



Biodiesel Production from Castor Oil in the Liquid Phase using Acidic Alumina as a Catalyst

K. Shanmugalakshmi, M. A. Mary Thangam, J. Ilavarasi Jeyamalar, C. Kannan*

Department of Chemistry, Manonmaniam Sundaranar University, Tirunelveli, TN, India

Received: 18.11.2018 Accepted: 02.12.2018 Published: 30-03-2019

*chellapandiankannan@gmail.com



ABSTRACT

Biodiesel is technically defined as alkyl esters of long-chain fatty acids, derived from vegetable oils or animal fats. It is an eco-friendly fuel, compared to petroleum-based hydrocarbons. This renewable and biodegradable advantage makes biodiesel a good sustainable energy carrier. It is usually produced by a trans-esterification reaction of vegetable or waste oil with low molecular weight alcohol, such as ethanol and methanol. In this work, ethanol has been used for the production of biodiesel, by using castor oil as a source material and acidic alumina as a catalyst. Experimental conditions like time, temperature, molar ratio and catalyst dosage were optimized to obtain maximum conversion. The product obtained has been characterized by FT-IR and NMR techniques.

Keywords: Alumina; Biodiesel; Catalyst; Energy.

1. INTRODUCTION

Biodiesel is technically defined as alkyl (usually methyl and ethyl) esters of long-chain fatty acids derived from vegetable oils or animal fats. When used as fuel in diesel engines and heating systems, biodiesel has many merits, such as high energy density, more favorable combustion emission profile and improved lubricating properties. It is also an environment-friendly fuel compared to petroleum-based diesel, as biodiesel is renewable, biodegradable, non-toxic and free of sulfur and aromatics (Yamane *et al.* 2001).

The demand for petroleum-based fuels is fast increasing; if the present consumption patterns continue, these resources will be consumed in a few years. Hence, efforts are being made to explore the alternative source of energy. Currently, biodiesel is becoming one of the best alternative fuel in most countries. Directly or blended edible or non-edible oil can be used in diesel engines, though it can create problems in engines because of its high viscosity (Pramanik, 2003; Knothe *et al.* 2005). Biodiesel is produced using edible oil, non-edible oil and animal fats by acid- or base-catalyzed trans-esterification with ethanol or methanol (Murugesan *et al.* 2009; Ma and Hanna, 1999).

In the present work, focus has been laid upon the trans-esterification of castor oil with ethanol in the presence of alumina as a catalyst. The castor nut, which contains approximately 90% of ricinoleic acid, abundantly available in India, has been used as a source material for the current research.

2. MATERIALS AND METHODS

2.1 Catalytic Reaction

Acidic alumina was used as the catalyst for the synthesis of biodiesel; castor oil and ethanol were taken as reactants. The acidic alumina and ethanol were purchased from Lobachem Pvt. Ltd., India. Its molecular formula is Al_2O_3 and the molecular weight is 101.96 g/mol. The particle size of acidic alumina is 70-230 mesh and its pH is 3.5 to 5. The reaction mixture was taken in a two-necked 100 ml round-bottom flask and it was placed in an electrical heating mantle with an energy regulator. The central neck of the flask was fitted with a condenser, and to the side, the neck was fixed with a mercury well for the thermometer. The flask was heated gently and at a controlled temperature. The product formed was in the form of biodiesel and residual glycerol. Then the product mixture was filtered and separated from the catalyst.

2.2 Material Characterization

The structure of the catalyst was determined using the JASCO-410 FT-IR Spectrometer and a Fourier Transform Infrared (FT-IR) analyzer. The dried carbon sample was mixed with potassium bromide for this analysis (KBr). The spectra were acquired in the range of $400\text{-}4000\text{ cm}^{-1}$. The FT-IR spectra of acidic alumina are shown in Fig. 1. A peak at 1605 cm^{-1} can be attributed to Al-O-Al asymmetric stretching. The corresponding symmetric stretching vibration has been observed at 606 cm^{-1} . It was confirmed that the acidic alumina has no tetrahedral framework. The strong peak at 3640 cm^{-1} can

be attributed to Al-OH stretching mode. This OH was an active site for trans-esterification reaction.

