

Process Optimization and Kinetics of Biodiesel Production from Renewable Raw Materials

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Abstract

Kinetics of biodiesel production from renewable raw material like soybean oil deodoriser distillate (SBODD) and methanol (MeOH) in the presence of biocatalyst Novozyme 40013 (lipase from *Candida antarctica*) has been studied in the present research investigation along with optimization of reaction parameters like molar ratio of alcohol to SBODD, temperature and catalyst concentration. 5:1 molar ratios of alcohol to SBODD, 60°C temperature with 5% concentration of catalyst for 3 hrs of reaction duration are the optimum conditions identified which contributed 93.24% conversion. Pseudo homogeneous kinetic model has been used to fit the experimental data and results have been analysed on the basis of model data. Equilibrium constants (K_{obs}) have been evaluated through this kinetic model at different temperatures and different molar ratios. By fitting the experimental data, the pre exponential factor and the activation energy of the esterification reaction have been determined also. Kinetic analyses are in good agreement with experimental results.

Keywords: Biodiesel, *Candida Antarctica*, Kinetic model, SBODD, Equilibrium constant.

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INTRODUCTION

Renewable fuels are getting more important for the last few decades due to decrement of non-renewable fuels, gradual environmental degradation and its biodegradability [1,2]. Biodiesel is considered to be one of the most important renewable fuels which is a promising alternative to fossil fuels due to its ecofriendly nature, low toxic emission, less process hazards and minimization or no byproducts [3, 4]. It can also significantly reduce exhaust emissions like hydrocarbons, carbon monoxide and particulate matters at any ratios of blends with diesel fuel [5]. Different raw materials have been used for the synthesis of biodiesel using chemical or biochemical catalyst and performance characteristics have been compared with diesel fuel. Nandi et al compared the performance characteristics of biocatalysts for the production of biodiesel from bioresources [6]. They also compared the production efficiency using chemical and biochemical catalyst [7]. Arumugam and Ponnusami prepared biodiesel from waste sardine oil and evaluated engine performance by enzymatic transesterification method [8]. Waste oil was also used by Taher H et al. [9] for biodiesel production in ionic liquid media using biocatalytic method. Kinetics of biodiesel production was also analysed by different researchers using

different raw materials chemically or enzymatically. Firdaus et al identified a kinetic model for biodiesel production using biocatalyst [10]. Jain and Sharma discussed the kinetics of biodiesel production from of *Jatropha Curcas* oil [11]. The kinetic behaviour of esterification or transesterification reaction for the production of biodiesel was also studied by Zeng et al. [12], Konwar et al. [13] and Vujicic et al. [14]. Present author also studied the effect of mass transfer kinetics for biodiesel production from *Jatropha Curcas* oil [15]. But the production of biodiesel from renewable raw materials is the most important thinking in the present scenario with regard to environmental stability and future generations.

In the present research investigation, a cheap renewable raw material, SBODD, mostly utilised for low quality soap production, is utilised for biodiesel production in the presence of biocatalyst Novozyme 40013 (lipase from *Candida antarctica*) with controlled addition of methanol as alcohol. Reaction parameters were optimised for the maximum production of biodiesel. Kinetics of the reaction was studied with a view to identify the rate constants with regard to temperature, activation energy and frequency factor through the experimental results.

EXPERIMENTAL

The SBODD used in this study was provided by M/s. A.S. Oil Mills, Burdwan, West Bengal, India. The enzyme used in the following studies was Novozyme 40013 (*Candida antarctica*) immobilized lipase which was a kind gift of Novozyme South Asia Pvt. Ltd. Bangalore, India. The chemicals used in this work were methanol and hexane purchased from S.D. Fine Chemicals (Mumbai, India). Except otherwise specified all other chemicals used were A.R. Grade.

Initially, SBODD was taken in an Erlenmeyer flask and heated up to 80°C to drive off moisture by continuous stirring for about 1 h. After that, enzyme Novozyme 40013 was added and continuously stirred in the presence of alcohol maintaining proper reaction conditions. Alcohol was added in stepwise manner in an appropriate proportion using solvent hexane fitted with a water condenser and stirred by a magnetic stirrer at a specified temperature for 3 hours. Stepwise addition of methanol was allowed to minimize the deactivation of enzyme.

