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Modeling of esterification-pervaporation integrated system of acrylic acid with ethanol

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Abstract

Kinetic model for esterification of acrylic acid with ethanol using sulphuric acid (H_2SO_4) as a catalyst coupled pervaporation process was established in this work. The major effects of different parameters such as reaction temperature, ratios of initial molar quantity of reactants, membrane area, catalyst concentration and membrane permeability on the esterification reaction and the permeation kinetics of water removed by pervaporation were taken into consideration in this kinetic model. The developed model equations are solved by the ODE solver, ode45 implemented in the MATLAB. The esterification of acrylic acid with ethanol usingH_2SO_4 was carried out at a temperature range of 50–70°C, catalyst concentration of 1-3% of reaction mixture and initial reactant molar ratio of 1:1-1:3. The conversion of acrylic acid or yield of ethyl acrylate was enhanced in a pervaporation reactor as compared to a conventional reactor. The result indicates that the esterification pervaporation integrated system accelerates the rate of ester formation by removing water.

Keywords: Pervaporation, Esterification, Membrane, Modeling, Acrylic acid.

Introduction

Nowadays, merging reactor with separation unit has become a current trend in the chemical industry in order to obtain more efficient processes and lower energy consumption[1]. This combination is advantageous for the production of esters from esterification reaction as this reaction is thermodynamically limited. Pervaporation process shifts the chemical equilibrium towards the production of ester by removing water continuously. Pervaporation (PV) is useful for dehydration of organicchemicals[2].

Moreover, PV enhances both conversion and reaction rates as it can remove water simultaneously from the reactor. Mathematical modeling of coupled reaction-membrane systems has attracted great interest because it can provide an insight into the industrial design and optimal operation of theseprocesses[3].

In present work the resulting ester ethyl acrylate from the esterification reaction between acrylic acid and ethyl alcohol can be used as a reactive building block to produce coatings and inks, adhesives, sealants, textiles, plastics and elastomers[4,5]. Pervaporation membrane reactors assisted with esterification have been studied of acrylic acid and n-butanol[6], lactic acid and iso-propanol[7], acetic acid and iso-propanol[8], acetic acid and iso-butanol[9], acetic acid and ethanol[10], lactic acid and ethanol[11]. Limited work related to esterification- pervaporation hybrid system of acrylic acid with ethanol has been available on literature[12]. Truong et al. 2013[12] used a polymer based membrane to improve the synthesis of acrylic esters and investigated the chemical stability of the membrane.

In present paper experiments were conducted for esterification of acrylic acid with ethanol integrated with pervaporation and without pervaporation. Modeling of the esterification reaction coupled with PV process has also been presented for the esterification of acrylic acid with ethanol. The model was validated using experimental data. Besides, the effect of various process variables, such as process temperature (T), initial mole ratio of reactants (MR), and the ratio of the effective membrane area over the volume of reacting mixture (S/V),catalyst content (C_C) on the performance of pervaporation reactor for esterification reaction were discussed.

Materials and methods

The hydrophilic PVA membrane, used in this work was supplied by Permionics Membranes Pvt. Ltd., India. All reactants (acrylic acid, ethanol) and catalyst (sulfuric acid) were of analytical grade with purity higher than 99% and obtained from Merck.

The experimental set-up used for the PV couple desterification reaction was performed in situ batch operation mode. The membrane was placed just below the reactor in a particular cell. The effective membrane area which was in contact with the feed mixture was 78.5 cm^2. Reactants were added to the reactor along with catalyst and heated up to the desired reaction temperature. The stirrer was started at 300 rpm speed for the proper mixing of reaction mixture. A thermostat has been used to maintain the temperature within the accuracy of ±1°C during the reaction. With the help of hydrophilic membrane (PVA), water was separated from the feed mixture simultaneously. The

pressure on the permeate side was held constant at 5 mbar and chiller temperature was maintained at -5°C. During the experiment samples were withdrawn from the reactor at regular intervals.

Samples collected from the reactor and the permeate were analyzed by NUCON series 5700 gas chromatograph (GC) with porapak column (id 2mm, od 1/8", length 2 m) hydrogen gas taken as carrier gas with flow rate 60 ml/min equipped with a TCD detector. Sample has injected in chromatograph with amount of 1µl. To obtain accurate results, each sample was analyzed two times.

