

J. Surface Sci. Technol., Vol 30, No. 1-2, pp. 45-58, 2014
© 2014 Indian Society for Surface Science and Technology, India.

An Effective Heterogeneous Catalyst from Waste Material for the Biodiesel Production

AJAY K. ARORA, SUNIL RAJ M. P.**, TANMAY MANDAL, J. CHRISTOPHER, SURESH K. PURI* and ANURAG A. GUPTA

Indian Oil Corporation Ltd, R & D Centre, Sector 13, Faridabad-121 007, India

***Research Associate, Indian Oil Corporation Ltd, R & D Centre, Sector 13, Faridabad-121 007, India*

Abstract — The aim of this study was to develop an environmentally benign catalyst from natural waste material for the transesterification of vegetable oils. An ABO_3 perovskite type metal oxide based robust catalyst was developed using egg shell and evaluated for effective conversion of vegetable oil to biodiesel.

Keywords : *Heterogeneous Catalysts, Natural waste, Biodiesel.*

INTRODUCTION

Since the demand for petroleum fuels are escalating at a substantial rate and with diminishing availability of crude oil, an alternative source of energy is essentially required. Biodiesel is an attractive alternative energy source to fossil fuel due to its excellent properties such as lower exhaust emission, superior lubricity, lower toxicity, biodegradability etc. Biodiesel is synthesized by the transesterification of vegetable oils by using acidic/basic homogeneous/heterogeneous catalysts. Homogeneous catalysts [1,2] such as NaOH, KOH, etc. are most widely used for the transesterification of vegetable oils commercially since they are relatively cheap, have high activity performance under moderate reaction conditions. However homogeneous catalysts are having several disadvantages such as soap formation, complicated product separation and purification [3–9], which eventually decrease the biodiesel yield. The removal of homogeneous catalysts is technically difficult and brings extra cost to the final

*Author for correspondence. E-mail : purisk@indianoil.in, Tel: +91-129-2294211, Fax : +91-129-2284666

product. In addition, the difficulty for recycling and the generation of large waste amounts make the traditional catalysts less favorable.

Supercritical method [10,11] is fast and catalyst free, however it requires high temperature and pressure and high capital investment. Enzyme catalyzed transesterification [12–14] is also not economically viable due to its low reaction rate and high cost.

Heterogeneous catalysts received much attention recently because it can overcome many problems associated with homogeneous catalysts [15–17]. These are environmentally benign, non-corrosive catalyst and the product separation process is much easier. Moreover the purity of the byproduct, glycerine is very high. Solid acid catalysts have advantages as they can perform esterification and transesterification simultaneously and can tolerate water and free fatty acid present during transesterification of vegetable oils. However it is also having some disadvantages that the reaction rate is very slow and there are adverse reaction conditions. Solid basic catalysts are more active than acidic catalysts. Biodiesel had been synthesized from vegetable oils by using varied solid catalysts and feedstock types [18–20]. Kawashima *et al* [21] reported preparation of CaZrO_3 catalyst from laboratory grade chemicals and evaluated by biodiesel production from rapeseed oil. The surface area of the catalyst was $1.8 \text{ m}^2/\text{g}$ and the maximum biodiesel yield obtained was 91%.

Macedo *et al* [22] synthesized Al_2O_3 -SnO and Al_2O_3 -ZnO catalysts and studied their effectiveness for the transesterification of soybean oil. They have achieved biodiesel yields of about 80% from soybean oil after 4 h at 60°C using 5 wt% of catalyst concentration. Babu *et al.*²³ examined the transesterification activities of coprecipitated Mg-La oxides obtained by precipitating both nitrate precursors with KOH/ K_2CO_3 , which contained MgO, La_2O_3 , and La_2MgO_x phases. They have obtained 100% conversion of sunflower oil using Mg-La oxide (Mg/Al = 3 by weight) within 2.2 h, even at room temperature, using 5 wt% catalyst and a methanol/oil molar ratio of 20 : 1.

Our presents study demonstrates the preparation of ABO_3 perovskite type catalyst using egg shell as key raw material and evaluation of the catalyst performance by the transesterification of soybean oil. The reactions were conducted by varying the catalyst concentration, oil to methanol molar ratio and moisture content of oil to optimize the reaction conditions. The durability and recyclability of the catalyst was validated by carrying out the repeated cycles of biodiesel preparation with recovered catalysts and characterizing catalyst structure by XRD spectroscopy.

EXPERIMENTAL**Reagents and materials :**

Commercial edible grade soybean oil was purchased from local market and used without further purification. Other chemicals viz. zirconium dioxide (97%) (Loba Chemie), methanol and hexane (analytical grade solvents, Merck, India) were of lab grade. The properties of soybean oil and methanol are given in Table 1. Eggshells were collected from local market and cleaned to remove protein and other interfering substances by washing 3-4 times with warm water. Washed shells were dried overnight in an oven at 110°C to remove traces of water.

TABLE 1.