During the reaction, continuous sampling and analysis were done by withdrawing the sample in to a capped vial and removing enzyme through centrifugation. The progress of reaction or production of biodiesel was monitored by thin layer chromatographic (TLC) method and the typical yield of

each reaction product was determined by column chromatography. TLC was done by 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 [16]. The composition of methyl esters was determined by column chromatography using silicic acid as an adsorbent and 160 mL of hexane-diethyl ether: 99:1 as eluting solvent [17]. After completion of reaction, the enzyme was washed with hexane, dried and reused for the next experiment. Values are reported as mean \pm s.d., where n=3 (n=no of observations).

RESULTS AND DISCUSSION

Optimization of process conditions

The physicochemical properties and fatty acid profiles of SBODD are shown in Table 1. It is shown that FFAs are the major component of SBODD. They represent approximately 87.27% of the SBODD on weight basis. High Iodine value indicates higher amount of unsaturated FFAs in the SBODD which is also reflected in the fatty acid composition. Apart from FFAs, SBODD contains some amount of neutral glycerides and unsaponifiable matters. The biodiesel production process was optimized by varying the molar ratio of MeOH to SBODD, analysing the effect of temperature and by changing the amount of biocatalyst.

Table-1: Physicochemical properties of SBODD

| Characteristics | Amount | Characteristics | Amount |
|---------------------|-------------------|-------------------------------------|-------------------|
| Total acidity (wt%) | 87.27 \pm 0.301 | Iodine value (I ₂ /100g) | 74.34 \pm 0.195 |
| C 16:0 | 26.9 \pm 0.111 | Neutral glycerides (wt%) | 8.86 \pm 0.049 |
| C 18:0 | 2.3 \pm 0.017 | Unsaponifiable matters (wt%) | 3.82 \pm 0.025 |
| C 18:1 | 37.3 \pm 0.118 | | |
| C 18:2 | 33.1 \pm 0.171 | | |

Effect of molar ratio of MeOH to SBODD: The conversion of biodiesel production was analysed by varying the moles of alcohol with fixed amount of SBODD at temperature 60°C using 5% (wt/wt) biocatalyst for 3 hours. Figure 1 shows that maximum conversion was achieved at 5:1 molar ratio of MeOH to SBODD.

Stepwise addition of methanol has been the most important strategy to avoid lipase denaturation. Deactivation of enzyme has been prevented by keeping the alcohol concentration low. Two consecutive addition of methanol has been arranged. Stepwise addition also improves the conversion of biodiesel from SBODD.

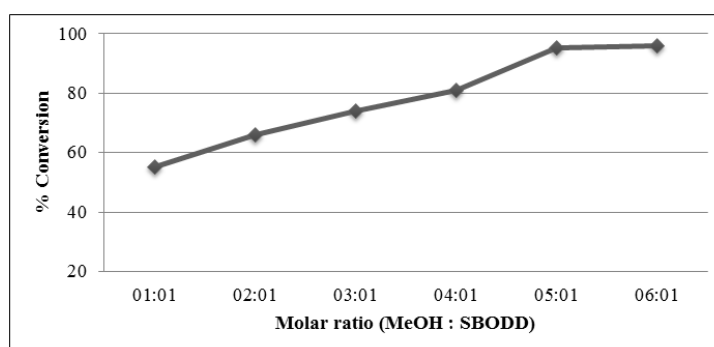


Fig-1: Effect of molar ratio of MeOH to SBODD for biodiesel production at 60°C, 180 min and 5% enzyme catalyst NS40013

Effect of reaction temperature: Figure 2 shows the effect of reaction temperature for biodiesel production with 5:1 molar ratio of MeOH: SBODD, 180 min and 5% concentration of enzyme catalyst. Temperature variation analysed in our study ranges from 40 – 70⁰ C and experiments showed that maximum biodiesel was obtained at a temperature of 60⁰C. Increasing temperature did not enhance rather decrement occurred at higher temperature. It may be due to deactivation of enzyme at higher temperature.

