

Effect of Mixing Intensity for Biodiesel Production from Coconut Acid Oil

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ABSTRACT

Mixing intensity plays an important role for transesterification reaction between coconut acid oil and methanol for the production of biodiesel. Variation of mixing intensity from 400 to 700 rpm at a temperature of 65°C using 6:1 molar ratio of methanol and coconut acid oil (CAO) for 8 hours of reaction in the presence of enzyme Novozyme 40013 shows that 600 rpm is the optimum stirring rate for maximum conversion of biodiesel. Mixing intensity variation has been studied w.r.t. molar ratio, duration of reaction and enzyme concentration for the reaction system. Another study of variation of mixing intensity was observed w.r.t. glycerides concentration in the reaction medium. Maximum conversion of triacylglycerol (TAG), diacylglycerol (DAG) and monoacylglycerol (MAG) to biodiesel has been observed at 600 rpm of mixing intensity maintaining other optimum reaction parameters. Final composition of biodiesel has been analysed and 94.16% conversion has been achieved along with the presence of minor amounts of TAG, DAG and MAG.

Keywords:Biodiesel, coconut acid oil, diacylglycerol, mixing intensity, monoacylglycerol, Novozyme 40013, triacylglycerol.

1. INTRODUCTION

Optimum conversion of biodiesel from different raw materials depends on several parameters and mixing intensity is one of the important parameters which directs the collision of reactant molecules. Variation of mixing intensity in a reaction system increases or decreases the number of collisions between the reactants which helps the optimum conversion of the desired products. Production of biodiesel from different raw materials has been studied by several researchers and different parameters have also been studied. Stirring and mixing has been studied by Peiter et al. (1) and showed that 350 rpm is the optimum stirring speed in the absence of baffle for soy biodiesel production. The effect of agitation on alkali catalyzed methanolysis of sunflower oil was studied by Stamenkovic et al (2). Waste canola oil was analysed for biodiesel production w.r.t. different reaction parameters by Hossain et al (3). Nazario et al (4) evaluated the stirring procedure for the production of biodiesel from castor oil and identified the best conditions for a yield of 99.3%. The effect of mixing intensity through mathematical modeling has also been studied by several researchers. Brasio et al (5) studied the modeling the effect of mixing in biodiesel production and in this work, a modeling strategy is presented in order to predict the effect of mixing conditions in the transesterification process. Frascari et al (6) optimized the mechanical agitation and evaluation of the mass-transfer resistance of KOH-catalyzed transesterification of sunflower oil with methanol for biodiesel production. Lowering of mass transfer resistance in the production of biodiesel production was studied by Li et al (7) and Langmuir-Hinshelwood model was used to establish a rate equation for the transesterification of soybean oil with methanol in the stirring packed-bed reactor.

The effect of agitation intensity on alkali-catalyzed methanolysis of sunflower oil was studied by Stamenkovic et al (8) and showed that the rate of reaction occurring at the interface has been enhanced progressively. Present authors optimized the biodiesel production process and studied the kinetics of biodiesel production from soybean oil deodoriser distillate and methanol (9). Nandi and Mallick also optimized the production parameters of biodiesel from Palm fatty acid distillate and studied the blended properties (10). Present author also studied the biodiesel production process from waste cooking oil (11), coconut acid oil (12), Neem oil (13), jojoba oil (14), jatropha curcas oil (15) etc. Effect of stirring in case of hydrogenation of non-oxygenated bio-oil was studied by Supramonob et al (16) and showed that hydrogenation should have been operated at stirrer speed in between 650 and 800 rpm. Static mixing reactor was used by Tulliza et al (17) for the production of palm oil biodiesel and showed that the number of modules used in the static mixing reactor can enhance the mixing intensity by reducing the amount of catalyst. Effect of mixing for the biodiesel production from different sources was also studied by Klofutar et al (18), Reyes et al (19), Sungwornpatansakul et al (20), Thompson and He (21). But very few studies have been made for the effect of mixing intensity for enzymatic

bio-diesel production from coconut acid oil. In the present research investigation, coconut acid oil is used as a raw material for identifying the effect of stirring for bio-diesel production in the presence of enzyme catalyst and analysis showed good outcomes.

