths coated with Z or MZ or CZ were placed in a reactor specially designed in our laboratory (Supplementary Data, Fig. S1) to accommodate honeycomb monolithic catalyst along with 20 g of unesterified WCO and methanol (molar ratio of WCO: methanol = 1:6). The glass reactor consisted of a ring at the bottom to accommodate both a magnetic stirrer and a honeycomb.

The mixture was subjected to microwave irradiation in a microwave reactor (Labmatrix India Ltd) equipped with a water cooled condenser, a magnetic stirrer with a power of 800 W. The reactions were carried out for a particular interval of time at 60 °C. After the reaction time, the HC catalyst was separated by filtration from the reaction mixture and the resulting reaction mixture was transferred to a separation flask. The upper layer (biodiesel) was separated from the bottom layer (glycerol). The crude biodiesel was washed with deionized water for purification and analysed by GC-MS (Hewlett Packard HP-624) fitted with a column bearing description; HP-624, 30 m \times 25 μm \times 0.25 μm .

Synthesis of biodiesel by conventional heating (using HC catalysts)

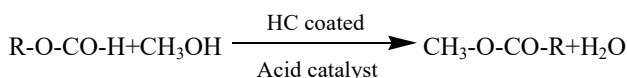
Biodiesel production using conventional heating process was carried out in two steps (Scheme 1). Since the WCO used for the present work consisted of high %FFA (12.4 mg KOH/g), it was reduced to a lower permissible value by acid catalyzed esterification. Therefore, the first step involved acid catalyzed esterification of WCO with methanol (WCO: methanol = 1:6) over HC-acid catalyst (AZ) to reduce the percentage of free fatty acid (acid value) and the second step was the production of biodiesel via base catalyzed transesterification of WCO over HC-base catalyst (MZ or CZ).

The acid value of the esterified WCO was determined by the acid-base titration method¹⁵ using 0.5 N NaOH solution. The following equation was used to calculate the acid value: Acid value = $(X_1 - X_2) / X_1$, where X_1 is the volume of base (NaOH solution) required for pure WCO, and X_2 is the volume of base (NaOH solution) required for WCO after esterification.

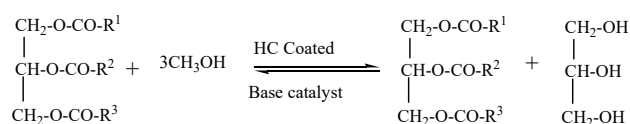
The reactions (both esterification and transesterification) were carried out with 20 g of WCO. Methanol and the HCs coated with solid

acid/base catalysts (Z or MZ or CZ/ AZ) were placed in a specially designed reactor with a ring at the bottom to accommodate the HC catalyst and refluxed at reflux temperature (~60 °C) for a particular period of time on a magnetic stirrer cum hot plate. After the completion of both esterification and transesterification steps the reaction mixture consisting of biodiesel was analyzed using GC-MS.

Step 1: Acid catalyzed esterification of WCO



Step 2: Base catalysed transesterification of esterified WCO



Scheme 1

Results and Discussion

The total surface basicity (TSB) and basic site distribution of the HC catalysts measured by CO₂-TPD method are given in Table 1. Pure zirconia was found to be least basic followed by MZ and CZ [16]. i.e., CZ is most basic than either pure Z or MZ. Further, CZ consisted of ‘moderate, strong as well as very strong’ basic sites whereas MZ consisted of ‘moderate and strong’ basic sites. The surface acidity (SA) of AZ measured by NH₃-TPD was found to be 0.78 mmols/g.

