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Intensification of Esterification of Acetic Acid with Ethanol by Pervaporation Reactor: Modeling and Simulation

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Abstract. Pervaporation has appeared as an energy efficient and highly selective separation process in the recent past for the reaction and separation. Conversion and productivity can be intensified by coupling the reaction with pervaporation, i.e. Pervaporation reactor. In the present study, modeling and simulation of esterification reaction of acetic acid and ethanol coupled with pervaporation were carried out. The model was verified by comparison with available experimental data and a good agreement was found. Effects of change of temperature and initial reactant ratio on the conversion rate were also studied and general trend was postulated.

Keywords: Pervaporation reactor, Esterification, Modeling, Simulation

1. Introduction

To develop the new process designs and rearrangement of present process designs are of increasing importance to industry. Pervaporation has become a promising technology and potentially useful in applications like dehydration, removal or recovery of organic solutions from aqueous in recent years. Pervaporation as a hybrid separation process, i.e., in combination with another separation technology is often applied these days, with pervaporation-distillation systems and pervaporation membrane reactor being prominent industrial [1]. The use of membranes in the chemical industries has received considerable attention. Since membranes permit selective permeation, the conversion of thermodynamically limited reactions can be enhanced. By applying a hybrid process, such as esterification -pervaporation, It is possible to shift the equilibrium towards higher reaction yields and considerable savings can also be made in pervaporation reactor [2-3].Ethyl acetate is an important raw material finding many applications in chemical industry[4]. In the literature several studies of pervaporation coupled esterification based on water removal by using various hydrophilic membranes, while ethyl acetate removal was not much investigated [5], discussion on the design issue of pervaporation reactors for esterification[2], modeling of pervaporation reactor for esterification of acetic acid with *n*-butanol, benzyl alcohol acetylation have been reported.

In the present paper, the generalized mathematical model is being formulated and simulated for the esterification reaction of acetic acid and ethanol using hydrophobic membrane. The model was validated using available experimental data. The effect of various process parameters temperature, reactant ratio, etc has been studied.

2. Model Formulation

2.1. Assumptions

The esterification reaction between the acetic acid and ethanol follows a first order kinetics with respect to each reactant but overall follows second order reaction kinetics. The fluxes of all other elements except

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ethyl acetate present at any time are assumed to be zero. The polydimethylsiloxane membrane used allows only ethyl acetate to pass through it. All the other elements have negligible fluxes. The permeability coefficients, k_{pv1} and k_{pv2}, of the membrane are assumed to be constant with respect to the ester concentrations. The permeability coefficients depend only on the type of membrane and other constituents of the reaction mixture. The variation of the volume of the reactor is assumed to be negligible.

2.2. Governing Equations

The governing equations for the esterification of acetic acid and ethanol are given below [7, 8].

Esterification reaction of acetic acid and ethanol to give ethyl acetate and water can be schematically represented by:

$$A + B \leftrightarrow R + W$$

Acetic acid Ethanol Ethyl acetate Water

The pervaporation reactor is in semi-batch mode as ethyl acetate is continuously removed from the reaction mixture using pervaporation.

The rate of ethyl acetate formation by esterification reaction can be written as:

$$r_R = k_1 C_A C_B - k_1 C_R C_W$$

The variation of volume of the reactor is neglected. Hence the ethyl acetate balance in pervaporation reactor can be:

$$\frac{dC_R}{dt} = (k_1 C_A C_B - k_2 C_R C_W) - \frac{S}{V} J_R$$

The relation between flux and ethyl acetate concentration is nonlinear and not constant throughout the reaction, the following relation can be used.

$$J_R = k_{pv_1} C_R - k_{pv_2} C_R^2$$

Normally, the concentration of water, acetic acid and ethanol in permeate were negligible as compared to ethyl acetate. Hence the material balance for the water, acetic acid and ethanol can be:

$$\frac{dC_W}{dt} = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = (k_1 C_A C_B - k_1 C_R C_W)$$

Above equation represents the homogeneous esterification reaction rate equation without catalyst and the reaction with catalyst can be written as:

$$A + B + C \leftrightarrow R + W + C$$

The reaction also occurs without the catalyst and the rate of the reaction with catalyst is directly proportional to the catalyst concentration. Hence, the overall rate of disappearance of component B can be given by:

$$-\frac{dC_B}{dt} = k_{obs}(C_A C_B - \frac{C_R C_W}{K})$$

The value of k_{obs} depends on the catalyst concentration and reaction temperature. Also the balance equation for ester becomes,

$$\frac{dC_R}{dt} = k_{obs}\left(C_A C_B - \frac{C_R C_W}{K}\right) - \frac{S}{V} J_R$$

The conversion of ethanol can be given by:

$$X_B = \frac{C_{B_O} - C_B}{C_{B_O}}$$

The values of rate constants were taken from available thermodynamic and experimental data [5, 9]

3. Results and Discussion

3.1. Model Verification

The Comparison of experimental and model results for acetic acid conversion are shown in Fig.1 to 6. Model was verified by comparing modeled results with available experimental data of Hasanoglu et al. [5] for the conditions of temperature T= 50 ^{o}C, 60 ^{o}C and 70^{o}C, and initial reactant ratios of M= 1 and 1.5.