Properties of reactants

Properties	Soybean oil	Methanol
Molecular Weight	750–800 g/mol	32.04 g/mol
Kinematic Viscosity @ 40°C	32 cSt	–
Total Acid Number (TAN)	0.5 mgKOH/g	Negligible
Density	0.91 g/cm ³	0.785–0.795 g/cm ³
Moisture	Negligible	600 ppm
Assay	97%	99%
Appearance	Yellow viscous liquid	Colorless liquid

Catalyst Preparation :

The CaZrO₃ catalyst was prepared by using egg shell and ZrO₂. The prepared catalyst is an ABO₃ type metal oxide with perovskite structure, where A is an alkaline-earth metal, alkali metal, or rare earth metal and B is a transition metal. ZrO₂ and waste eggshell were used as the raw materials. The eggshells were washed and calcined at 550°C for 3 h before use. Those used eggshells were taken as the source of calcium carbonate. CaZrO₃ was prepared by mixing 1 : 1 molar ratio of calcined eggshells and ZrO₂ in a mortar for 10-15 min. The mixture was then calcined at 1150°C for 5 h. The prepared catalyst, CaZrO₃ was kept in desiccator.

Catalyst Characterization :

The synthesized catalyst was characterized by X-Ray Diffraction, IR spectroscopy, TGA, SEM analysis etc. Structure and crystalline nature of the catalyst was investigated by 18 KW X-Ray Diffractometer (Rigaku, Japan). XRD patterns were

recorded at 50 KV and 250 mA, at a scan rate of $2^\circ/\text{min}$ with a step size of 0.01° at 2θ within the range of 5 to 75° . The XRD patterns (Fig. 1) obtained were matched with the JCPDS data to find out formation of CaZrO_3 complex. Minor peaks of ZrO_2 were also observed.

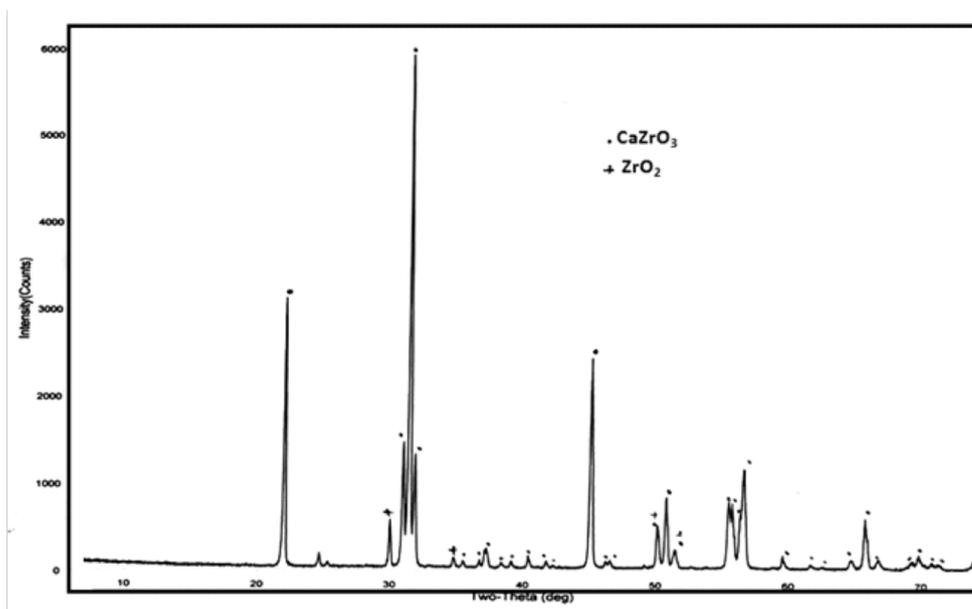


Fig. 1. XRD pattern of CaZrO_3 .

Infra-Red spectrum of the catalyst was recorded with KBr in the range of 400 – 4000 cm^{-1} by Perkin Elmer FT-IR spectrometer. Fig. 2 shows a strong band at 545 cm^{-1} of Zr-O stretching frequency of CaZrO_3 complex.

Thermogravimetric analysis is a technique in which the weight loss of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Thermogravimetric Analysis of the catalyst was performed in the temperature range from room temperature to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ by TGA model 2960 thermal analyzing machine (TA Instruments, USA) under a flow of nitrogen. Fig. 3 showed that the weight loss at 697 – 768°C corresponds to the loss of CO_2 by the decomposition of calcium carbonate in the precursor to form CaO phase which reacts with other active ingredient ZrO_2 to form CaZrO_3 .