The XRD patterns of HC catalysts (Z, MZ & CZ) are shown in Fig. 1. Z consists of reflections due to its monoclinic and tetragonal phases. However, the XRD pattern of MZ showed characteristic reflections due to MgO as well as reflections due to tetragonal phase of zirconia. The XRD pattern of CZ consists of peaks pertaining to tetragonal phase of zirconia and peaks

corresponding to CaO. Further, the XRD pattern of AZ consisted of reflections pertaining to rhombohedral alumina and tetragonal phase of zirconia. Interestingly, no reflections corresponding to monoclinic phase of zirconia are seen in the XRD patterns of MZ or CZ or AZ. This indicates that structure stabilizing effect of CaO, MgO and Al₂O₃ on ZrO₂ and also infers that the catalysts are in the form of mixed oxides.

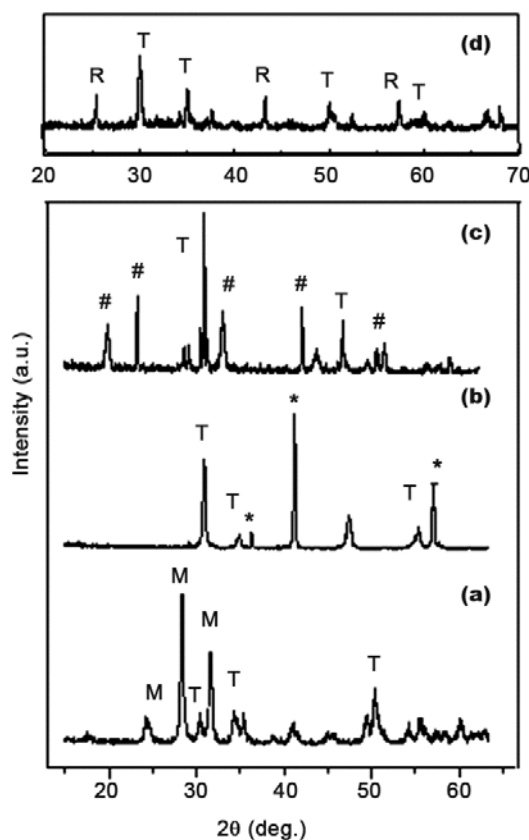


Fig. 1—XRD patterns of (1) Z, (2) MZ, (3) CZ, and, (4) AZ. [M- monoclinic ZrO₂, T- tetragonal ZrO₂, * - MgO, # - CaO, R – rhombohedral Al₂O₃].

Table 1—TSB, basic site distribution of the HC catalysts and the yield (%) of biodiesel

HC catalyst	Basic site distribution (mmol/g)				TSB (mmol/g)	Yield of biodiesel ^a (%)
	Weak	Moderate	Strong	Very strong		
Z	0.07	0.28	-	-	0.35	31 (29)
MZ	-	0.19	1.04	-	1.23	98 (96)
CZ	-	0.17	0.98	0.29	1.44	83 (262)
AZ ^b	-	-	-	-	0.78 (SA)	3.3 (% FFA)

^aReact cond.:Reaction time = 10 min for microwave heating and 2 h for conventional heating; reaction temp. = 60 °C; weight of catalyst = ~0.2 g coated on HC; weight of WCO = 20 g; molar ratio of WCO: methanol = 1:6. Numbers in the parenthesis represent the yield (%) of biodiesel obtained after conventional heating under the reaction conditions as mentioned above.

^bSurface acidity and %FFA over AZ catalyst after 2 h of esterification.