The operating conditions for the gas chromatograph are: i. Temperature (°C), ii. Injector: 150, iii. Detector: 180, iv. Oven: 180.

Modeling of the membranereactor: The mathematical model of a hybrid system of a batch reactor for esterification coupled with pervaporation is based on three aspects: (a) reaction kinetics of esterification, (b) membrane perm selectivity in pervaporation, and (c) mass balance.

The esterification reaction between acrylic acid (A) and ethyl alcohol (B) to produce ethyl acrylate (E) and water (W) can be represented by an elementary reversible reaction having second order. The reaction can be written as follows:

$$A + B \rightleftharpoons E + W$$

The rate expression for second order reversible reaction can be written as:

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A C_B C_C - k_{-1} C_E C_W C_C \quad (1)$$

Where: C_A, C_B, C_E, C_W and C_C represents the concentration (mol/m^3) of acrylic acid, ethanol, ethyl acrylate, water and catalyst respectively. k_1 and k_{-1} are the forward and backward reaction rate constants and t is the reaction time.

The change in concentration of acrylic acid, ethyl alcohol, ester and water can be deduced from the material balance and can be presented as

$$r_i = \frac{-dC_A}{dt} = \frac{-dC_B}{dt} = \frac{dC_E}{dt} = \frac{dC_W}{dt} = k_1 C_A C_B C_C - k_{-1} C_E C_W C_C \quad (2)$$

To consider non-ideal thermodynamic behavior of the reaction mixtures, the chemical activities instead of concentrations can be used in the reaction rate equation:

$$r_i = k_1 C_A \gamma_A C_B \gamma_B C_C - k_{-1} C_E \gamma_E C_W \gamma_W C_C \quad (3)$$

Where, γ_A, γ_B, γ_E and γ_W represent the activity coefficient of acrylic acid, ethanol, ethyl acrylate, water and catalyst respectively.

Equation (3) can be written as

$$-r_i = \frac{d(C_i)}{dt} = k_1 C_C \left(\gamma_A \gamma_B C_A C_B - \frac{\gamma_E \gamma_W C_E C_W}{K_{eq}} \right) \quad (4)$$

Where: the equilibrium constant, K_{eq} can be calculated from the given equation below as

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{\gamma_E C_E \gamma_W C_W}{\gamma_A C_A \gamma_B C_B} \quad (4)$$

For simplifying the mathematical model following assumptions can be made: i. constant selectivity of the PVA membrane, ii. isothermal reaction and pervaporation, iii. constant catalyst activity, and iv. the partial molar volume in a mixture is the same as that of a pure component[3].

By combining pervaporation with the esterification, the change of concentration can be written as follows:

$$\frac{d(C_i)}{dt} = r_i - \frac{S}{V_0} J_i \quad (5)$$

In present work a hydrophilic PVA membrane was used so the partial fluxes of components acrylic acid, ethanol and ethyl acrylate were neglected ($J_{Ethanol} \sim J_{Acid} \sim J_{ester} \sim 0$). The water balance in the PV coupled reactor can be written as:

$$\frac{d(C_W)}{dt} = k_1 C_C \left(\gamma_A \gamma_B C_A C_B - \frac{\gamma_E \gamma_W C_E C_W}{K_{eq}} \right) - \frac{S}{V_0} J_W \quad (6)$$

The relationship between flux and feed water concentration is nonlinear and varies throughout the reaction. Hence the following modified relation can be used [2].

$$J_W = k_{PV1} C_W - k_{PV2} C_W^2 \quad (7)$$

Where: k_{PV1} and k_{PV2} are empirical constants.

Solution methodology: The model equations described in the previous section consists of non-linear differential equations. These ODEs along are solved by an ODE solver, ode45 in Matlab, to get the solutions of concentration profile of reactants and product. The set of kinetic parameters are estimated by a nonlinear optimization technique. The error between the model and experimental data serves as the objective function to be minimized by using combination of optimization routine *fmincon* and Genetic Algorithm from the Matlab Optimization Toolbox. The objective function of the optimization problem is

$$\phi = \sum_{i=1}^{NC} \left(C_i^{cal} - C_i^{\exp} \right)^2 \quad (8)$$

Where: NC is the number of experimental data points for concentration of acrylic acid. The kinetic parameters are obtained by solving the model equation based on the successive guess values of the kinetic parameters.