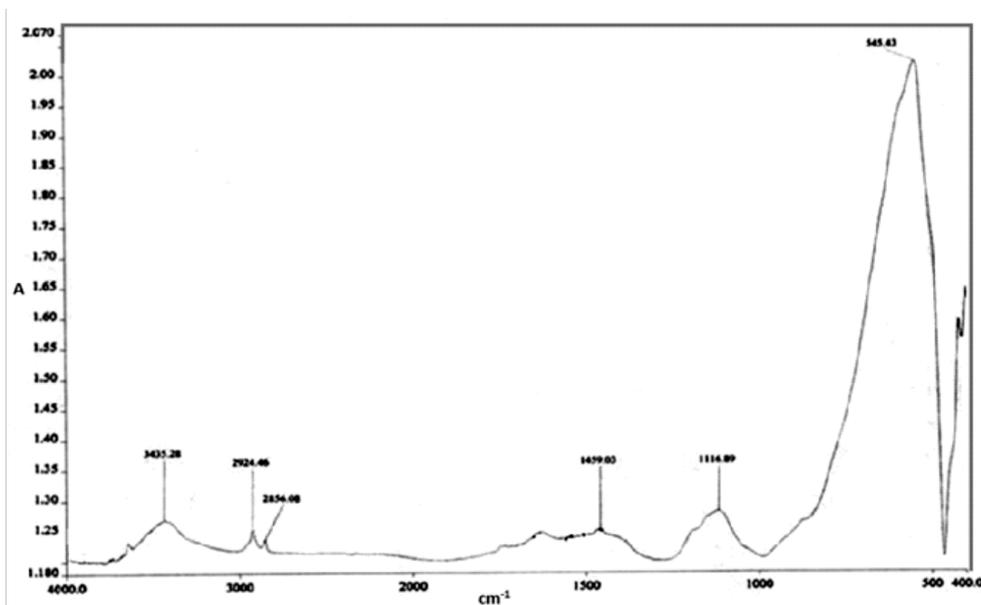
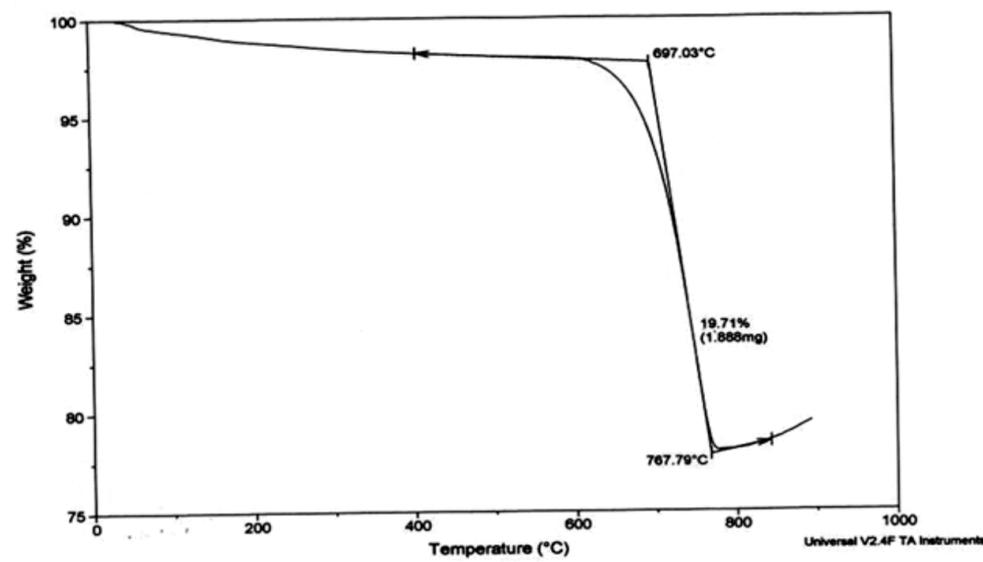


Fig. 2. IR Spectra of CaZrO₃.

BET surface area, pore size and pore volume were estimated from the N₂-adsorption/desorption isotherm, measured by Micromeritics ASAP2010 Porosimeter. Pore-size and pore volume were obtained from the analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett-Joyner-Halenda) method. Surface area of synthesized CaZrO₃ is found to be 21.0 m²/g. Pore size and pore volume are 49 Å and 0.03 cm³/g respectively. High pore size enhances possibilities of reactivity of reacting species during transesterification.

SEM micrographs were obtained with a Hitachi S3400N scanning electron microscope utilizing an electron beam accelerated at 300 V to 30 KV. The particle size of the catalyst was found in the range of 1.2–4.2 μm.

Basic strength of the catalyst was determined by using Hammett indicators. The Hammett indicators used were neutral red (H₋ = 6.8), bromothymol blue (H₋ = 7.2), phenolphthalein (H₋ = 9.3), 2,4-dinitroaniline (H₋ = 15.0). Typically, 25 mg of the catalyst was mixed with 5 ml of a solution of Hammett indicators diluted with methanol and kept for 2 h. After the equilibration, the color of the catalyst was noted. The basic strength (H₋) of the CaZrO₃ was in the range of 6.8–9.3.

Fig. 3. TGA Diagram of CaZrO₃.