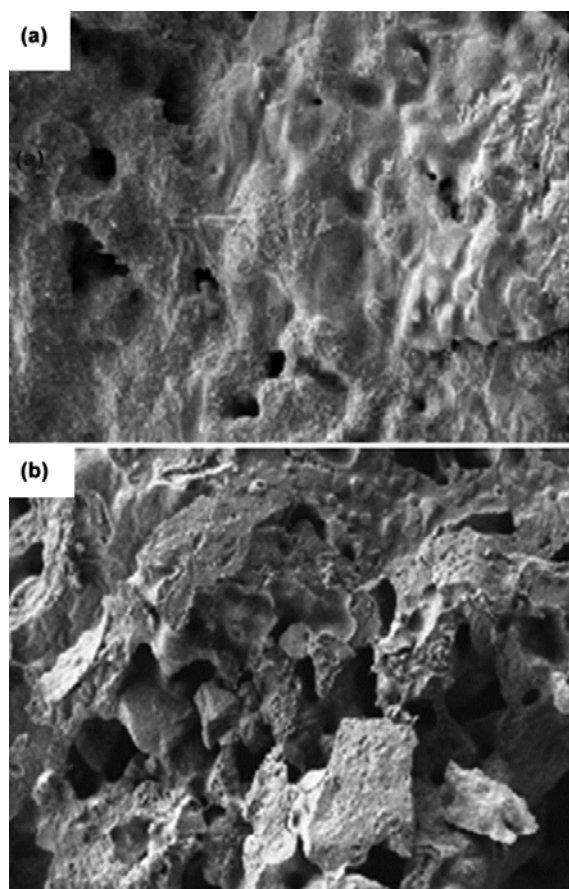


Fig. 2—SEM images of (a) MZ, and, (b) CZ. [Magnification = 2000X; 10 μ m].

SEM images of HC catalysts coated with MZ and CZ are shown in Fig. 2. The images show appearances indicating a strong, adherent and almost uniform coating of the active catalyst on the surface of the HC. This indicates that the method used to coat the catalyst on the HC is suitable enough to obtain an efficient coat. Similar SEM images were obtained for Z and AZ catalysts (Supplementary Data, Fig. S2).

Microwave assisted synthesis of biodiesel

In order to find out a suitable catalyst, direct transesterification¹⁰ (without reducing the %FFA) of WCO was carried out over HCs coated with Z, MZ and CZ catalysts and the results are shown in Table 1. A correlation between the surface basicity and the yield of biodiesel was observed, i.e., Z being least basic gave less yield of biodiesel when compared to either MZ or CZ. Further, the quality of biodiesel (after separating glycerol) was found to depend on the basic site distribution of the catalysts. Soap formation

was not observed during MW or conventional heating method. Both Z and MZ showed 100% selectivity towards the formation of glycerol separated biodiesel, whereas over CZ catalyst, in addition to biodiesel by-products other than glycerol (as recorded by GC-MS) were also produced. Therefore, CZ catalyst was less selective towards the production of biodiesel than either Z or MZ. Therefore, for further studies MZ was selected as the catalyst as it produced reasonably good yield of biodiesel with 100% selectivity. When the transesterification of WCO was carried out over bare HC under microwave irradiation, a very low yield (11%) was observed which indicates that the transesterification is a catalyzed reaction.

Conventional heating method of synthesis of biodiesel

Before carrying out transesterification, the WCO was subjected to esterification with methanol over a solid acid catalyst (AZ). Esterification reaction was carried out to reduce the %FFA in WCO from 12.4 mg KOH/g. The reaction was carried out by using 20 g of WCO in a molar ratio of WCO:methanol at 1:6 at a reaction temperature of 60 °C for 2 h. After the esterification reaction, the %FFA (acid value) was found to be 3.3 mg KOH/g. The thus obtained esterified WCO was then subjected to transesterification over basic catalysts for the synthesis of biodiesel.

Synthesis of biodiesel via transesterification was carried out by conventional heating method on a magnetic stirrer cum hot plate over all the HC catalysts studied in the present work. It was noticed that the yield of biodiesel (for a reaction time of 10 min) was low with conventional heating when compared to the yield of biodiesel obtained under microwave conditions. For instance, over MZ catalyst, 98% of biodiesel was obtained under microwave irradiation in 10 min whereas only 32% biodiesel was obtained in 10 min under conventional heating method. Further, to obtain ~96% of biodiesel under conventional heating method it took ~2 h. Therefore, microwave assisted synthesis of biodiesel is more beneficial than conventional heating method in terms of increased yield of biodiesel in shorter reaction times.