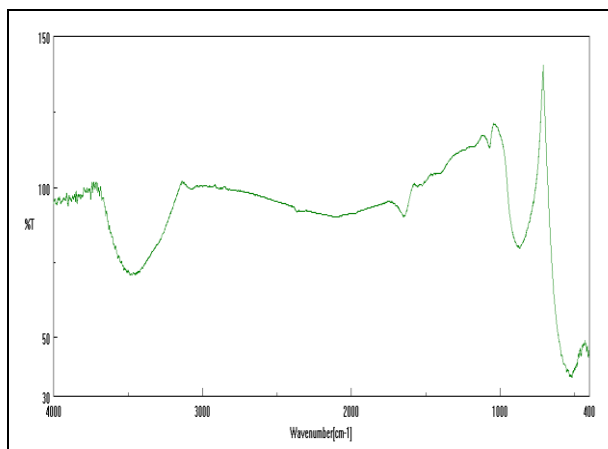


Fig. 1: FT-IR spectrum of acidic alumina

3. RESULT AND DISCUSSION

The trans-esterification of castor oil was carried out over low-cost and non-hazardous acidic alumina catalysts in the liquid phase. The conversion of castor oil increased rapidly above 120-150 °C. The time required for the trans-esterification of castor oil, the effect of temperature, the contact time, the effect of alcohol to oil mole ratio and the effect of catalyst dosage were optimized to achieve better conversion.

3.1 Effect of Time

The castor oil trans-esterification reaction can be studied at different time intervals. It may be noticed that approximately 28% of product conversion observed within the first one hour. The percentage of conversion increased with the increase in time and attained a maximum conversion at 3 h. For further increase in time there is no significant increment in the trans-esterification reaction. The conversion was 33.8% at 3 h, indicating the formation of trans-esterification reaction occurs rapidly in the presence of acidic alumina (Fig. 2).

3.2 Effect of Temperature

The temperature effect of castor oil with ethanol trans-esterification reaction over-acidic alumina was shown in Fig. 3. The temperature effect has been studied from 60-200 °C. The conversion of the reaction is 20% from 60-150 °C. For further increase in temperature, the conversion of castor oil significantly increased, up to 150 °C. This study has proved that the optimum temperature for the castor oil conversion was 150 °C.

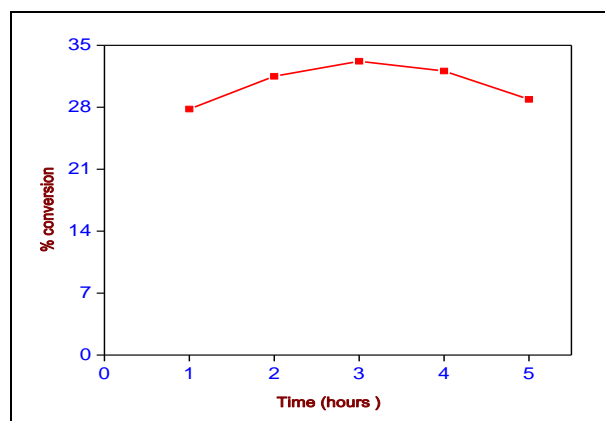


Fig. 2: Effect of Time on castor oil trans-esterification reaction over acidic alumina (Castor oil - 5 ml, Ethanol - 0.9 ml (1:3 mole ratio), Temperature - 150 °C, catalyst weight - 0.1 g)