Biodiesel Preparation Process :

Soybean oil, methanol and catalyst were taken in a 750 ml Stainless steel high pressure reactor equipped with a PID controller, stirrer, and pressure gauge. The reaction mixture was heated to 170°C at 80 bar pressure and stirred at a rate of 310–320 rpm. The progress of the reactions was monitored by thin layer chromatography using a mixture of hexane, diethyl ether and glacial acetic acid (85 : 13.5 : 1.5) as eluent. After completion of the reaction catalyst was recovered by filtration and washed with methanol and hexane to remove residual ester and glycerol. Filtrate was allowed to equilibrate to allow separation of two phases. Upper phase contained the ester in methanol, and the lower phase contained the glycerol byproduct. After phase separation, the upper phase was passed through a column of acidic alumina followed by evaporation of solvent in rotary evaporator to yield biodiesel.

Characterization and Evaluation of Synthesized Biodiesel :

Physico-chemical properties (Table 2) of synthesized biodiesel were evaluated as per IS 15607/ASTM D6751 standards. Acid value and moisture content were measured by ASTM D974 and ASTM D2709 methods respectively. Kinematic viscosity was determined with Cannon-Fenske viscometers following ASTM D445 method. All viscosity data reported are mean of triplicate determination. Flash point was measured

TABLE 2.

Physico-chemical properties of synthesized biodiesel

Properties	IS 15607 test method	IS 15607 limits	Soybean oil methyl ester
Kinematic Viscosity at 40°C (cSt)	IS 1448 P : 25	2.5–6.0	4.23
Density at 15°C (g/cm ³)	EN 14103	0.8–0.9	0.83
Acid value (mgKOH/g)	IS 1448 P : 1/Sec.1	Max. 0.50	0.446
Flash Point (°C)	IS 1448 P : 21	Min. 120	159
Sulphated ash (mass %)	IS 14448 P : 4	Max. 0.02	0.002
Water and sediment (vol. %)	D2709	Max. 0.05	0.04
Carbon residue (mass %)	D4530	Max. 0.05	0.022
Copper corrosion	IS 1448 P : 15	Max. 1	1
Free Glycerol, (mass %)	D6584	Max. 0.02	0.0055
Total Glycerol, (mass %)	D6584	Max. 0.25	0.0920
Oxidation stability, h*	EN 14112	Min. 6 h	3.20

*Can be improved by adding antioxidants like DBPC etc.

by Pensky-Martens closed cup apparatus following standard method ASTM D93 and oxidation stability was determined by Rancimat apparatus following EN 14112 method. Density at 15°C was determined by ISO 3675 method.

The synthesized biodiesel was analyzed by GPC, GC, IR Spectroscopy and NMR Spectroscopy. The quantification of FAME was done by Gel Permeation Chromatography (GPC) analysis of biodiesel on Waters 515 HPLC equipment fitted with a UV and RI detector. A styragel stainless steel column of 60 cm × 7.5 mm having pore size of 100 Å was used with tetrahydrofuran as the mobile phase at a flow rate of 1 ml/minute. Gel Permeation Chromatogram was confirmed the conversion rate of 96.3% for soybean to biodiesel and 3.7% of fat.

Ester content and glycerine content were determined by Gas Chromatography (Perkin Elmer Clarus-500). Gas Chromatograph equipped with split/splitless injector and flame ionization detector. For ester content, split ratio of 1 : 50 and injector and FID detector temperature of 300°C were used for helium carrier (ultra high pure grade) with a fused silica capillary column CP-Wax 52 BD (30 m × 0.32 mm id × 0.25 µm).

Glycerine content was determined by a Carlo Erba model HRGC 5300 equipped with split/splitless injector and flame ionization detector (FID) using ASTM 6584 method. The non polar capillary column consisted of 5% phenol and 95% polymethylsiloxane (15 m × 0.32 mm id × 0.1 μm film thickness). The temperature of injector and detector was 350°C and 380°C respectively with split ratio of 20 : 1. The free glycerine, monoglycerides and total glycerides of synthesized biodiesel were 55 ppm, 865 ppm and 920 ppm respectively. However, ester content of biodiesel obtained was 96.4 wt%.

Nuclear magnetic resonance spectroscopy is a powerful and theoretically complex analytical tool for determining the structure of organic compounds. ¹H NMR of synthesized biodiesel confirms the biodiesel purity of 94%.

RESULTS AND DISCUSSION

Effect of variation of oil to methanol molar ratio on biodiesel yield and reaction time. In this present study, effect of molar ratio of oil to methanol on biodiesel yield and reaction time was evaluated with 10 wt% catalyst concentration at a reaction temperature of 170°C and pressure of 80 bar. The oil to methanol ratio was varied from 1 : 15 to 1 : 30. Stoichiometrically 3 moles of methanol is needed for complete transesterification of 1 mol of triglyceride to get 3 moles of FAME. From the experimental studies it was found that the excess amount of methanol will shift the equilibrium to forward direction (product side). The maximum biodiesel yield (95%) was obtained with 1 : 25 molar ratio of oil to methanol in 3 h with 10 wt% of catalyst concentration at 170°C and 80 bar pressure (Fig. 4b). There was no significant increase in biodiesel yield beyond this ratio (Fig. 4a).