In order to study the non-ideality associated with the reaction mixture, we need to consider the activity coefficients along with the concentrations to determine the equilibrium constant. Here we considered UNIFAC method to determine the activity coefficients. The coefficients are directly obtained from Aspen Plus software.

Results and discussion

The main parameters which affect the esterification-PV aided process can be classified into three groups: i. Factors affecting only the esterification kinetics: catalyst concentration, and initial molar ratio of methanol to salicylic acid. ii. Factors affecting only the pervaporation kinetics: ratio of effective membrane area to volume of reaction mixture. iii. Factors affecting both the esterification and pervaporation kinetics: temperature.

The esterification reactions were carried out in aninsitu pervaporation membrane reactor with and without pervaporation. The experiments were carried out by changing different process parameters such as temperature (50-70^{o}C), initial mole ratio of acrylic acid to ethanol (1:1-1:3), catalyst concentration (1-3%) and the ratio between the effective membrane area and reaction volume (14.13-25.505 m^{-1}) were carried out. The results are discussed in further section.

For the validation of the developed model the obtained results are compared with experimental data and are presented in Figure-1. The suggested model predicted results were in good agreement with the experimental data. It was observed that the PV intensified the conversion of acrylic acid for the PV coupled esterification reaction than for the esterification without PV. For this experiment the operating conditions are considered as reaction temperature of 50°C, molar ratio of reactants of 1:1 and catalyst loading of 3% (vol). Acrylic acid conversion was increased from its equilibrium value of 46% to 57.2% in 7 hr by using PVA membrane reactor.

The increment in the amount of the any reactant shifts the chemical equilibrium towards the product side. Figure-2 presents the effect of initial mole ratio of acrylic acidto ethanol, MR, on the performance of the pervaporation-esterification coupled reactor. The simulations were carried out under the operating conditions as temperature of 60°C, C_C of 3%, *S/V* of 14.13 m^{-1}. The reaction rate of esterification increases with an increase in amount of ethanol. The conversion increased from 78% to 98.8% with changing molar ratio from 1:1 to 1:3.

In esterification catalyst concentration is also another way to accelerate reaction rate. For the analysis, the catalyst concentration was varied from 1 to 3% of initial volume of the reacting mixture. The simulation results for conversion of acrylic acid during esterification aided PV process over various catalyst loadings were presented in Figure-3. It can be seen that as catalyst concentration increased the conversion of acrylic acid increases due to the availability of more H^+ ions enhancing conversion. A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products[5].

An increase in the temperature enhances the esterification reaction because a higher temperature favors both water removal by pervaporation and the rate of reaction[3]. Effect of temperature on the esterification-PV process of acrylic acid and ethanol was studied for the fixed molar ratio of acrylic acid to ethanol of 1:1 and 3% (vol) of catalyst by varying temperature from 50 to 70°C. Figure-4 shows that increasing in temperature increases the conversion of acrylic acid. The accelerating of the rate of reaction with the increase of the temperature for the forward reaction was faster than the backward process.

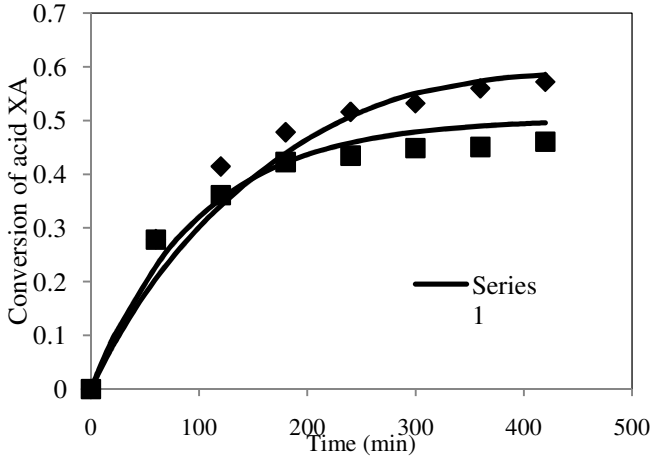

Figure-1: Dependence of conversion on time with and without PV. The solid lines indicate the values predicted by the kinetic model. (T=50°C, C_C=3%, MR=1:1, S/V=14.13m^{-1}).