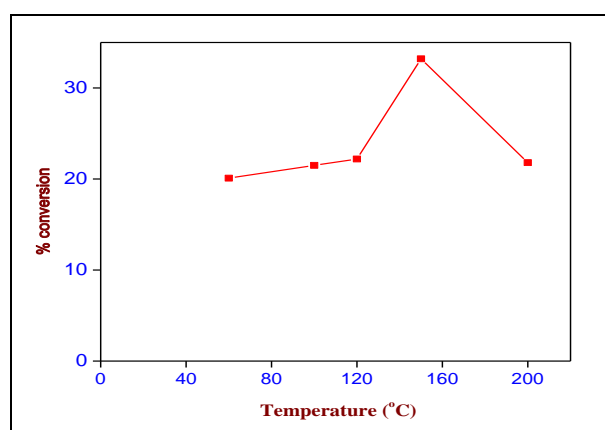


Fig. 3: Effect of Temperature on castor oil with ethanol trans-esterification reaction over acidic alumina (Catalyst weight - 0.1 g, Castor oil - 5 ml, Ethanol - 0.9 ml (1:3 mole ratio), Time - 3 h)

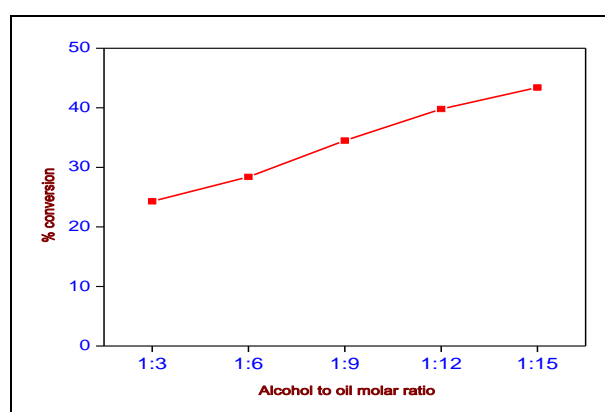


Fig. 4: Effect of castor oil with ethanol dosage on trans-esterification reaction over acidic alumina (Time - 3 h, Catalyst weight - 0.1 g, Temperature - 150 °C)

3.3 Effect of Molar Ratio

The effect of mole ratio of castor oil and ethanol over-acidic alumina in the liquid phase is shown in Fig. 4. The effect of mole ratio of castor oil and ethanol has been studied from 1:3 to 1:15. The conversion was maximum at 1:15 mole ratio; this indicated that when the mole ratio increased, the percentage of the product also increased.

3.4 Effect of Catalyst Dosage

Catalyst dosage effect on castor oil with ethanol trans-esterification reaction over acidic alumina in the liquid phase at 150 °C has been studied to find out the linear relationship between the active sites present on the surface of catalyst and castor oil trans-esterification reaction (Fig. 5). In this study, the percentage of conversion of biodiesel increased with increasing catalyst amount. This clearly proved that castor oil trans-esterification has a linear relationship with the catalyst amount. When the catalyst amount increased, the active sites and the surface of the catalyst also increased. Hence the conversion of castor oil increased with the increase in the catalyst amount.

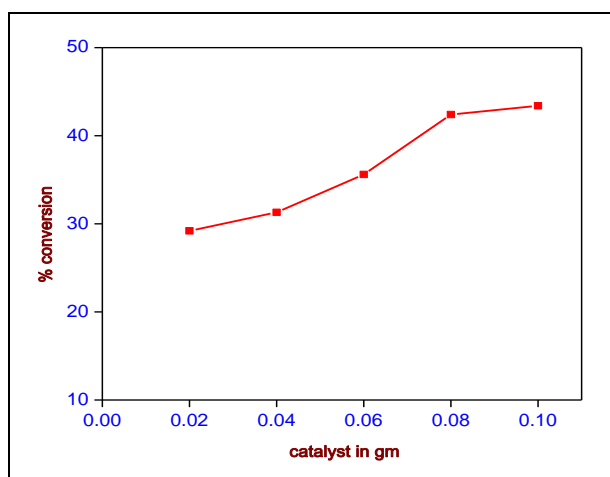


Fig. 5: Effect of catalyst amount on castor oil trans-esterification reaction over acidic alumina (Castor oil - 5 ml, Time - 3 h, Temperature - 150 °C)