Effect of variation of catalyst concentration on biodiesel yield and reaction time :

Transesterification reactions were carried out at different catalyst concentrations (5, 7, 10 and 12% wt/wt of vegetable oil) for different reaction conditions. It was found that maximum yield was obtained with a minimum reaction time of 3 h at 10 wt% of catalyst concentration (Fig. 5a & b). There was no reduction in reaction time beyond this catalyst concentration. However with further increase in the catalyst concentration the biodiesel yield decreased.

Effect of moisture content on biodiesel yield and reaction time :

The effects of moisture content in vegetable oil on biodiesel yield and reaction time were investigated by the transesterification reaction conducted by taking different amount of water (1 and 2%) in soybean oil. The rate of reaction was slowed down with water and reduction in product yield also was observed (Fig. 6a & b).

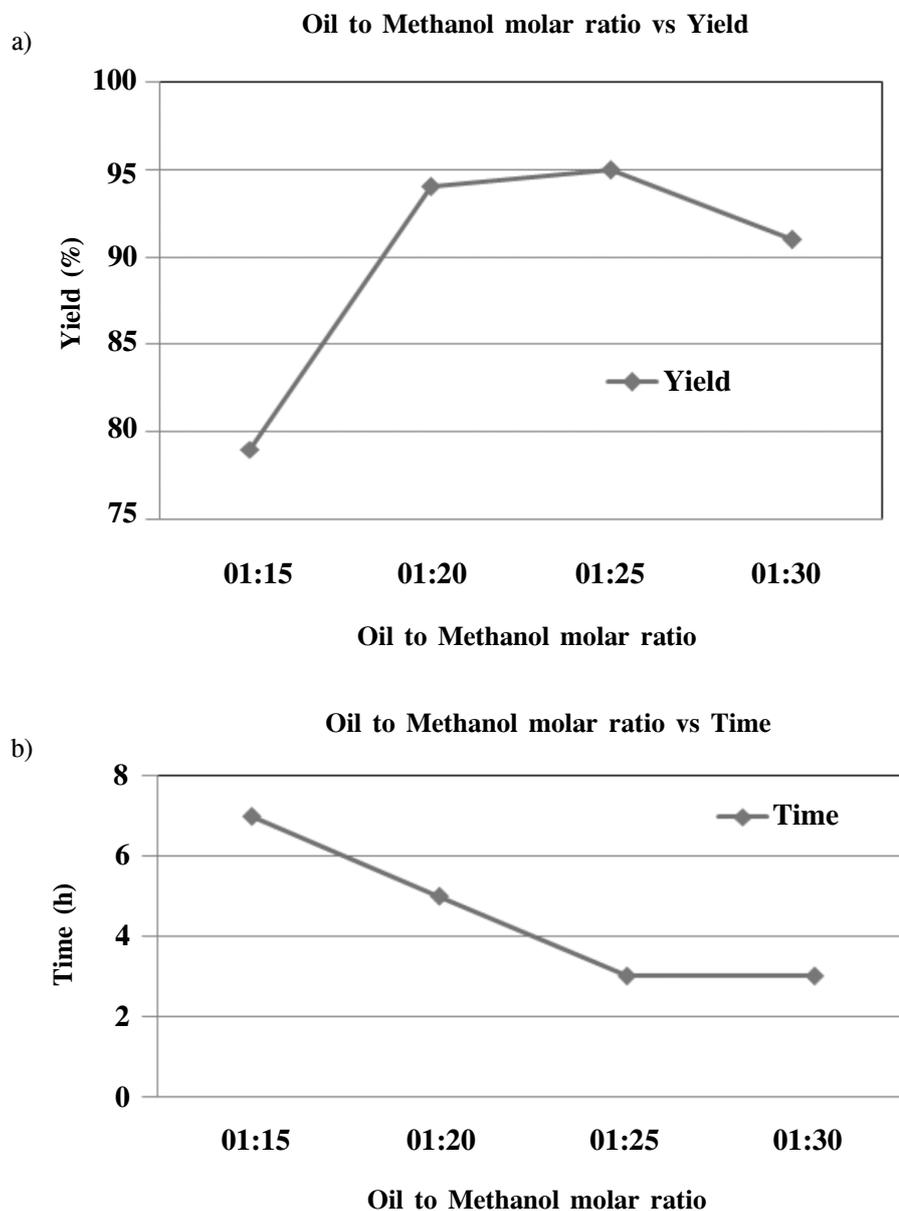


Fig. 4. Effect of variation molar ratio of oil to methanol on (a) Biodiesel Yield and (b) Reaction time.