2. EXPERIMENTAL

A. Materials

CAO was obtained from Edible Products (I) Pvt. Ltd. The enzyme Novozyme 40013, an immobilized nonspecific lipase from *Candida antarctica* with ester synthesis activity of 10000 propyl laurate unit/g, was a gift of Novozyme South Asia Pvt. Ltd., Bangalore, India. The chemicals such as monoglycerides and diglycerides were purchased from Scientific and Laboratory Instrument Co., Kolkata. Except otherwise specified all other chemicals were A.R. Grade.

B. Methods

Initially 250 mL of crude CAO was taken in an Erlenmeyer flask and heated up to 80⁰ C to drive off moisture by continuous stirring for about 1 h. After that, transesterification reaction was studied by changing the mixing intensity with stepwise addition of alcohol in an appropriate proportion using solvent hexane fitted with a water condenser and stirred by a magnetic stirrer at a specified temperature for 8 hours maintaining other reaction conditions. Immobilized enzyme Novozyme 40013 was added in definite proportion (w/w) in the reaction mixture. Stepwise addition of alcohol was allowed to minimize the deactivation of enzyme.

For the analysis of the products, definite amount of samples were withdrawn into a capped vial at suitable intervals. After that, the samples were centrifuged for 15 min 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. The progress of reaction was first monitored by thin layer chromatographic (TLC) method after spotting the lipid mixture on a silica-gel G plate (0.2 mm thick) using hexane-diethyl ether-acetic acid (90:10:1) as a developing solvent. The lipid spots were identified by iodine absorption with triacylglycerol (TAG), diacylglycerol (DAG), monoacylglycerol (MAG) and BD as standard. The typical yield of each reaction product was determined separately by column chromatography using silicic acid as an adsorbent and 160 mL of hexane-diethyl ether: 99:1 as eluting solvent. After completion of reaction, the enzyme was washed with hexane, dried and reused for the next experiment. Bio-diesel characterization was done according to the American Standard Testing Method (ASTM).

Values are reported as mean \pm s.d., where n=3 (n=no of observation).

3. RESULTS AND DISCUSSIONS

C. Analysis of CAO

Table 1 shows the composition of fatty acids, neutral glycerides and unsaponifiable matters present in CAO. It was observed from Table 1 that CAO contains higher amount of FFAs (72.56%) which mainly includes medium chain fatty acids like lauric acid and myristic acid. Among other acids, palmitic acid, oleic acid, capric acid and caprylic acid predominate. Among the neutral glycerides (26.34%), amount TAGs are higher than MAGs and DAGs.

Table 1: Composition of CAO

Component	Amount (%w/w)	Component	Amount (% w/w)
FFAs (Total)	72.56 \pm 1.127	Unsap. matters	1.1
Lauric acid (C 12:0)	53.08 \pm 1.006	Neutral Glycerides	26.34 \pm 0.834
Myristic acid (C 14:0)	19.77 \pm 0.952	MAG	13.51 \pm 0.017
Palmitic acid (C 16:0)	6.62 \pm 0.023	DAG	33.10 \pm 0.034
Stearic acid (C 18:0)	2.13 \pm 0.016	TAG	53.37 \pm 0.712
Oleic acid (C 18:1)	4.21 \pm 0.011		
Linoleic acid (C 18:2)	2.74 \pm 0.012		
Caprylic acid (C 8:0)	4.97 \pm 0.017		
Capric acid (C 10:0)	6.12 \pm 0.028		

D. Analysis of mixing intensity w.r.t. molar ratio

Variation of mixing intensity with respect to molar ratio of alcohol and CAO has been studied as shown in Figure 1. Mixing intensity or stirring of the reaction mixture plays a vital role for the necessary collision between substrate and enzyme to get optimum conversion of product. Proper mixing by optimum stirring actually helps to transfer the reactants from the bulk of the reaction zone to the external surface of enzyme and finally into the pores of active sites.