3.5 Characterization of Castor Oil and Biodiesel

3.5.1 FT-IR spectrum of castor oil

FT-IR spectrum of castor oil, shown in Fig. 6, has revealed that castor oil contained a hydroxyl component at 3409 cm^{-1} . The peaks at 2928-2855 cm^{-1} , 1744 cm^{-1} and 1462 cm^{-1} , corresponding to CH, C=O and C=C stretching, respectively. Thus, FT-IR has proved the structure of castor oil.

3.5.2 FT-IR spectrum of biodiesel

The FT-IR spectra of the synthesized biodiesel over acidic alumina in the liquid phase is presented in Fig. 7 to validate the biodiesel structure. The ester group was observed from 1740 cm^{-1} and the peak at 1176 cm^{-1} represented the CH_2 stretching band. The C=C group was observed at 2357 cm^{-1} and the peak at 2930 cm^{-1} represented CH, C=O and CH stretching bands (Mushtaq Ahmad *et al.* 2011; Kumar Ved and Kand Padam, 2013). The intense band near 1740 cm^{-1} has represented the ester group present in the biodiesel.

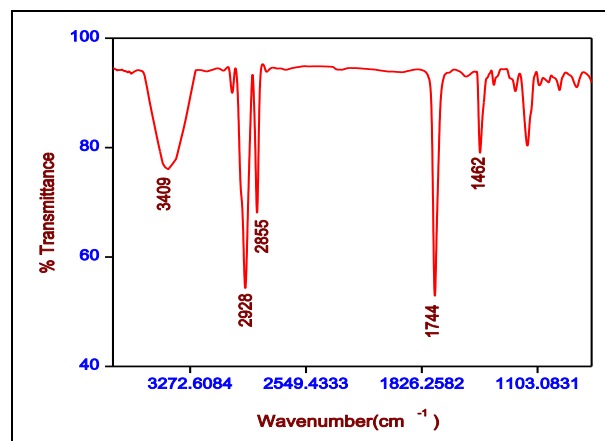


Fig. 6: FT-IR spectrum of castor oil

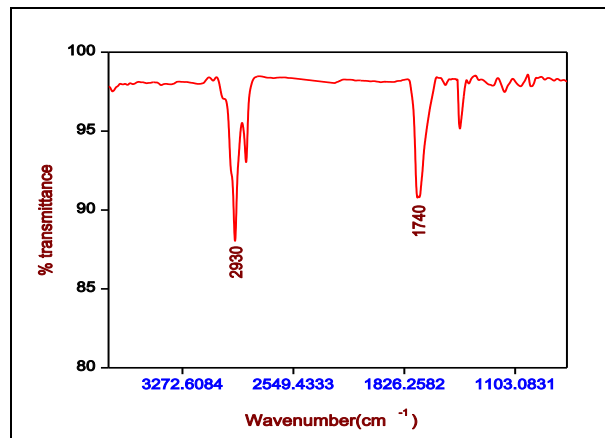


Fig. 7: FT-IR spectrum of biodiesel

The synthesized biodiesel was characterized by ^1H NMR spectroscopy, shown in Fig. 8. In the ^1H NMR spectrum, the strong peak at 3 - 4 ppm has indicated the ethyl ester formation. The peak obtained at 2.1 ppm resulted from the protons on the CH_2 groups adjacent to the ethyl ester. $\alpha\text{-CH}_2$ protons have appeared at 2.23 ppm. These observed peaks from ^1H NMR spectrum have proved the formation of biodiesel in the liquid phase over acidic alumina as the catalyst.

