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ENZYMATIC ESTERIFICATION ENHANCED BY PERVAPORATION

Summary. This paper presents study of enzymatic esterification of oleic-acid and i-amyl alcohol. Product of such reaction, i-amyl-oleate is widely used as bio-lubricant, (easily degradable compound). It was suggested that the mechanism of reaction obeys so called "Random Bi-Bi". Mathematical models of this reaction and the reaction integrated with pervaporation process was build. Several simulations carried out show that this integration can efficiently enhance the process.

ENZYMATYCZNA ESTRYFIKACJA WSPOMAGANA PROCESEM PERWAPORACJI

Streszczenie. W pracy przebadano katalizowaną enzymatycznie reakcję estryfikacji kwasu oleinowego za pomocą alkoholu amylowego. Powstający w trakcie takiej reakcji ester jest środkiem stosowanym jako biodegradowalny olej do maszyn precyzyjnych. Określony został mechanizm ww. reakcji - „Random Bi-Bi". W oparciu o ten mechanizm dobrano równanie kinetyki. Wykorzystując to równanie oraz równanie kinetyki procesu perwaporacji przeprowadzono teoretyczną integrację procesów: estryfikacji i perwaporacji, której celem jest usuwanie (na bieżąco) wody ze środowiska reakcji. Integracja taka, jak wykazały przeprowadzone obliczenia, może dać wymierny efekt w postaci czystego produktu i ominięcia konieczności stosowania rektyfikacji ekstrakcyjnej.

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1. Introduction

Ester types of natural lubricants have significant advantages compared to the synthetic one. These biolubricants are non-toxic, biologically degradable, environmental-safe, low-price compounds, which can be easily recycled [1]. Their production is based on the esterification of long-chain acids and short chain alcohols, both of natural origin. Fatty acids can be obtained by hydrolysis of plant oils [2], while short chain acids are the components of fusel oil: by-product of ethanol fermentation [3]. The esterification is catalysed by lipase enzymes, and can be realised under mild conditions [4].

Our aim was to study the enzymatic esterification of oleic acid and i-amyl-alcohol (main compound of fusel oil) from the kinetic point of view. During the esterification water is produced as a by-product, which has a disadvantageous effect on the reaction rate and the enzyme activity beyond a certain level [5]. To enhance the effectiveness of the process water should be removed. One of the most promising techniques is pervaporation, which can be on-line integrated into the reaction system. Such integration can be realized in the form of membrane reactor as it was studied in this work.

2. Modeling of the process

2.1. Reaction model

The Random Bi - Bi (Chaldene) was chosen as the proper reaction mechanism.

$$E + B + A \begin{matrix} \xleftrightarrow{K'_A} \\ \xleftrightarrow{K'_B} \end{matrix} \begin{matrix} EA + B \xleftrightarrow{K_B} \\ EB + A \xleftrightarrow{K_A} \end{matrix} EAB \xrightarrow{k} E + P + Q$$

This mechanism can be mathematically described as follows:

$$\frac{1}{r} = \left[\frac{K'_A K_B}{X_A X_B} + \frac{K_B}{X_B} + \frac{K_A}{X_A} + 1 \right] \frac{1}{r_{max}} \tag{1}$$

after recalculation we can find the reaction rate of ester or water produced during the reaction:

$$r = \left(\frac{dX}{d\tau} \right)_R = \frac{k \cdot X_{E0} \cdot X_A \cdot X_B}{K'_A K_B + K_B X_A + K_A X_B + X_A \cdot X_B} \tag{2}$$

2.2. Process model

Modern hydrophilic membranes can be characterized as highly selective. By using such membranes as PERVAP1005 by GFT it is possible to obtain the permeate composed almost only of water. Molar rate of water removed from the reaction mixture by pervaporation can be assumed as the product of permeability coefficient and water concentration:

$$n_W = A \cdot P_W \cdot X_W \tag{3}$$

The change of water concentration during the process is associated with the amount of water created in the reaction and removed by pervaporation. For the combination of pervaporation with the reaction system we can define the profile of water concentration starting with water mass balance:

$$\frac{d(N \cdot X_W)}{d\tau} = r \cdot N - n_W \tag{4}$$

Taking into account that, it is practically only water which passes through the membrane we can assume that the total mass balance is:

$$\frac{dN}{d\tau} = -n_W \tag{5}$$

After introduction (3) into (4)

$$N\frac{dX_W}{d\tau} + X_W\frac{dN}{d\tau} = r \cdot N - A\,P_W X_W \tag{6}$$

and transformation we get:

$$\frac{dX_W}{d\tau} = \frac{A\,P_W X_W (X_W - 1)}{N} + r \tag{7}$$

By introducing (2) into (7) we finally obtain water concentration profile in the membrane reactor:

$$\left(\frac{dX_W}{d\tau}\right)_P = \frac{A\,P_W X_W (X_W - 1)}{N} + \frac{k \cdot X_{E0} \cdot X_A \cdot X_B}{K_A' K_B + K_B X_A + K_A X_B + X_A \cdot X_B} \tag{8}$$

3. Experimental estimation of reaction and pervaporation parameters

3.1. Materials and Methods

Oleic acid used in the experiments were purchased from Reanal Ltd. (Hungary), while i-amyl-alcohol – main component of fusel oil – was received as a gift of Distillery Ltd., Győr

(Hungary). Novozym 435 immobilised lipase enzyme was a kind gift from Novo Nordisk (Denmark).

Esterification reactions were carried out in New Brunswick G24 shaking incubator in 500 rpm at 40 °C temperature in 25 ml volumes. The reactions were followed by gas chromatography and titration. Hewlett Packard 5890 A gas chromatograph equipped with HP-FFAP (30 m x 0.53 mm x 1.0 μm) column connected with HP 3396 A integrator was used for determination of ester concentrations. Conditions: oven temperature 200 °C, temperature of injector and detector 250 °C, split pressure 60 kPa, carrier gas (N_2) 28 ml/min. Titration with 0.1 alcoholic KOH solution (using phenolphthalein indicator) was applied to measure the amounts of oleic acid. Water content of the reaction mixtures were checked by Mettler DL 35 automatic Karl-Fischer titrator

3.2. Equilibrium and reaction rate constants

Estimation of the value of constants in the equation describing reaction rate requires linearization of that equation:

$$\frac{1}{r} = \left[\frac{K_A' K_B}{X_B r_{max}} + \frac{K_A}{r_{max}}\right]\frac{1}{X_A} + \left[\frac{K_B}{X_B} + 1\right]\frac{1}{r_{max}} \tag{9}$$

Based on (9), 1/r can be plotted against $1/X_A$ at several different, but within one series of experiments constant X_B. It should give straight lines

$$\text{with slope} = \left[\frac{K_A' K_B}{X_B} + K_A\right]\frac{1}{r_{max}} \tag{10}$$

$$\text{and intercept} = \left[\frac{K_B}{X_B} + 1\right]\frac{1}{r_{max}} \tag{11}$$

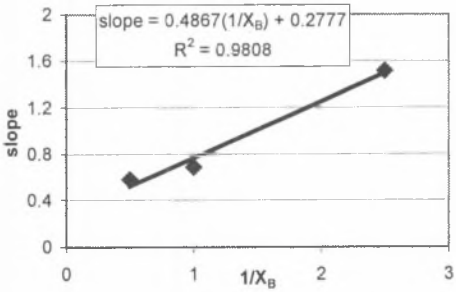

Fig.1. Graphical analysis of constants

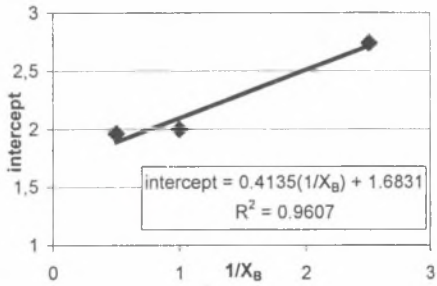

Fig.2. Graphical analysis of constants

From (10) we see that a plot of different slope values against $1/X_B$ gives a straight line with slope of $K'_A K_B/r_{max}$ and intercept of K_A/r_{max}. Similarly from (11) plot of different intercepts against $1/X_B$ is linear with slope of K_B/r_{max} and intercept of $1/r_{max}$. The appropriate values of slopes and intercepts are shown in figures 1 and 2. These figures present also Pearson correlation factors R^2 which gives us the deviation of experimental data from the straight line. Arranging the system of simple equations it is easily to calculate the constants values:

$K_A = 0.1650$ $K_B = 0.2457$ $K'_A = 1.177$ $r_{max} = k\, X_{E0} = 0.5941$

3.2.1. Permeation coefficient

Flux of the organic compound through that membrane can be neglected with acceptable error. Within the range of 0 ÷ 20% water (by weight) it could be assumed that the flux of water is linearly related with its concentration. Permeation coefficient of water was estimated in several water – organic mixtures [6]. Average value: P_W = 64,03 [mol/m^2 h] was found with standard deviation δ = 0,081.

4. Results and conclusions

Kinetic model was verified by independent experiments where initial ratio of alcohol to ester was set to 0.4 : 0.2. The concentration profile of ester produced during the reaction can be observed in figure 3. Next figure 4. shows simulation of water concentration profile in membrane reactor. Several ratios of membrane area to the volume of reaction mixture were used A/V = 0.01, 0.05 and 0.1 [m^2/dm^3]. It can be easily noticed that water can be completely removed from the reaction mixture after 20 hours with reasonable ratio of the reaction volume to the membrane area. Ratio A/V is a very important factor for industrial plant design.

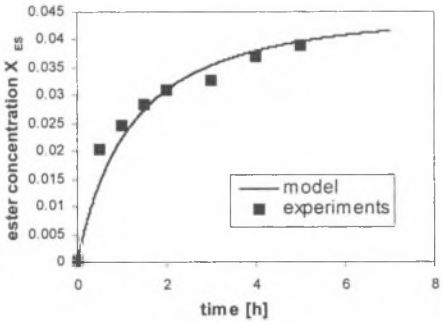

Fig.3. Ester concentration in reaction mixture

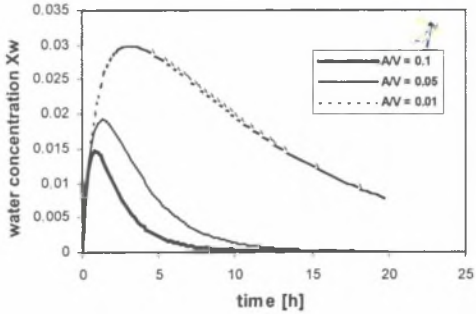

Fig.4. Simulation of water concentration in membrane reactor

In further study the proposed model of integrated process (esterification-pervaporation) will be verified experimentally.

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Streszczenie

W pracy tej przebadano katalizowaną enzymatycznie reakcję estryfikacji kwasu oleinowego za pomocą alkoholu amylowego. Przeprowadzono 9 serii eksperymentów przy następujących początkowych stosunkach molowych substratów:

- alkohol i-amylowy: 0,4 ; 1 ; 2
- kwas oleinowy: 0.2 ; 0.5 ; 1

Na podstawie tych eksperymentów określono mechanizm reakcji jako tzw. „Random Bi-Bi". Przyjęte dla powyższego mechanizmu równanie kinetyki reakcji (1) poddano linearyzacji (9) i metodą analizy graficznej (rys.1 i 2) wyznaczono wartości stałych równowagi oraz stałych kinetycznych: $K_A = 0.1650$; $K_B = 0.2457$; $K'_A = 1.177$; $r_{max} = k\ X_{E0} = 0.5941$. Określony w ten sposób model matematyczny reakcji (2) poddano weryfikacji na bazie niezależnego eksperymentu, rys. 3. Równanie (2) oraz często stosowane [6] równanie transportu wody poprzez membrany hydrofilowe (3) posłużyło następnie do zbudowania modelu matematycznego zintegrowanego procesu estryfikacja-perwaporacja (8). Przeprowadzono za jego pomocą szereg symulacji usuwania wody ze środowiska reakcji za pomocą procesu perwaporacji, rys.4. Integracja taka, jak wykazały symulacje, może dać wymierny efekt w postaci czystego produktu i ominięcia konieczności stosowania rektyfikacji ekstrakcyjnej.