Effect of catalyst concentration: Concentration of enzyme plays a vital role for the conversion of biodiesel production because as catalyst helps to decrease the activation energy of the reaction which

ultimately speeded up the conversion reaction. In our study, the effect of concentration of enzyme has been analysed by enhancing the amount of enzyme from 1-6% maintaining the same reaction parameters i.e. Temperature 60⁰C, molar ratio of methanol to SBODD 5:1 for 180 minutes which are indicated in Figure 3. It has been observed from the figure that maximum biodiesel was obtained with 5% (w/w) concentration of NS 40013. Enhancing concentration of enzyme did not show any significant increase in production as, in higher percentage of enzyme, agglomeration of enzyme may occur. Due to agglomeration of enzyme, some of the active sites of the enzyme may be blocked and conversion rate decreases.

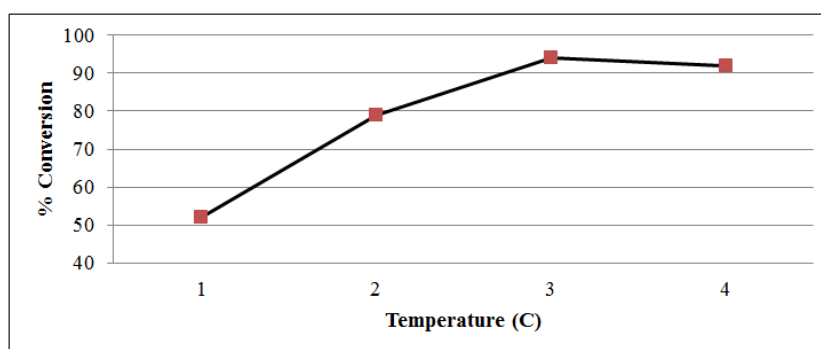


Fig-2: Effect of reaction temperature for biodiesel production at

5:1 molar ratio of MeOH: SBODD, 180 min and 5% enzyme catalyst NS40013 (1→40⁰C, 2→50⁰C, 3→60⁰C, 4→70⁰C)

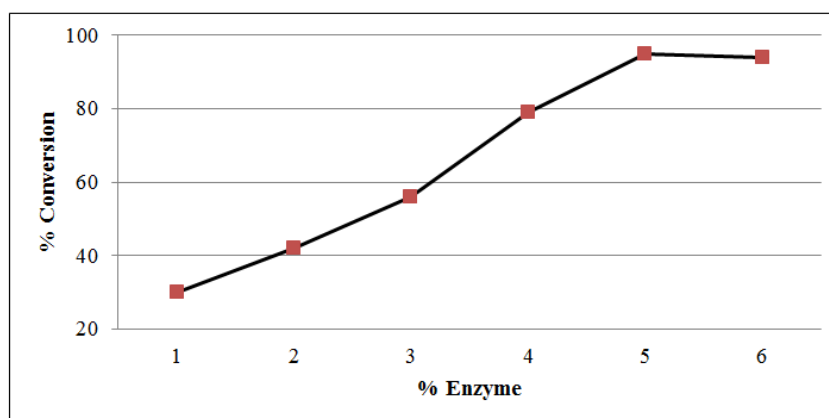


Fig-3: Effect of enzyme concentration for biodiesel production at

5:1 molar ratio of MeOH: SBODD, 180 min at 60⁰C temperature

Kinetic studies: Saha and Streat 1999 identified pseudo-homogeneous first order and second order models for polar reacting system. In our study, same model was followed to explain our kinetic results available for different temperatures, catalyst concentration and molar ratios of reactants. Biodiesel was produced by considering different molar ratios of MeOH and SBODD and the values of pseudo-first order

rate constant (K_{obs}) have been determined and plotted against molar ratios of MeOH: SBODD. It has been observed from the Figure 4 that rate constant increases linearly with molar ratios of MeOH: SBODD up to 5:1. On further increasing the molar ratio, there was no observable change in the rate constant which indicates the optimum ratio of MeOH: SBODD is 5:1.