From Figure 1, it has been observed that increasing mixing intensity from 300 to 700 rpm enhances the conversion of biodiesel subject to the molar ratio of alcohol to CAO and 600 rpm was identified as the optimum mixing intensity for maximum conversion of BD from CAO using 6:1 molar ratio of methanol and CAO for 8 hours of reaction. So lower mixing intensity prevents the proper interaction between substrates as well as amount of alcohol w.r.t CAO also is vital for maximum achievement of product. After achieving optimum conversion at 600 rpm stirring, no further enhancement of conversion was observed by increasing the agitation with increasing amount of alcohol. For this conversion, the reaction temperature was maintained as 65⁰C.

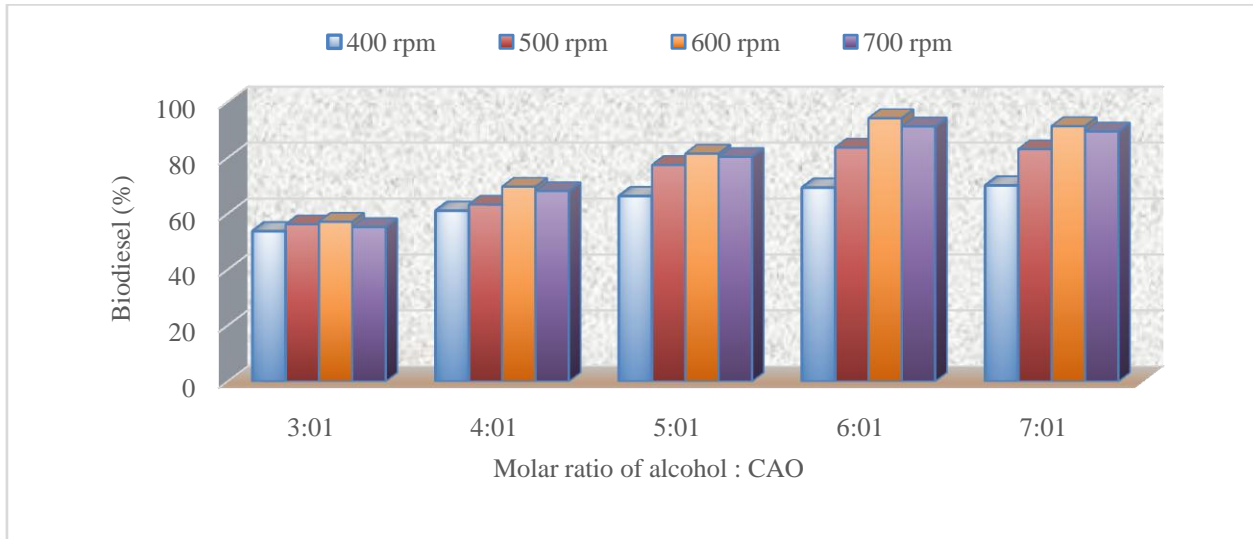


Figure 1. Effect of variation of mixing intensity for BD production w.r.t molar ratio of alcohol and CAO

E. Analysis of mixing intensity w.r.t. duration of reaction

Mixing intensity vs duration of reaction plays an important role for the conversion of biodiesel production from CAO and methanol. Enhancing duration of reaction increases the contact time between reactants with biocatalyst. It has been observed from Figure 2 that with the increasing of duration of reaction, production of biodiesel increases and maximum conversion has been achieved after 8 hrs of reaction with 600 rpm of mixing intensity maintaining other reaction conditions. 9 hrs of reaction duration with 600 rpm mixing intensity does not enhance the productivity of the transesterification reaction. This may be due to the fact that increasing time does not increase the collision between active sites of enzyme and reactants and so productivity remains same or less.