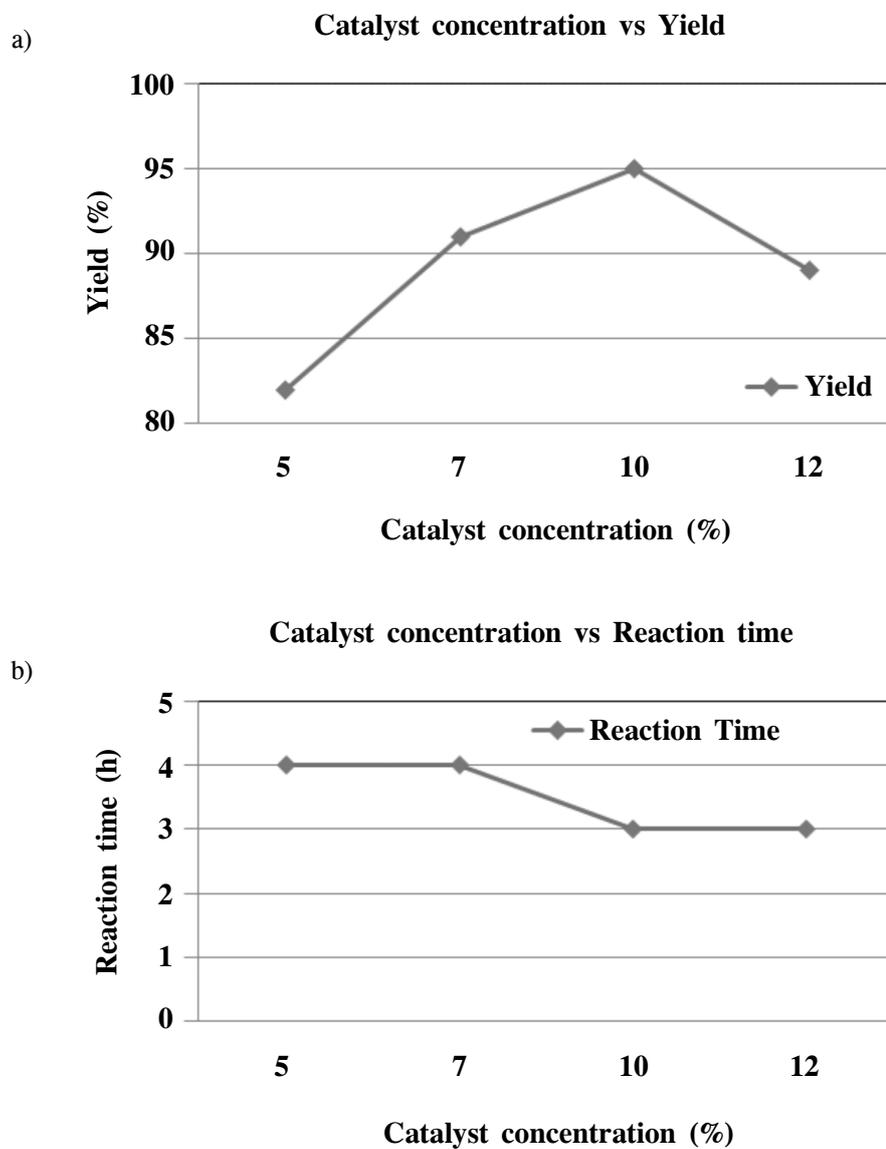


Fig. 5. Effect of variation of Catalyst concentration on (a) Biodiesel Yield and (b) Reaction Time.