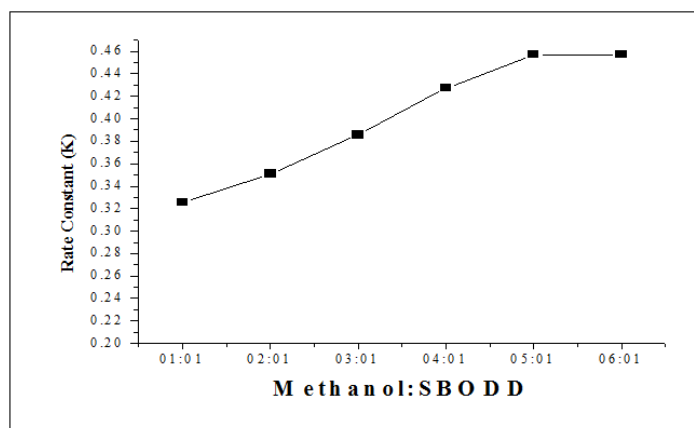


Fig-4: Plot of K_{obs} (min^{-1}) vs molar ratio of MeOH: SBODD at 60°C .

The effect of temperature on the rate of production of biodiesel from SBODD was also analysed by changing the temperature from $40\text{--}70^{\circ}\text{C}$ at 5:1 molar ratio of methanol and SBODD. The values of rate constants (K_{obs}) at different temperature are given in

Table 2. It has been observed from Table 2 that optimum rate constant value has been obtained at temperature 60°C . Further enhancement of temperature actually decreases the rate constant value as enzyme has been deactivated due to higher temperature.

Table-2: K_{obs} at different temperature for biodiesel production

| Temperature ($^{\circ}\text{C}$) | K_{obs} (min^{-1}) |
|------------------------------------|---------------------------------|
| 40 | 0.3256 |
| 45 | 0.3511 |
| 50 | 0.3856 |
| 55 | 0.4274 |
| 60 | 0.4573 |
| 70 | 0.4427 |

Activation energy and frequency factor: The energy of activation for the reaction was also evaluated from the slope of Arrhenius plot (Fig. 5) of $\log K$ vs $1/T$

and was found to be $30.677 \text{ kJ mol}^{-1}$. The frequency factor obtained from the kinetic results was $1.41 \times 10^5 \text{ collisions s}^{-1}$.

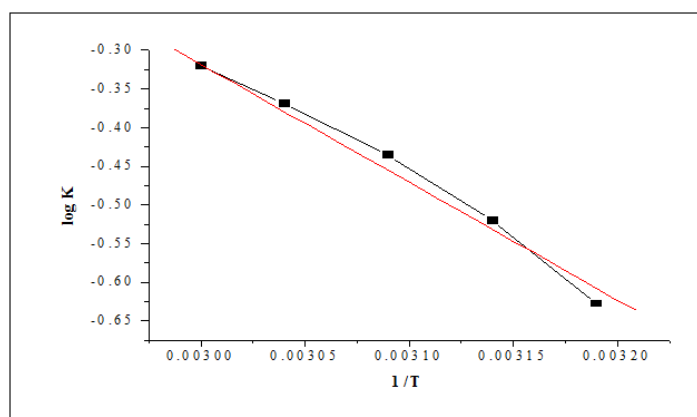


Fig-5: Plot of $\log K_{obs}$ vs $1/T$

CONCLUSION

Production of biodiesel from relatively low cost renewable materials has been optimized for the process conditions. The maximum conversion of SBODD to biodiesel was obtained at a molar ratio of 5:1 (MeOH: SBODD), 5% catalyst at 60°C for 180 min. A pseudo-homogeneous kinetic model was employed for fitting the experimental results and it is in agreement with the observed optimum conditions. The activation energy and frequency factor for the experimental

condition of conversion of biodiesel from SBODD and methanol for the forward reaction were found to be $30.677 \text{ kJ mol}^{-1}$ and $1.41 \times 10^5 \text{ collisions s}^{-1}$ respectively.

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