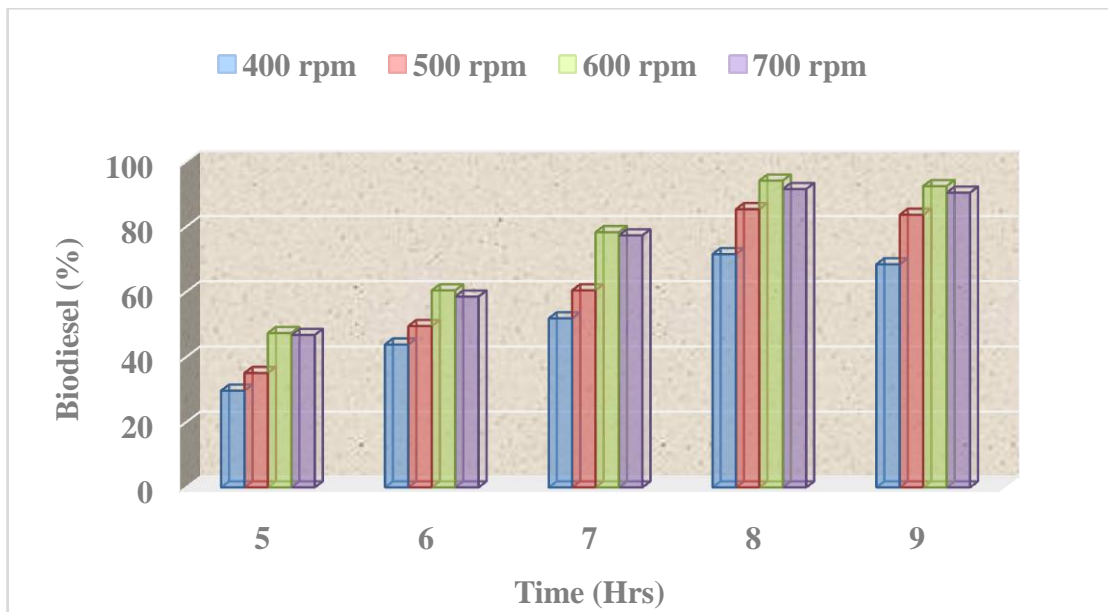


Figure 2. Effect of variation of mixing intensity for BD production w.r.t duration of reaction

F. Analysis of mixing intensity w.r.t. enzyme concentration

Catalyst concentration plays a vital role for conversion of biodiesel from CAO and methanol. Increasing the concentration of enzyme enhances the conversion with increasing mixing intensity but the optimum conversion has been achieved at 6% concentration of enzyme with 600 rpm of mixing intensity. At 7% concentration of enzyme, the conversion of product did not enhance by increasing the mixing intensity. This may be due to the fact that increasing enzyme concentration may agglomerate the enzyme which prevents the proper contact between active sites of enzyme and reactants. Mixing intensity actually helps to prevent the coagulation of catalyst but higher mixing intensity like 700 rpm with higher concentration of enzyme did not favor the reaction. Before reaching this parametric values, optimum production has been achieved as evidenced from Figure 3.

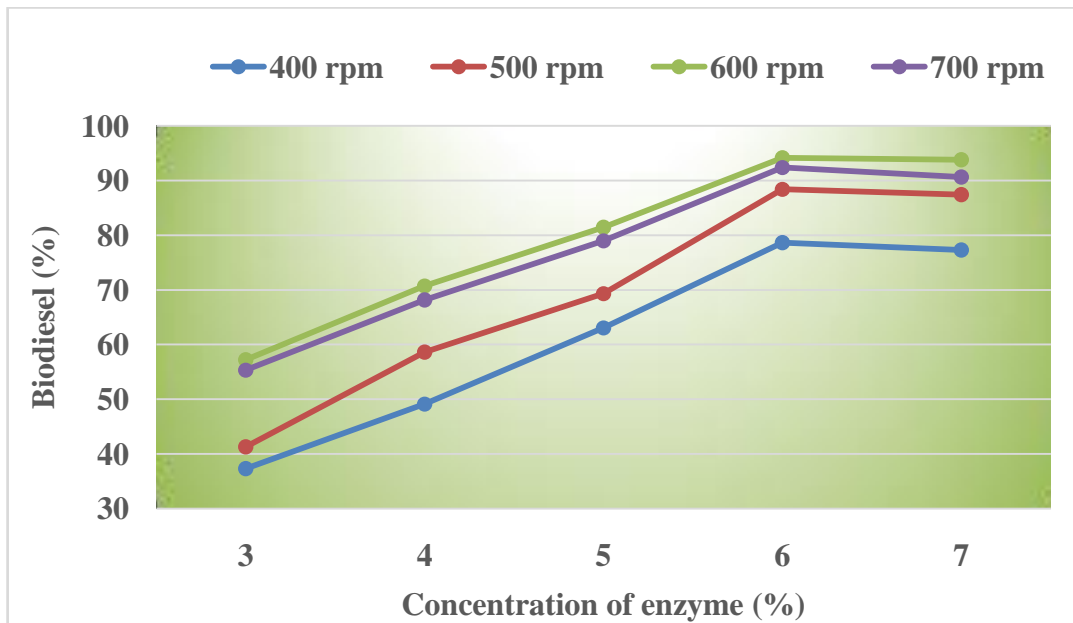


Figure 3. Effect of variation of mixing intensity for BD production w.r.t concentration of enzyme