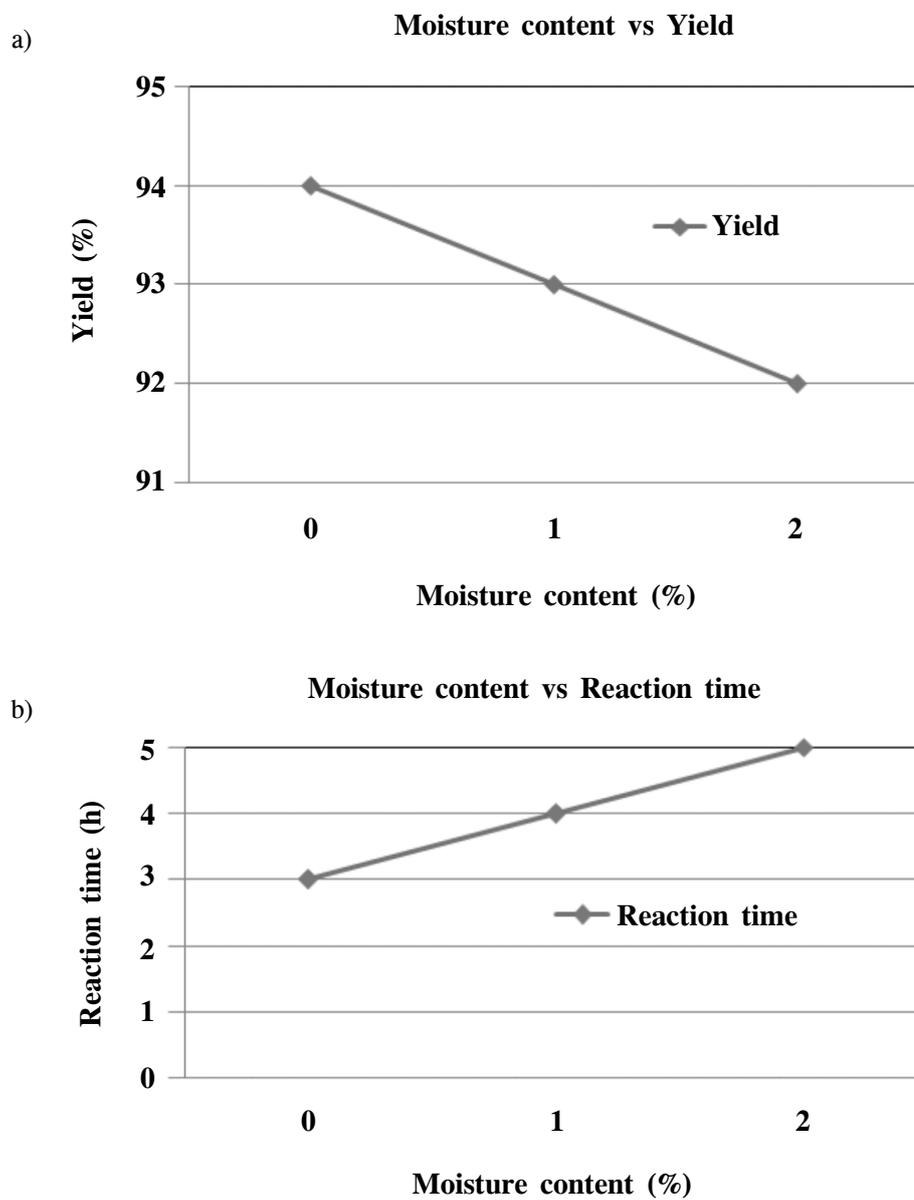


Fig. 6. Effect of moisture content on (a) Biodiesel Yield and (b) Reaction Time.

Recyclability Study of CaZrO₃ :

Recyclability of lab synthesized CaZrO₃ catalyst was examined by carrying out repeated cycles of synthesis of biodiesel with recovered catalyst. The recovered catalyst was exhaustively washed with methanol and hexane and dried overnight at 100°C. Biodiesel synthesis was carried out 3 repeated cycles using the recovered catalyst. The Fig. 7 shows that the catalyst retained its structure even after 3rd cycle and was able to provide more than 90% of yield in all those four consecutive cycles.

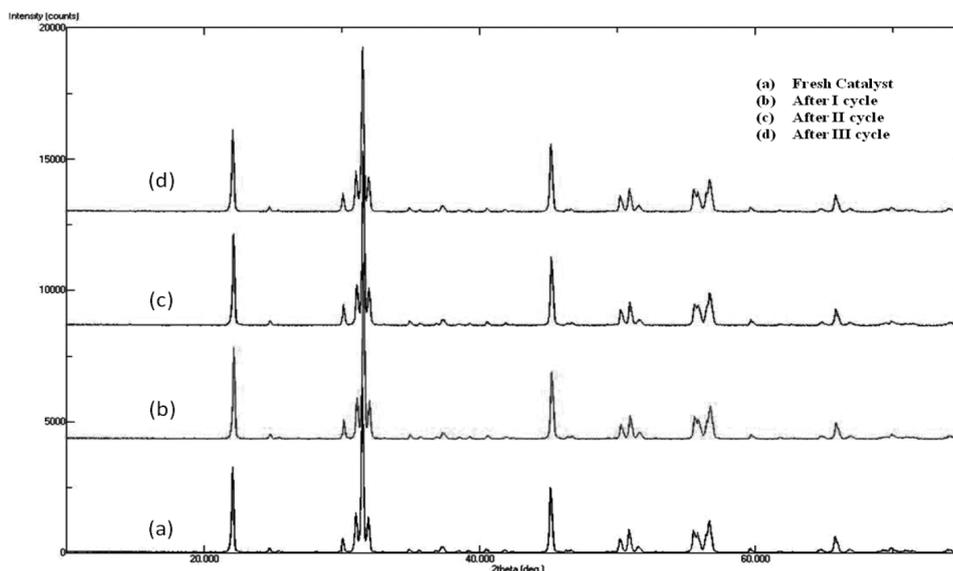


Fig. 7. XRD Patterns of Fresh and Recovered CaZrO₃.

CONCLUSIONS

This present study demonstrates the development of an environmentally benign Perovskite type catalyst, CaZrO₃ from natural waste material (the egg shells). The high surface area (21.0 m²/g) of the developed catalyst was found to be very effective for the preparation of biodiesel from soybean oil. The maximum biodiesel yield (94.4%) was obtained at 170°C and 80 bar pressure with 1 : 25 molar ratio of oil to methanol using 10 wt% catalyst concentration in reaction time of 3 h. The catalyst showed high activity and durability over repeated cycles. So it can be concluded that

Ca-Zr based catalyst has the potential to be used as an effective catalyst for carrying out biodiesel production from vegetable oils.

ACKNOWLEDGEMENTS

We would like to thank the management of IOC R&D Centre for granting permission to publish this work.