Effect of molar ratio of WCO: Methanol on the yield of biodiesel

Transesterification of WCO was carried out over MZ catalyst by varying the molar ratio of WCO: methanol in the range 1:4 to 1:8 and the results are shown in Figure 3(a). It can be seen that the yield

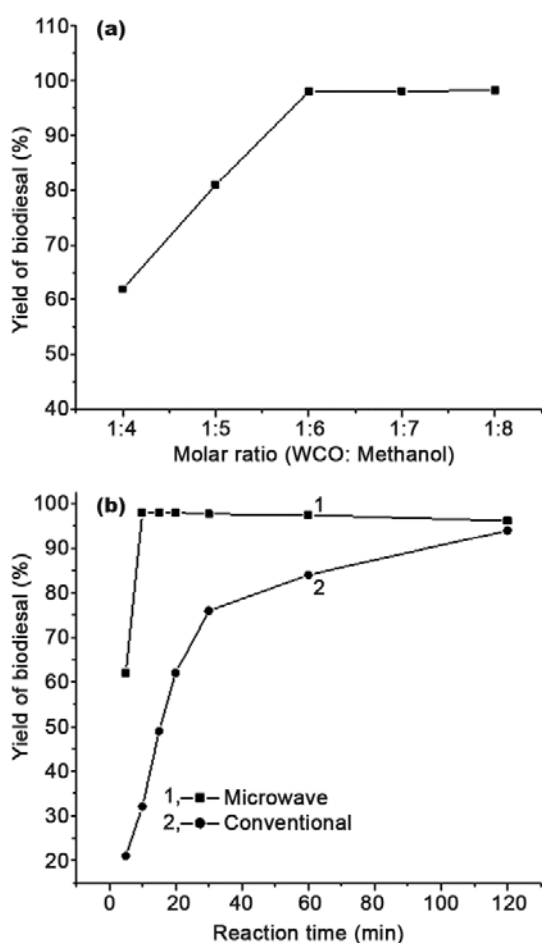


Fig. 3— (a). Effect of molar ratio of WCO-to-methanol on the yield of biodiesel over MZ catalyst. (b) Effect of reaction time on the yield of biodiesel over MZ catalyst.

of biodiesel increased when the molar ratio of WCO: methanol was increased from 1:4 till 1:6 beyond which no reasonable change in the yield of biodiesel was observed. Hence, for further studies molar of WCO: methanol was chosen as 1:6.

Effect of reaction time on the yield of biodiesel

Biodiesel synthesis was carried out with WCO by varying the reaction time ranging from 5 min to 2 h over MZ catalyst and the results are presented in Figure 3(b). As can be seen from the figure that the yield of biodiesel reached ~98% in a reaction time of only 10 min when the transesterification was carried out using microwave irradiation. However, in conventional heating method, nearly 2 h of reaction time was required to obtain ~96% of biodiesel over MZ catalyst. Hence microwave irradiation method is more advantageous in terms of reduced reaction times from hours to minutes.

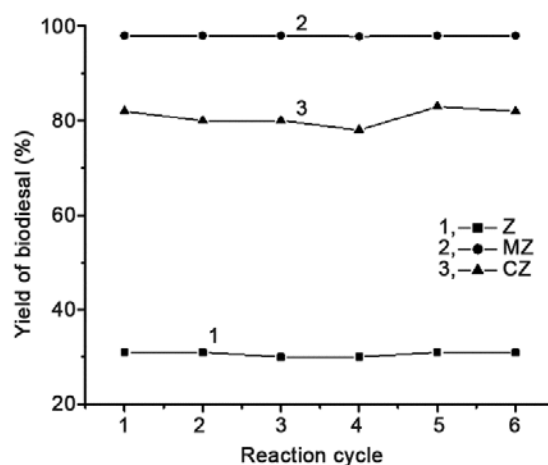


Fig. 4—Effect of reusability of HC catalysts on the yield of biodiesel under microwave irradiation.

