Biodiesel from Jatropha Curcas oil: An enzymatic approach

Sumit Nandi[1], Rupa Bhattacharyya[2] and Sreyoshi Chatterjee[3]

[1,2] *Department of Chemistry, Narula Institute of Technology, 81, Nilgunj Road, Agarpara, Kolkata-700109, West Bengal*

[3] *Department of Mechanical Science, Narula Institute of Technology, 81, Nilgunj Road, Agarpara, Kolkata-700109, West Bengal*

ABSTRACT

Biodiesel is considered as one of the significant alternative energy sources in the future world as an environment friendly, renewable and non toxic fuel. Biodiesel can be produced from different vegetable oils but the most suitable and cost effective source is non edible vegetable oil of the fruits of Jatropha Curcas plant. Productivity of biodiesel from Jatropha Curcas oil through transesterification reaction with methanol depends on molar ratio of oil to methanol, reaction temperature, catalyst concentration and stirrer speed or mixing effect of the reaction system. In the present research investigation, biodiesel is prepared from Jatropha Curcas oil with methanol using non-specific enzyme NS40013 (Candida antarctica) and the effects of reaction parameters on the productivity of biodiesel have been studied. The physical properties such as density, flash point, kinematic viscosity, cloud point and pour point for Jatropha Curcas methyl ester and diesel fuel have been compared. The conformity of results between biodiesel and diesel fuel suggests the use of biodiesel in the engine without any modification.

Keywords: Biodiesel, Lipase enzyme, Jatropha Curcas oil, Enzymatic transesterification.

1. INTRODUCTION

The depleting condition of world petroleum reserves, recent increase in petroleum prices and concern on the availability of petroleum have generated great interest in alternative source of fuel for diesel engines. Biodiesel (BD) may be a promising option as it is obtained by chemical transesterification process from vegetable oils or animal fats and an alcohol and can be used in diesel engines. **BD is the only alternative fuel that runs in any conventional, unmodified diesel engine. BD can be used alone or mixed with petroleum based diesel in any proportions. It is** a renewable, biodegradable and non-toxic fuel. It is also **safe to handle and transport as it has a flash point higher than that of petroleum diesel and able to extend engine life because of its superior lubricating properties.**

BD can be produced from different vegetable oils but the most promising source is the non edible oil of Jatropha Curcas plant. BD from Jatropha Curcas Oil (JCO) does not hamper on food supply.

Also this plant can be grown in both non tropical regions and in waste or barren land and grows on almost any terrain, even on gravelly, sandy and saline soils and under adverse climatic condition. The seed contains 27-40% oil that can be processed to produce high quality of biodiesel. BD from JCO using chemical catalyst has been studied by several researchers. Hawash et al [1] transesterified JCO to BD using calcium oxide as a solid base catalyst under supercritical conditions. Berchmans and Hirata [2] investigated production of BD from crude JCO using two stage transesterification process using acid catalyst in the first stage and base catalyst in the second stage. Raja et al [3] shows that alkaline catalyzed transesterification of JCO with methanol produces higher percentage of BD under definite parametric conditions. But there are several drawbacks associated with the chemical catalyst. It is energy intensive, unwanted side products are generated from the use of alkali catalyst and there are problems regarding separation of products. Hence better and alternative method of production is the use of enzyme as catalyst due to its reusability, specificity, thermo stability, mild reaction conditions in terms of low temperature and its environmental friendliness [4, 5].

Production of BD from JCO using enzyme as catalyst has also been investigated by several researchers. Kumari et al [6] uses immobilized lipase from *Enterobactor aerogenes* using JCO in t-butanol solvent for BD production and they obtained 94% yield. Another study of Aransiola [7] presents the ethanolysis of both crude and pretreated JCO using immobilized lipase enzyme from *Pseudomonas cepacia* and maximum of 72.1wt% fatty acid ethyl ester is obtained at optimized conditions. Veny et al [8] produced BD from JCO through enzymatic synthesis in a re circulated packed bed reactor and they obtained highest methyl ester yield of 54% from lipase dosage of 10%. Preparation of BD from JCO has also been investigated by Zarie et al [9], Sash and Gupta [10], Shah et al [11], Wang et al [12] and they showed that BD can be produced from JCO using different lipases maintaining optimum reaction conditions.

In our research study, BD is produced from JCO using methanol as substrate as well as solvent with the help of non-specific enzyme NS40013 (*Candida antarctica*) and the effects of reaction parameters on the productivity of biodiesel have been studied. The physical properties of BD are compared with diesel fuel and the results shows close proximity of properties.