Fig.1 to 6 shows that conversions increase with temperature.

Table 1: Values and range of the various parameters used.

Parameter	**Notation and unit**	**Value/range**
Initial mole ratio of acetic acid and ethanol	$M_O = \frac{C_{A_O}}{C_{B_O}}$	1-1.5
Ratio of the effective membrane area over the volume of reacting mixture	$\frac{S}{V}(m^2/m^3)$	1-15
Equilibrium constant for temperature range 50-70 ^{O}C	$K = \frac{k_1}{k_2}$	2.41-5.14
Pervaporation constants	k_{pv_1} k_{pv_2}	0.0004 10^{-7}
Reaction Time	t(min)	400
Temperature	T(^{o}C)	50 –70
Catalyst concentration	Cc(g)	1-5

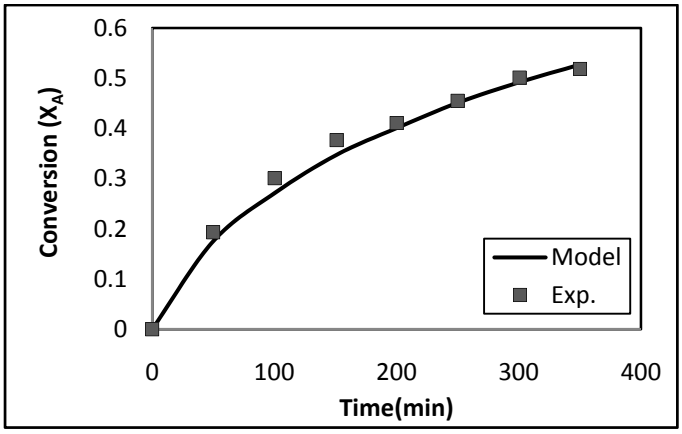

Fig. 1: Comparison of experimental and model results for acetic acid conversion (M = 1, T = 50^{o}C)

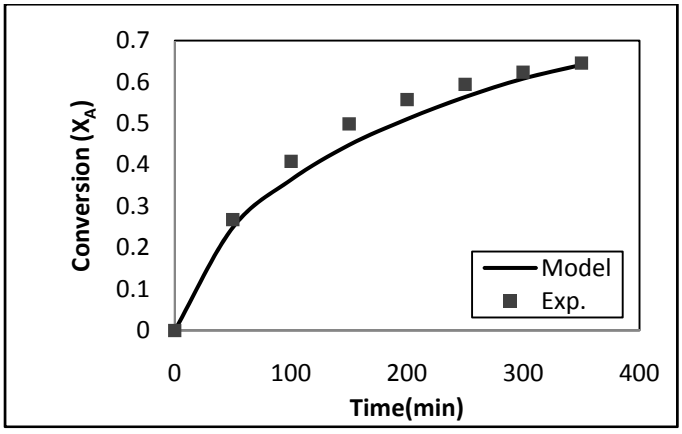

Fig. 2: Comparison of experimental and model results for acetic acid conversion (M = 1, T = 60^{o}C)

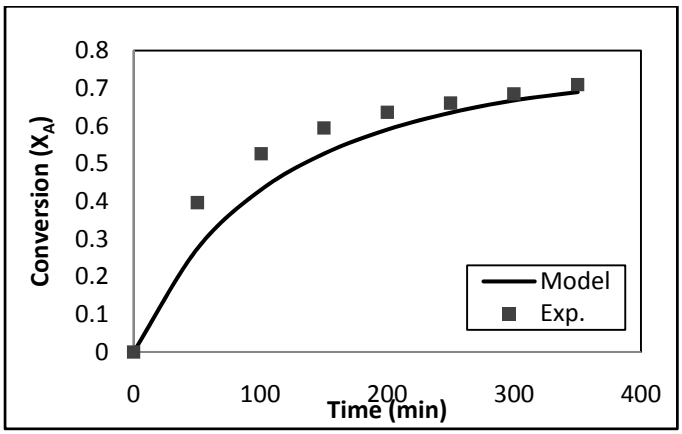

Fig. 3: Comparison of experimental and model results for acetic acid conversion (M = 1, T = 70°C)