Reactivation and reusability studies of catalysts (in microwave assisted biodiesel synthesis)

The HC catalysts (Z, MZ and CZ) were reactivated after the first cycle of the microwave assisted transesterification reaction of WCO. The used catalysts were separated from the reaction mixture by filtration, thoroughly washed with methanol and dried in a hot air oven at 120 °C for 2 h before its use in the second reaction cycle. Similar procedure was repeated after every reaction cycle for reactivation of the HC catalyst. Such reaction cycles were carried out for 6 times.

Among the HC catalysts used in the present study, Z and MZ were found to be more reusable for microwave-assisted transesterification of WCO and could be used for six reaction cycles (Fig. 4). However, the CZ catalyst was found to lose its catalytic activity gradually to a certain extent. The present study reveals that HC coated with MZ is more active, stable and efficient catalyst for the synthesis of biodiesel from WCO via microwave assisted transesterification. After the 4th cycle, when the HC catalysts were calcined for 1 h at 550 °C and reused in the 5th cycle, it was observed that all the catalysts including CZ regained their catalytic activity after calcination.

Conclusions

Biodiesel could be effectively produced from waste cooking oil over honeycomb monoliths coated with modified forms of zirconia such as MgO/ZrO₂ and CaO/ZrO₂ under microwave conditions. A correlation between the total surface basicity of the catalysts and the yield of biodiesel was observed. However, the selectivity of the biodiesel product was found to

depend on the basic site distribution on the zirconia catalysts. The solid acid $\text{Al}_2\text{O}_3/\text{ZrO}_2$ was found to effectively catalyze esterification of waste cooking oil to reduce the percentage of free fatty acid. Microwave assisted synthesis is a promising technique for biodiesel production in terms of shorter reaction time with high purity product yield compared to conventional heating method. Moreover, biodiesel synthesis can be synthesized in a single step process via microwave assisted method irrespective of the amount of free fatty acids present in the waste cooking oil. Catalysts coated on honeycomb monoliths were found to be efficient, economical and reusable.

Supplementary Data

Supplementary Data associated with this article, viz., Figs S1 and S2, are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_56A\(04\)373-378_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_56A(04)373-378_SupplData.pdf).

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References

- 1 Freedman B, Butterfield R O & Pryde E H, *J American Oil Chemists' Soc*, 63 (1986) 1375-.
- 2 Karmakar A, Karmakar S & Mukherjee S, *Biores Technol*, 101 (2010) 7201.
- 3 Ma F R & Hanna M A, *Biores Technol*, 70 (1999) 1.
- 4 Lang X, Dalai A K, N. Bakhshi N N & Reaney M J, *Biores Technol*, 80 (2002) 53.
- 5 Canakci M & Van Gerpen J, *J American Soc of Agri and Biolog Engineers*, 46 (2003) 945.
- 6 Patil P D, Gude V G, Reddy H K & Shuguang Deng, *J Environ Protection*, 3 (2012) 107.
- 7 Hassani M, Najafpour G D, Mohammadi M & Raeii M, *J Scient Ind Res*, 73 (2014) 129.
- 8 Dorado M P, Ballesteros E, Lopez F J & Mittelbach M, *Energy Fuels*, 18 (2004) 77.
- 9 Leadbeater N E & Stencel L M, *Energy Fuels*, 20 (2006) 2281.
- 10 Refaat A A, El Sheltawy S T & El Sherbiny S A, *J Adv Res*, 1 (2010) 309.
- 11 Azcan N & Danisman A, *Fuel*, 86 (2007) 2639.
- 12 Roy I & Gupta M N, *Curr Sci*, 85 (2003) 1685.
- 13 Nijhuis T A, Kreutzer M T, Romijn A C J, Kapteijn F & Moulijn J A, *J Chem Eng Sci*, 56 (2001) 823.
- 14 Venkatesh & Mohamed Shamshuddin S Z, *Indian J Chem*, 54A (2014) 843.
- 15 *AOCS Official Method Cd 3d-63, Acid Value*, (1999) (American Oil Chemists Society, Campain, USA).