2. MATERIALS

The JCO used in this study was provided by M/s. Arora Oils Ltd., Burdwan, West Bengal, India. The enzyme used in the following studies is Novozyme 435 (*Candida antarctica*) immobilized lipase which was a kind gift of Novozyme South Asia Pvt. Ltd. Bangalore, India. The chemicals used in this work such as methanol (99.8% pure) and hexane were purchased from S.D. Fine Chemicals (Mumbai, India). Except otherwise specified all other chemicals used were A.R. Grade.

3. EXPERIMENTAL METHODS

Transesterification reaction for BD production was carried out by taking JCO and methanol in an appropriate proportion in an Erlenmeyer flask (250 ml) fitted with a water condenser and stirred by a magnetic stirrer at different temperatures for 8 hours. To the reaction mixture immobilized enzyme was added in definite proportion (w/w).

For the analysis of the products, samples were taken from the reaction mixture at specified time intervals. The samples were centrifuged for 15 min at 20^0C to remove immobilized lipase. The supernatant part was taken in hexane and no leaching of enzyme was observed in this part. It was then evaporated to dryness and the products were isolated and their amounts were determined by thin layer chromatographic method. The enzyme was washed with hexane and reused for the next experiment. Biodiesel characterization was done according to the American Standard Testing Method.

4. RESULTS AND DISCUSSIONS

Effect of alcohol to oil molar ratio. The optimum concentration of methanol for BD production was investigated. The transesterification reaction was carried out at 50^0C using 5% (wt/wt) immobilized enzyme for 8 hours using different molar ratios as shown in Fig. 1. It has been observed from the figure that maximum biodiesel was obtained with a 4:1 molar ratio of methanol to JCO. Increasing concentration of methanol (5:1 or 6:1) did not enhance the reaction as evidenced from the figure. This may be due to the fact that the amount of substrates maintaining ratio 4:1 (methanol: JCO) actually occupies all the active sites of the enzyme. So further increase in amount of methanol did not enhance product percentage.

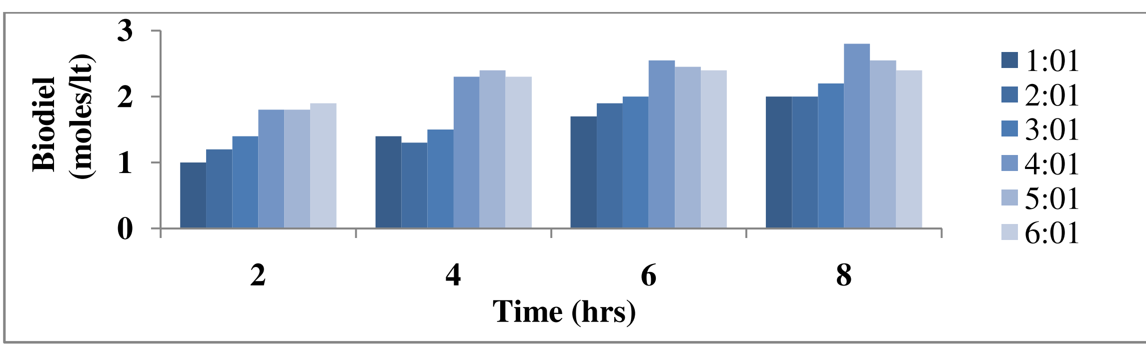

Fig.1. Effect of molar ratio of methanol to JCO on biodiesel production

Effect of reaction temperature. Reaction temperature is one of the important parameters for maximum conversion of product as activation energy plays a significant role for a reaction. Here, experiments were performed over the temperature range of 20 to 60^{0}C at 4:1 methanol: JCO molar ratio with 5% (w/w) enzyme for 8 hrs (Fig. 2). It is revealed from the figure that increasing temperature increases the conversion of BD production and a maximum production was obtained when the reaction temperature is maintained at 50^{0}C. After that increasing temperature decreases conversion of BD. This is due to the inactivation of enzyme NS 40013 beyond the temperature 50^{0}C as each enzyme is active up to a certain temperature beyond which it becomes deactivated. Higher temperature also volatilize methanol which hampers the proper ratio of methanol: JCO.