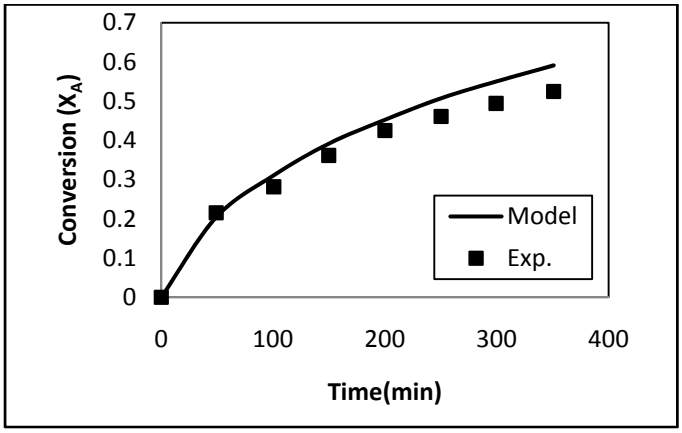

Fig. 4: Comparison of experimental and model results for acetic acid conversion (M = 1.5, T = 50°C)

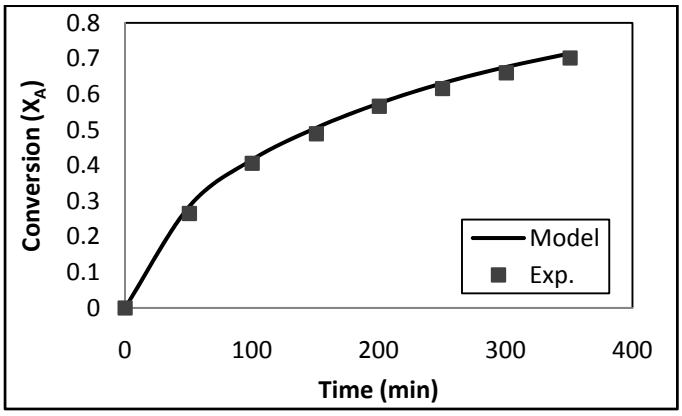

Fig. 5: Comparison of experimental and model results for acetic acid conversion (M = 1.5, T = 60°C)

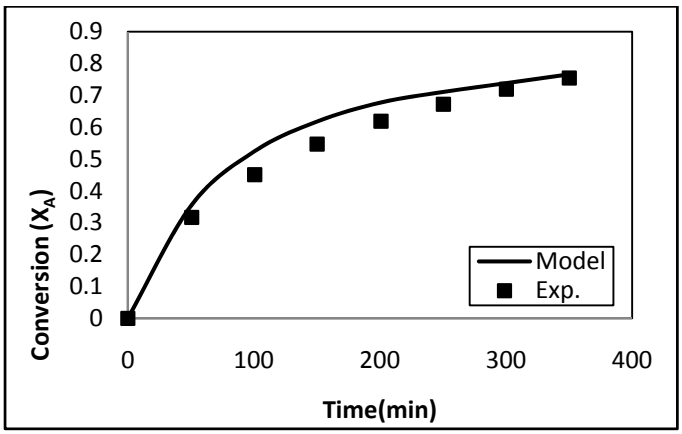

Fig. 6: Comparison of experimental and model results for acetic acid conversion (M = 1.5, T = 70°C)

4. Conclusion

The model equations for pervaporation reaction were developed based on the available reaction kinetics and pervaporation data for the esterification of acetic acid with ethanol. The simulation results were compared with the experimental data and good agreement between the values was found. The Conversion of acetic acid was enhanced by the increment of temperature and initial reactant ratio. The model presented can also be used for the other esterification reactions.

5. Nomenclature

C_A : Concentration of acetic acid in reactor (kmol/m^3)
C_{A0} : Initial concentration of acetic acid in reactor (kmol/m^3)
C_B : Concentration of ethanol in reactor (kmol/m^3)
C_C : Concentration of catalyst in reactor (kmol/m^3)
C_R : Concentration of ethyl acetate in reactor (kmol/m^3)
C_W : Concentration of water in reactor (kmol/m^3)
J_R : Ethyl acetate flux through membrane (kmol/m^{2}min)
k_1 : Forward reaction rate constant (m^3/kmol min)
k_2 : Backward reaction rate constant (m^3/kmol min)
k_{PV1} : Empirical constant in equation
k_{PV2} : Empirical constant in equation
k_{obs} : Observed kinetic constant (m^3/kmol min)
K : Equilibrium constant
r_W : Rate of formation of water by reaction (kmol/m^{3}min)
S : Area of membrane (m^2)
t : Reaction time (min)
V : Volume of reaction mixture (m^3)
X_B : Conversion of ethanol

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