G. Analysis of mixing intensity w.r.t. glycerides concentration

The principle of biodiesel production through transesterification reaction is the conversion of glycerides to methyl ester in the presence of catalyst by maintaining other reaction conditions. Here, the concentration of glycerides i.e. TAG, DAG, MAG has been analysed w.r.t. mixing intensity along with the amount of biodiesel after 8 hrs of reaction. It has been observed from Table 2 that minor amount of TAG, DAG and MAG are present in the final product when the reaction is carried out at 600 rpm of mixing intensity. It was found that with mixing intensity of 400 and 500 rpm, amount of TAG is much higher than DAG and MAG. It may be due to that fact that lower mixing intensity is not sufficient to convert TAG to DAG, MAG and biodiesel properly. But at higher mixing intensity at 600 and 700 rpm, the amount of TAG is less than DAG and MAG. In this case, due to rapid collision of TAG with methanol in the presence of enzyme, it has been converted to DAG, MAG and biodiesel. Apart from that, MAG amount enhances from initial value after 8 hrs of reaction when the reaction is carried out at 400 and 500 rpm. This is due to the conversion of TAG and DAG to MAG through biodiesel production.

Table 2. Analysis of mixing intensity w.r.t. glycerides and biodiesel for 8 hrs of reaction

Mixing intensity (rpm)	TAG (%)	DAG (%)	MAG (%)	Biodiesel (%)
400	10.17±0.065	7.32±0.012	6.87±0.007	69.36±0.621
500	8.54±0.034	3.13±0.009	4.67±0.011	81.67±0.801
600	1.76±0.011	1.92±0.007	2.07±0.023	94.16±1.012
700	2.15±0.013	2.98±0.010	2.58±0.019	91.23±0.876

Analysis of concentration glycerides during the production of biodiesel from CAO and methanol shows that concentration of TAG, DAG and MAG decrease with respect to time at 600 rpm of mixing intensity as shown in Figure 4. It has been observed from Figure 4 that after 8 hrs of reaction, minor amounts of TAG, DAG and MAG are present

in the reaction mixture. If the reaction is continued after 8 hrs then it has been experimentally observed that minor amounts of glycerides are still present in the final product mixture.