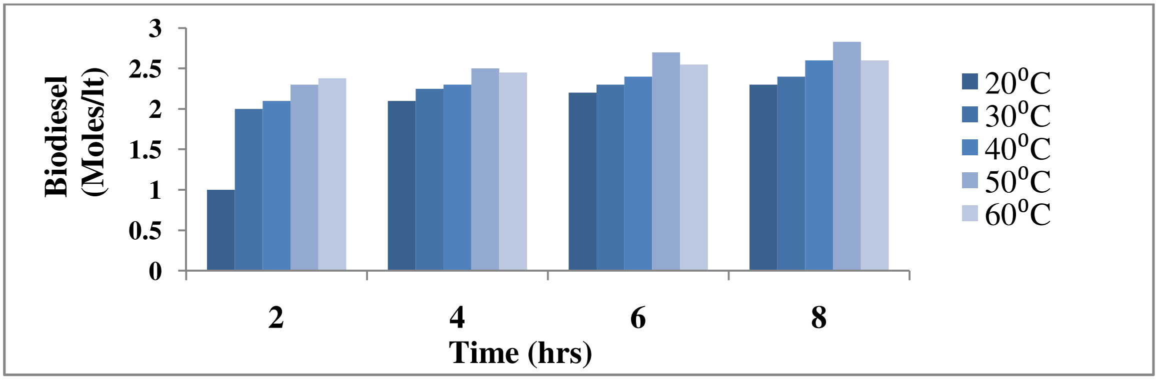

Fig.2. Effect of temperature on biodiesel production

Effect of enzyme concentration. Enzyme catalyst has the advantages that it does not produce mixture of by products as well as separation of product is much easier. Effect of enzyme concentration (Fig. 3) was investigated here for BD production. The enzyme concentration was varied from 2-6% at 4:1 methanol: JCO molar ratio maintaining a temperature of 50^{0}C for 8 hrs. Fig. 3 shows that increasing concentration of enzyme enhances BD production and we get maximum BD at 5% enzyme concentration. No significant increase in biodiesel production was observed upon further increase in the enzyme concentration. This may be due to the fact that higher amount of enzyme contributes higher amount of active sites but all active sites cannot be exposed to the substrates due to enzyme aggregation.

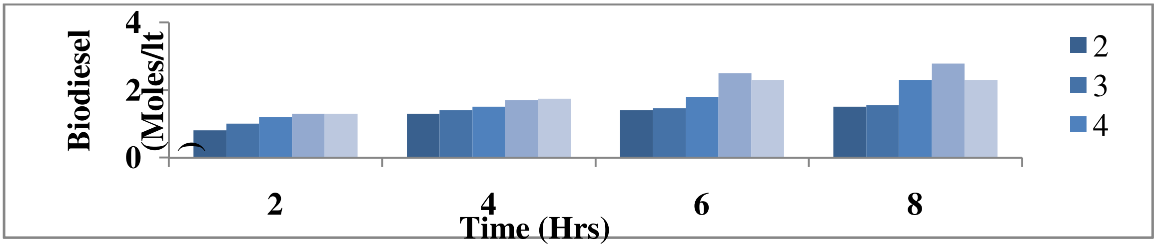

Fig.3. Effect of enzyme concentration (percentage) on biodiesel concentration

Effect of mixing intensity (stirrer speed). Mixing and transfer of reactants from the bulk liquid to the external surface of enzyme and finally in to the pores of active sites can only be obtained by optimum stirring. The effect of speed of agitation on conversion was investigated in the range of 200 to 800 rpm (Fig. 4). It was found that the percentage conversion increased with increasing stirring speed and reached maximum at 600 rpm maintaining other optimum parameters. Beyond that, no further enhancement of conversion was observed with increasing agitation. This may due to the fact that increasing mixing intensity hampers the proper contact of reactants with enzymes and / or decreases the time of contact between reactants and enzyme. So conversion decreases.

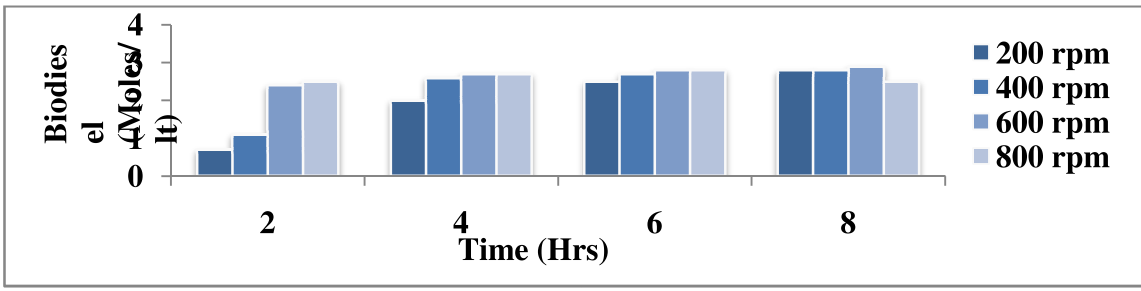

Fig.4. Effect of stirrer speed on biodiesel production

5. BIODIESEL CHARACTERIZATION

The fuel properties of Jatropha oil methyl ester are compared with biodiesel standards and it has been shown in Table 1. It is noteworthy that the characteristics of the Jatropha biodiesel are quite comparable with the standard.