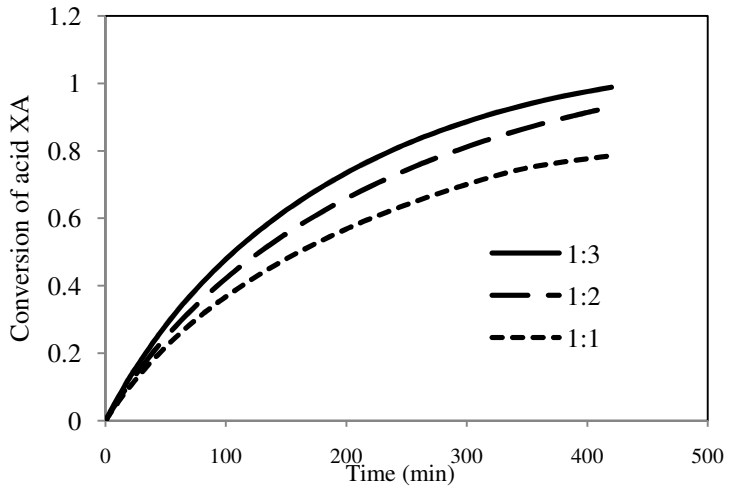

Figure-2: Effect of change in molar ratio on conversion of acrylic acid (T=60°C, C_C=3%, S/V=14.13m^{-1}).

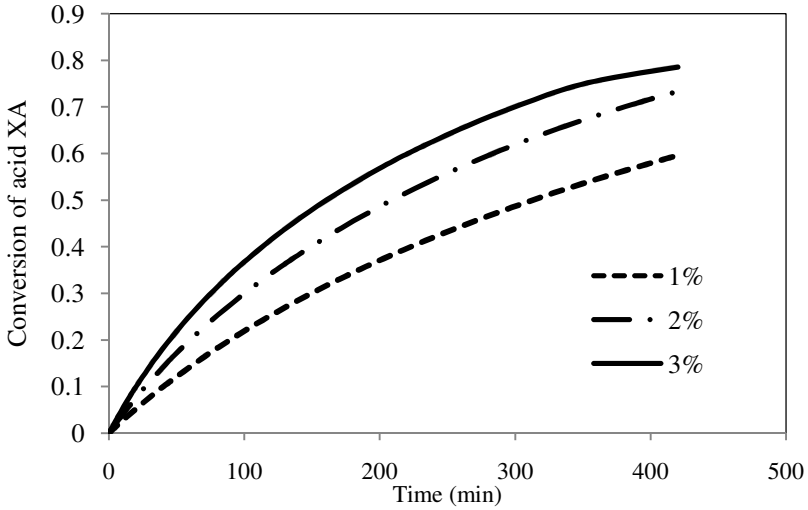

Figure-3: Effect of change in concentration of catalyst on conversion of acrylic acid (T=60°C, MR=1:1, S/V=14.13m^{-1}).

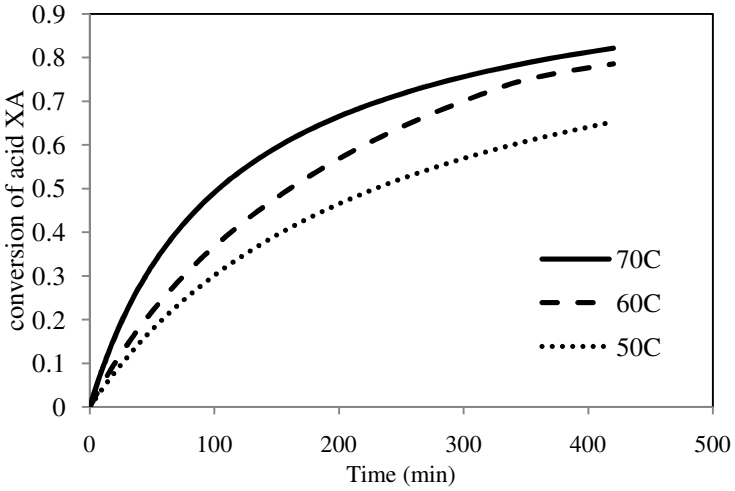

Figure-4: Effect of the reaction temperature on the conversion of the PV-aided esterification of acrylic acid and ethanol (MR= 1:1, C_C=3%, S/V=14.13m^{-1}).