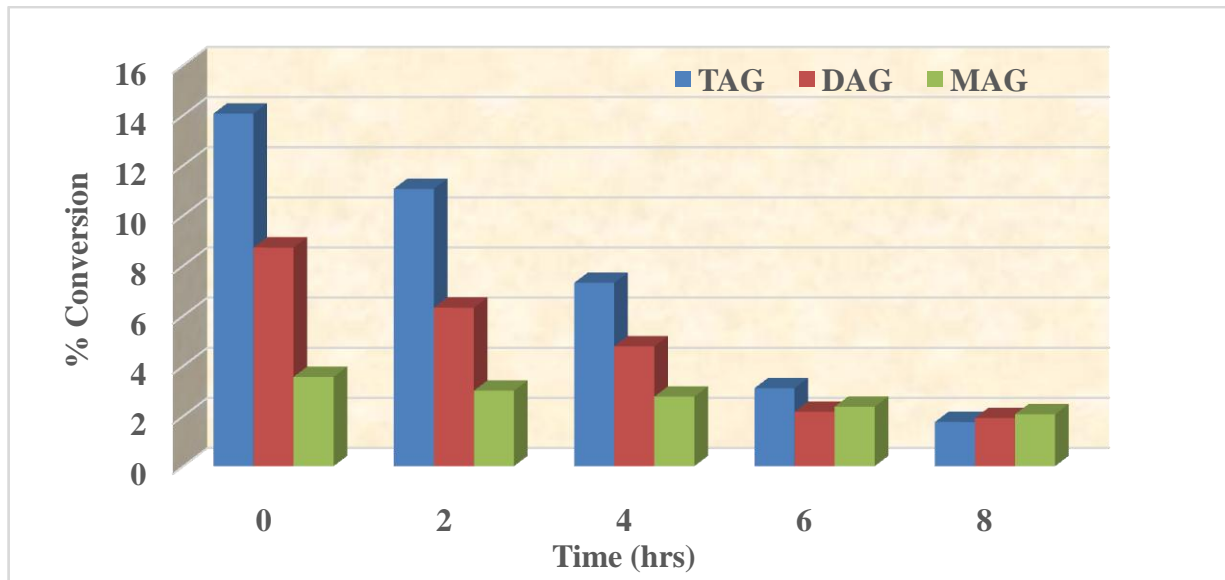


Figure4. Production of TAG, DAG and MAG during BD production at 600 rpm

Table 3 shows the total amount of glycerides during the transesterification reaction between CAO and methanol. It has been observed from Table 3 that after 8 hrs of reaction there is a slight increase of glycerides concentration. This may be due to that fact that at 600rpm, after 8 hrs of reaction, minor amount of biodiesel may be converted to glycerides as a reversible nature of the transesterification reaction.

Table 3. Total glycerides during biodiesel production from CAO and methanol at 600 rpm

Material	0 hr	2 hrs	4 hrs	6 hrs	8 hrs	10 hrs
Total glycerides (%)	26.34±0.031	20.39±0.029	14.86±0.033	7.65±0.015	5.75±0.024	5.78±0.022

Figure 5 shows the final composition of biodiesel after transesterification reaction between CAO and methanol at 600 rpm for 8 hrs at 65°C. From Figure 5, it has been established that final product contains minor amount of glyceride molecules which can be separated by applying different separation methodology for obtaining pure product.

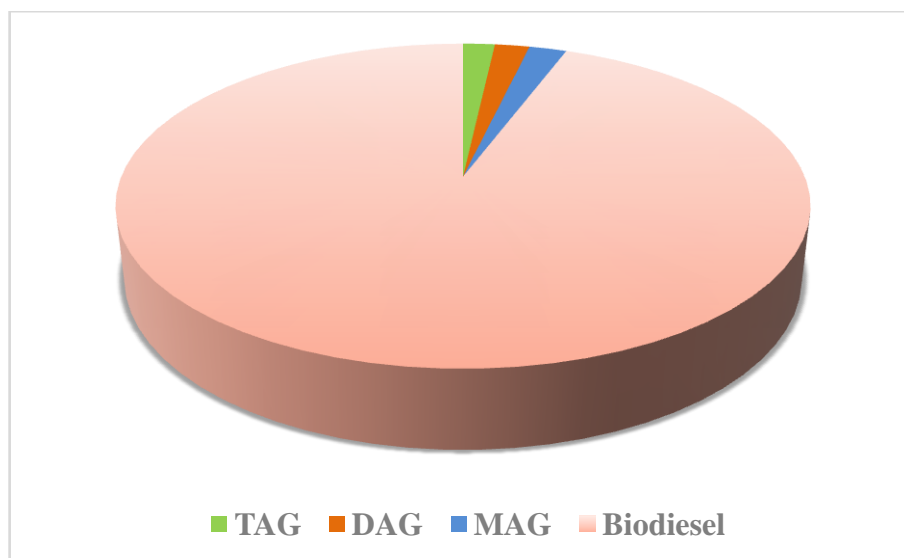


Figure 5. Final composition of biodiesel

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CONCLUSION

Mixing intensity plays a vital role for the conversion of biodiesel from coconut acid oil and methanol in the presence of enzyme catalyst. Different reaction parameters e.g. molar ratio of methanol to coconut acid oil, duration of reaction and enzyme concentration have been studied w.r.t. mixing intensity of the reaction mixture. Moreover, glycerides concentration has also been analysed w.r.t. mixing intensity during the reaction and ultimately, final composition of biodiesel has been identified. From the analysis of the present reaction, it has been concluded that proper stirring condition increases the productivity rate and identified parameters can be utilized for the production of alternative energy sources like biodiesel from suitable raw materials which can mitigate the scarcity of present energy crisis in future.

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