Table 1 Jatropha biodiesel characterization and biodiesel standards

Properties	Jatropha oil	Jatropha biodiesel	Biodiesel standard	Diesel fuel	Test method
Kinematic Viscosity (mm^2/s)	23.7	5.8	1.9 to 6.0	1.3-4.1	ASTMD-445
Flash point (^0C)	212	131	>120	60-80	ASTMD-93
Pour point (^0C)	8	4	-15 to 10	18	ASTMD-93
Specific gravity (15^0C)	0.932	0.87	0.86 to 0.90	0.82-0.95	-
Refractive index at 40 ^0C	1.61	1.48	1.34	1.45	-
Calorific value (MJ/kg)	37.56	36.9	33 to 40	45	ASTM-6751
Cloud point (^0C)	11	6	5	-	ASTMD-2500

6. CONCLUSION

The study presents the methanolysis of crude Jatropha Curcas oil using immobilized enzyme NS 40013 from *Candida Antarctica*. The effects of molar ratio of methanol to JCO, reaction temperature, enzyme concentration and stirrer speed have been studied. Maximum conversion (> 90%) of biodiesel was obtained at 4:1 molar ratio of methanol to JCO maintaining temperature at 50^0C and 600 rpm stirrer speed using 5% (w/w) concentration of NS40013 for 8 hrs. The excellent performance of the enzyme indicates that biodiesel from JCO can be produced in commercial scale with minimum process hazards. By product glycerol can be separated from the product biodiesel by easier method. Cost is one of the determining factors for biodiesel production using enzyme catalyst but recycling of immobilize enzyme is helpful for reducing cost. Immobilized enzyme can be recycled many more times s much as sixty times. So recycling or reusing of enzyme for biodiesel production is a cost effective approach. Properties of Jatropha biodiesel also match well with the biodiesel standard and diesel fuel indicating that lipase NS 40013 can be effectively utilized for biodiesel production from JCO as well as from other non edible oils. The results may be encouraging for the future researchers involved in biodiesel production enzymatically from other vegetable oils also.

REFERENCES

[1] Hawash S, Diwani G E, Kader E A. *Optimization of biodiesel from Jatropha oil by heterogeneous base catalyzed transesterification.* International Journal of Engineering Science and Technology 2011; 3(6): 5242-5251.

[2] Berchmans H J, Hirata S. *Biodiesel production from crude Jatropha Curcas L. seed oil with a high content of free fatty acids.* Bio resource Technology 2008; 99: 1716-1721.

[3] Raja S A, Smart D S R, Lee C L R. *Biodiesel production from Jatropha oil and its characterization.* Research Journal of Chemical Sciences 2011; 1(1): 81-87.

[4] Akoh C C, Chang S W, Lee G C, Shaw J F. *Enzymatic approach to biodiesel production*. Journal of Agricultural and Food Chemistry 2007; 55(22): 8995-9005.

[5] Al-Zuhair S, Ling F W, Jun L S. *Proposed kinetic mechanism of the production of biodiesel from palm oil using lipase*. Process Biochemistry 2007; 42(6): 951-960.

[6] Kumari A, Mahapatra P, Garlapati V K, Manerjee R. *Enzymatic transesterification of Jatropha oil.* Biotechnology for Biofuels 2009; 2: 1-7.

[7] Aransiola E F. *Lipase catalysed ethanolysis of Jatropha oil for biodiesel production.* Energy and Environment Research 2013; 3(1): 85-92.

[8] Veny H, Aroua M K, Sulaiman N M N. *Solvent free enzymatic transesterification of crude Jatropha oil in a packed bed reactor.* Proceedings of 2nd International Conference on Chemical, Biological and Environmental Engineering (ICBEE) 2010; 978-1-4244-8749-3/10 IEEE.

[9] Zarei A, Amin N A S, Kiakalaie A T, Jalilian H. *Biodiesel production with immobilized enzyme and effects of alcohol on the result.* Proceedings of 3rd International Conference on Chemistry and Chemical Engineering, IPCBEE, Singapore, 2012; 38: 141-144.

[10] Shah S, Gupta M N. *Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system.* Process Biochemistry. 2007; 42(3): 409-414.

[11] Shah S, Sharma S, Gupta M N. *Biodiesel preparation by lipase catalyzed transesterification of Jatropha oil*. Energy and Fuels. 2004; 18(1): 154-159.

[12] Wang R, Hanna M A, Zhou W W, Bhadury P S, Chen Q, Song B A, Yang S. *Production and selected fuel properties of biodiesel from promising non-edible oils: Euphorbia lathyris L., Sapium sebiferum L. and Jatropha Curcas L.* Bioresource Technology. 2011; 102 (2): 1194-1199.