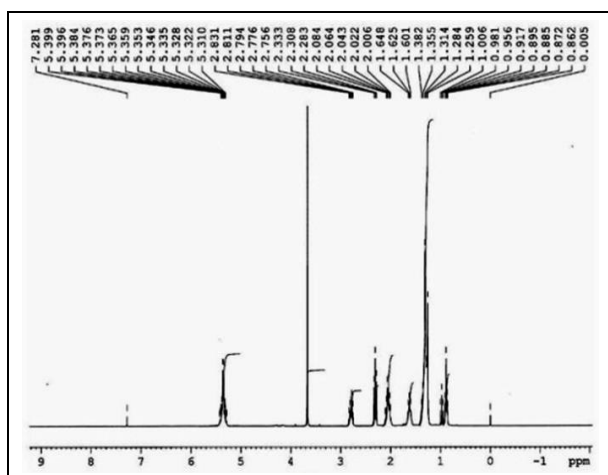


Fig. 8: ^1H NMR spectrum of biodiesel

4. CONCLUSION

In the present investigation, castor oil transesterification has been studied through the green chemistry method. The castor oil with ethanol transesterification over acidic alumina has been studied in the liquid phase. The experimental conditions like contact time, effect of temperature, amount of castor oil with ethanol ratio and catalyst amount have been optimized for maximum conversion. The contact time effect has been studied from 1 to 5 h and it was found that maximum conversion was attained at 3 h and no significant increment of conversion was found with further increase in time. The temperature effect has been studied from 60 to 150 °C and it was found that the conversion was maximum for 150 °C for biodiesel. The synthesized biodiesel was characterized by FT-IR spectrum. The ester group vibration (1745 cm^{-1}), CH_2 group vibration (1176 cm^{-1}), the $\text{C}=\text{C}$ group vibration (2357 cm^{-1}) and the CH stretching (2929 cm^{-1}) were observed in FT-IR spectrum. It has proved the formation of biodiesel.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

COPYRIGHT

This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC-BY) license (<http://creativecommons.org/licenses/by/4.0/>).



REFERENCES

- Knothe, Gerhard and Steidley R. K., Kinematic viscosity of biodiesel fuel component and related compounds. Influence of compound structure and comparison to petro-diesel fuel components, *Fuel*, 84(9), 1059-1065(2005).
<https://doi.org/10.1016/j.fuel.2005.01.016>
- Kumar Ved and Kant Padam, Study of physical and chemical properties of biodiesel from Sorghum Oil, *Res. J. Chem. Sci.*, 3(9) 64-68(2013).
- Ma F, Hanna A. M., Biodiesel production: A review, *Bioresource. Technol*, 70, 01-15(1999).
[https://doi.org/10.1016/S0960-8524\(99\)00025-5](https://doi.org/10.1016/S0960-8524(99)00025-5)
- Muragesan, A., Umarani, C., Chinnusamy, T. R., Krishanan, R., Subramanean, R. and Neluzchezhain, N., Production and analysis of biodiesel from non-edible oils: A Review, *Renewable and Sustainable Energy Reviews*, 13(4), 825-834(2009).
<https://doi.org/10.1016/j.rser.2008.02.003>
- Mushtaq Ahmad, Mir Ajab Khan, Muhammad Zafar and Shazia Sultana, Biodiesel from Non Edible Oil Seeds: A Renewable Source of Bioenergy, Economic Effects of Biofuel Production, 259-280(2011).
<https://doi.org/10.5772/24687>
- Pramanik, K., Properties and use of jatropha curcas oil and diesel fuel blend in compression ignition engine, *Renewable Energy*, 28, 239-248(2003).
[https://doi.org/10.1016/S0960-1481\(02\)00027-7](https://doi.org/10.1016/S0960-1481(02)00027-7)
- Yamane, K., Ueta, A. and Shimamoto, Y., Influence of physical and chemical properties of biodiesel fuels on injection, combustion and exhaust emission characteristics in a direct injection compression ignition engine, *Int. J. Engine Res.*, 2, 4, 249-261(2001).
<https://doi.org/10.1243/1468087011545460>