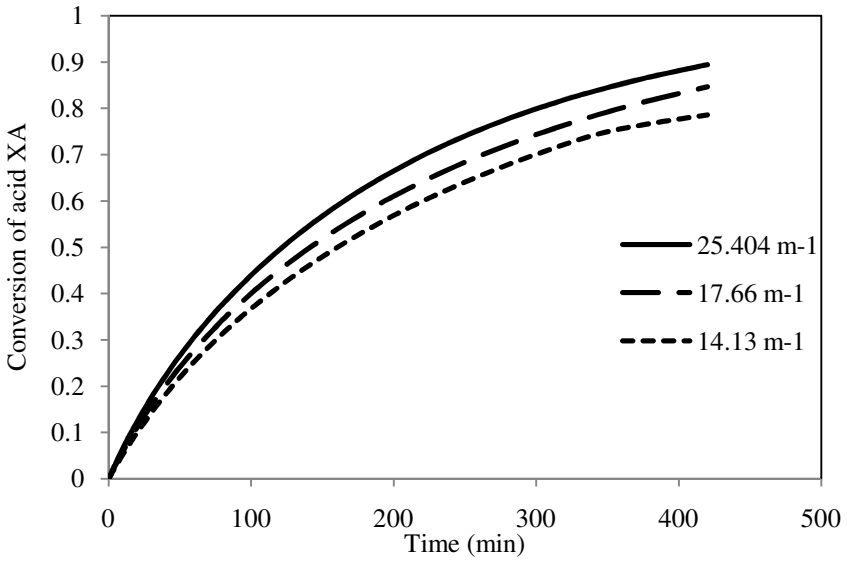

Figure-5: Effect of the ratio between the membrane area and reaction volume on the conversion of the PV coupled esterification of acrylic acid and ethanol (T=60°C, MR= 1:1, C_C=3%).

The larger membrane area could remove the byproduct water sufficiently, and thus the esterification was enhanced. Simulations were carried out with changing the ratio of membrane area to initial reaction volume as 14.13, 17.66 and 25.404 m^{-1} and the obtained results were presented in Figure-5. The values for the other operating parameters were the following: molar ratio of initial reactant, 1, catalyst loading, 3%, and reaction temperature 60°C. As increasing *S/V*, the water removal rate will be more and hence leading to enhanced conversion.

Conclusion

Conversion of reversible reaction is limited due to occurrence of chemical equilibrium. Hence these reactions are integrated with additional process to shift the chemical equilibrium thereby intensifying the conversion. In this work, a series of esterification reaction of acrylic acid and ethanol coupled with pervaporation were conducted at different operating temperature, catalyst concentration, initial composition, etc. Moreover, different ratios of the membrane area to reacting mixture volume were also studied. It was observed that these parameters have significant effect on the performance of the esterification–pervaporation integrated reactor. Pervaporation and reaction rate both can be increased with increase in operating temperature. The ester rate formation increases significantly with increase in catalyst concentration. When the *A*/*V*o ratio increases higher ester conversions were obtained.

Nomenclature: C_A= concentration of acrylic acid (mol/m^3), C_B= concentration of ethyl alcohol (mol/m^3), C_E= concentration of ethyl acrylate (mol/m^3), C_W= concentration of water (mol/m^3), C_C= concentration of catalyst (mol/m^3), γ_A= activity coefficient of acrylic acid, γ_B= activity coefficient of ethanol, γ_E= activity coefficient of ethyl acrylate, γ_W= activity coefficient of water, k_1 = forward reaction rate constant($(m^3)^2/kmol^2.min$), k_{-1} = backward reaction rate constant ($(m^3)^2/kmol^2.min$), t = reaction time (min), T = reaction temperature (°C), K_{eq} = equilibrium constant, S = membrane area (m^2), J = total flux ($gm/m^2.min$), R = rate constant (8.314 J/mol K), V = volume of initial reaction mixture.

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