Enzyme catalyzed synthesis of 2-ethylhexyl acrylate from acrylic acid and 2-ethylhexyl acrylate

Virendra Rathod,[a,] * Govind Waghmare[a]

[a] *Chemical Engineering Department, Institute of Chemical Technology, Matunga, Mumbai-40019, India.*

**Corresponding author: E-mail address-vk.rathod@ictmumbai.edu.in,*

Abstract: Enzymatic esterification of 2-ethylhexyl acrylate was investigated. Experiments were performed to study the effect of operating parameters such as molar ratio, enzyme loading, reaction temperature, and agitation speed. The kinetic model for esterification reaction was predicted and verified, the determined kinetic parameters were also reported. Experimental results showed good fit with the results predicted by Ping Pong Bi Bi mechanism with dead end inhibition by both the substrates. The reusability study revealed that enzyme retained 85% of its catalytic activity after five consecutive cycles.

Keywords: Enzymatic esterification, Ping-Pong bi bi model,

1. Introduction

Acrylic acid (AA) is an industrially important raw material frequently used in the manufacturing of valuable acrylic esters. Acrylic esters are considered to be very important chemicals because of their use in emulsion polymers, paint emulsions, adhesive, water based printing inks, construction chemicals etc. These esters also show excellent clarity, color retention, toughness, chemical inertness and UV stability. The presence of significant amounts of AA in the liquid discharge from the AA processing plant may cause adverse effect to aquatic life and their presence found to create the limitations for the waste water treatment applications using biological treatment and adsorption method 1. Though, various treatments for the processing of AA have been suggested such as; incineration, catalytic degradation, biodegradation, and adsorption, they are not that efficient, economical and also generate large amount of waste 2. Esterification is another method which can be used for the conversion of acrylic acid to valuable acrylate esters. Esterification using enzyme as catalyst has various advantages over conventional organic and inorganic catalyst like, mild operating conditions, and high selectivity.

The present study reports the esterification of acrylic acid by 2-ethylhexanol using enzyme catalyst in a batch system. The effect of various operating parameters such as molar ratio, catalyst loading, speed of rotation and reaction temperature was studied on the esterification reaction.

2. Experimental

Immobilized lipase *Candida Antarctica* lipase B (CAL-B) was used as catalyst. The enzyme was provided by Fermenta Biotech, India as "Fermase CALB 10000". All the reactions were carried out in a 50 cm^3 baffle glass reactor equipped with overhead stirrer with speed control system was used to agitate the reaction mixture. The reactor was submerged in a water bath equipped with temperature controller in order to maintain desired reaction temperature.

The calculated amount of reactants is first measured and then transferred to the reactor. Hydroquinone is also added to inhibit the undesirable free-radical polymerization of acrylic acids and its esters. The measured quantity of enzyme was then transferred to the reaction and addition of enzyme was considered as starting of the reaction. Periodically samples were taken and analyzed for acid value determination. The acid value was determined by titrimetric analysis and the results were calculated by the following equation,

$$\text{Acid value} = \frac{56.1 \times N \times V}{W}$$

Where, N is the strength of alkali required to neutralize the acid, V is the volume of KOH in milliliters and W is the weight of the sample in grams.

3. Results and discussion

The effect of substrate concentration on esterification reaction was studied by varying the concentration of alcohol at constant acid concentration. The percent conversion is found to increase with an increase in substrate concentration upto certain limit and at higher concentration the conversion get reduced. The inhibition of enzyme may be the reason of decreased conversion at higher alcohol concentration 3. The experimental data obtained shows good fit with the data simulated using Ping Pong bi bi mechanism with the inhibition by both the substrate (Fig. 1).

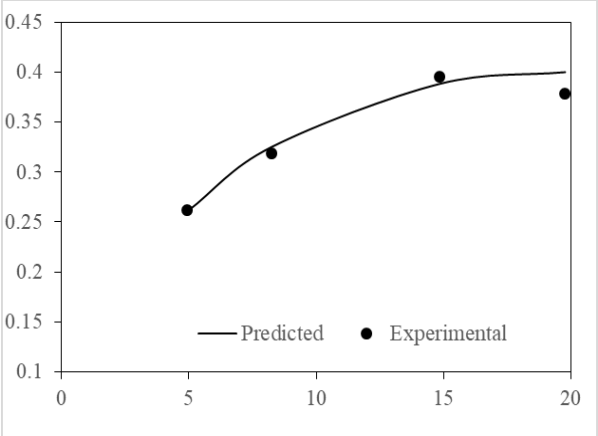

Figure 1. Initial reaction rate comparision between experimental and predicted model.

The inhibition suggested by the model was verified using Lineweaver–Burk double reciprocal plot for both the substrate. The kinetics parameters obtained were V_{max}= 0.52 (mol h^{-1}), K_{mA} = 8.6 × 10^{-3} (mol dm^{-3}), K_{mB} = 7 × 10^{-4} (mol dm^{-3}), K_{iA} = 0.12 (mol dm^{-3}) and K_{iB} = 7 × 10^{-4} (mol dm^{-3}). The effect of temperature was investigated at reaction temperature 40°C, 50°C, 60°C and 70°C. At higher temperature (70°C) the conversion have found to decrease as compared with the conversion at 60°C due to the thermal denaturation of enzyme minimizing its catalytic activity 4. The effect of enzyme loading was studied at 2, 3, 4 and 5% (w.r.t weight of substrate). Initially with increase in enzyme loading the percent conversion was increased from 72 at 2% to 93 at 4%. The increase was possibly due to the increased numbered of active enzyme sites that can form more number of enzyme-substrate complexes ultimately producing more product. Further increase in enzyme loading does not bring any significant difference in percent conversion, possibly due to the saturation of enzyme in the system due to this increased amount of enzyme will stay unattended. Also, the effect of agitation speed was studied and found that at higher speed of agitation the conversion was found to get reduced due to the breakage of bonding between the enzyme and the immobilization support. The reusability study was performed at obtained optimized parameters and found that the catalyst retain around 85 % of its catalytic activity after five consecutive cycles. The activation energy E_a was calculate using Arrhenius plot and it is found to be 29 kJ mol^{-1} which is found to be in good agreement with the reported literature for enzymatic reactions.

4. Conclusions

Enzyme catalyzed synthesis of 2-ethlyl hexyl acrylate from 2- ethyl hexanol and acrylic acid was reported successfully. Various reaction parameters were optimized as reaction temperature of 60°C, molar substrate ratio of 1:3, enzyme loading of 4%, and agitation speed of 400 rpm. A maximum conversion of about 86% was achieved in 15 h. The kinetic model is predicted and fitted with experimental data to obtain the kinetic parameters. Ping-Pong bi bi model with substrate inhibition by both the substrate at higher substrate concentration is found to show good fit with the experimental data. The reusability study of the biocatalyst at optimum conditions shows good reusability without much loss of its catalytic activity after consecutive 5 cycles.

References

1. M. Allison, K. Singh, J. Webb, S. Grant, Proc. Water Environ. Fed. 2011 (2011) 6554–6564.
2. D. Bhattacharyya, M.J. Allison, J.R. Webb, G.M. Zanatta, K.S. Singh, S.R. Grant, J. Hazardous, Toxic, Radioact. Waste. 17 (2012) 74–79.
3. Y. Shimada, J. Mol. Catal. B Enzym. 17 (2002) 133–142.
4. K. Nie, F. Xie, F. Wang, T. Tan, J. Mol. Catal. B Enzym. 43 (2006) 142–147.