REFERENCES

1. H. Lu, Y. Liu, H. Zhou, Y. Yang, M. Chen and B. Liang, Production of biodiesel from *Jatropha curcas* L. oil, *Comput Chem. Eng.*, 33, 1091–1096 (2009).
2. A. B. Chhetri, M. S. Tango, S. M. Budge, K. C. Watts and M. R. Islam, Non-edible plant oils as new sources for biodiesel production, *Int. J. Mol. Sci.*, 9, 169–180 (2008).
3. B. Freedman, R. O. Butterfield and E. H. Pryde, Transesterification kinetics of soybean oil, *J. Am. Oil Chem. Soc.*, 63, 1375–1380 (1986).
4. R. Stern and G. Hillion, Purification of esters, *Eur. Pat. Appl.*, EP 356317, 1990.
5. M. Canakci, The potential of restaurant waste lipids as biodiesel feedstocks, *Biores Technol.*, 98, 183–190 (2007).
6. D. Y. C. Leung and Y. Guo, Transesterification of neat and used frying oil : Optimization for biodiesel production, *Fuel Process Technol.*, 87, 883–890 (2006).
7. G. Madras, C. Kolluru and R. Kumar, Synthesis of biodiesel in supercritical fluids, *Fuel*, 83, 2029–2033 (2004).
8. N. S. Kitakawa, H. Honda, H. Kuribayashi, T. Toda and T. Fukumura et al, Biodiesel production using anionic ion-exchange resin as heterogeneous catalyst, *Biores Technol.*, 98, 416–421 (2007).
9. M. I. Al-Widyan and A. O. Al-Shyoukh, Experimental evaluation of the transesterification of waste palm oil into biodiesel, *Biores Technol.*, 85, 253–256 (2002).
10. G. W. Huber, S. Iborra and A. Corma, Synthesis of Transportation Fuels from Biomass : Chemistry, Catalysts and Engineering, *Chem. Rev.*, 106, 4044–4098 (2006).
11. A. Demirbas, Progress and recent trends in biofuels, *Progr. Energy Combust Sci.*, 33, 1–18 (2007).
12. (a) S. V. Ranganathan, S. L. Narasimhan and K. Muthukumar, An overview of enzymatic production of biodiesel, *Biores Technol.*, 99, 3975–3981 (2008); (b) N. Dizge, C. Aydiner, D. Y. Imer, M. Bayramoglu and A. Tanriseven et al, Biodiesel

- production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer, *Biores Technol.*, 100, 1983–1991 (2009).
13. Z. Helwani, M. R. Othman, N. Aziz, J. Kim and W. J. N. Fernando, Solid catalysis for transesterification of triglycerides with methanol, *Appl. Catal. A.*, 363, 1–10 (2009).
 14. D. Y. C. Leung, B. C. P. Koo and Y. Guo, Degradation of biodiesel under different storage conditions, *Biores Technol.*, 97, 250–256 (2006).
 15. G. R. Peterson and W. P. Scarrah, Rapeseed oil transesterification by heterogeneous catalysis, *J. Am. Oil Chem. Soc.*, 61, 1593–1597 (1984).
 16. G. J. Suppes, K. Bockwinkel, S. Lucas, J. B. Bots, M. H. Mason and J. A. Heppert, Calcium carbonate catalyzed alcoholysis of fats and oils, *J. Am. Oil Chem. Soc.*, 78, 139–145 (2001).
 17. S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, *Biores Technol.*, 70, 249–253 (1999).
 18. R. Sarin, M. Sharma, S. Sinharay and R. K. Malhotra, Jatropha-Palm biodiesel blends : An optimum mix for Asia, *Fuel*, 86, 1365–1371 (2007).
 19. S. Semwal, A. K. Arora, R. P. Badoni and D. K. Tuli, Biodiesel production using heterogeneous catalysts, *Biores Technol.*, 102, 2151–2161 (2011).
 20. S. Semwal, A. K. Arora, S. Prakash, S. K. Puri and D. K. Tuli, Preparation of novel catalyst composition from natural waste for biodiesel production, *Journal of Scientific and Industrial Research*, 70, 1054–1060 (2011).
 21. A. Kawashima, K. Matsubara and K. Honda, Development of heterogeneous base catalysts for biodiesel production, *Biores Technol.*, 99, 3439–3443 (2008).
 22. C. C. S. Macedo, F. R. Abreu, A. P. Tavares, M. B. Alves, L. F. Zara, J. C. Rubim, P. A. Z. Suarez, New heterogeneous metal-oxides based catalyst for vegetable oil transesterification, *J. Braz Chem. Soc.*, 17, 1291–1296 (2006).
 23. N. S. Babu, R. Sree, P. S. S. Prasad, N. Lingaiah, Room-Temperature Transesterification of Edible and Nonedible Oils Using a Heterogeneous Strong Basic Mg/La Catalyst, *Energy & Fuels*, 22, 1965–1971 (2008).