

Modeling of a Batch Catalytic Reactive Distillation Process Using a Multi-Scale Approach of Pore Diffusion and Non-Equilibrium Rate Based Model

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ABSTRACT: Reactive distillation is carried out to produce methyl acetate from acetic acid and methanol using Indion180 as a solid ion-exchange resin catalyst in a simple distillation apparatus. Unlike the reboiler-column combination, a simple distillation apparatus is used to conduct reactive distillation where the vapors are condensed and collected as the catalytic reaction is proceeding in the reboiler flask. The aim is to quantitatively measure the distillate's purity in terms of the methyl acetate's mole fraction in it. The composition of instantaneous distillate, cumulative distillate, and of the reactant mixture in the reboiler is measured continuously. The temperature in the reboiler as well as the electrical energy supplied to it is also measured as a function of time. A non-equilibrium evaporation rate-based model is proposed to predict the kinetics of the distillate and reboiler composition as well as the temperature. The reaction rate of the solid-catalyzed esterification process is modeled as per the pore diffusion model for the heterogeneous parts as well as homogeneous reactions. No previous studies are available on this concept of reaction kinetics in combination with the evaporation rate for reactive distillation. The experiment was conducted in simple distillation mode with nearly a constant heat input rate and developed a mathematical model for the obtained distillate composition. The overall model of reactive distillation is validated with the help of very few adjustable parameters found by minimizing the error between experimental data and model prediction.

KEYWORDS: Kinetics; Distillation; Multiscale; Diffusion; Batch; Mathematical Modeling.

INTRODUCTION

The chosen system of study is methyl acetate's production by catalytic esterification. Methyl acetate, a widely used chemical, is commonly produced from a liquid-state reaction between acetic acid and methanol. The products are methyl acetate and water as shown in the following equation.



Without a catalyst, the above liquid state reaction is very slow [1]. It is found from our studies also that a conversion

of only 10% is reached for a large reaction time of around 7-8 hours even at an elevated temperature of 60 °C. However, it is found that the reaction rate increases several times due to the addition of a homogeneous catalyst such as sulphuric acid or even higher by the addition of a solid ion-exchange resin catalyst such as Amberlyst catalyst [1-6]. For example, a conversion of 70% is achieved in just 3 hours by utilizing Indian 180 at the temperature of 60 °C [7].

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Although the reaction rate increases, it is a reversible reaction and therefore the conversion reaches a constant value after some reaction time owing to equilibrium. This reaction time to reach equilibrium in a batch mode depends substantially on the catalyst loading and temperature of the reaction mixture. This aspect is well predicted by our earlier proposed model [7].

Interestingly the boiling point of the product methyl acetate at normal pressure is 56 °C whereas the boiling point of other product water is 100 °C and that of the reactants are 118°C for acetic acid and 65°C for the methanol. Hence the reactants-products mixture could be evaporated slowly and the vapors can be condensed to obtain a distillate that is rich in methyl acetate. The reason is that the boiling point of the methyl acetate is the least among all the four components of reactants and products. It may be noted that there may be lower boiling azeotropes but they do not form in the present reactive distillation process due to perturbation of composition owing to reaction. Methanol and methyl acetate mixture form a lower boiling azeotrope. The lower boiling azeotropes have a composition different from the reboiler composition throughout the reactive distillation. Such a system is an ideal one for studying reactive distillation where distillation is carried out simultaneously as the reaction proceeds. This process of reactive distillation would greatly reduce the thermal energy requirement per unit quantity of product produced compared to the process of reaction followed by distillation. If we could model this challenging kinetics of reactive distillation then one could design a highly energy-efficient reactive distillation column.

A number of previous studies represent the hurdles experienced and uncertainties involved in modeling reactive distillation either in batch, semi-batch, or continuous column [8-13]. There are recent studies on evaporation rate-based models and reactive distillation in general [14-18]. The objective of the present work is to explore and develop a non-equilibrium evaporation rate-based model along with pore diffusion reaction kinetics to predict the dynamics obtained during reactive distillation carried out in a simple distillation apparatus. It is a novel experiment in the aspect of energy measurement as well as a mathematical model that predicts directly the dynamics of the distillate's composition for a given mode of heat supply.

EXPERIMENTAL SECTION

Chemicals

The reactants used are methanol with a purity of 99%

w/w and acetic acid with purity of 99.95% w/w supplied by SD Fine Chemicals Ltd., Mumbai, India.

Catalyst

The solid acid catalyst used for the heterogeneous esterification reaction is Indion 180 which is supplied by Ion-Exchange India Limited, Mumbai, India. Indion 180 has cross-linked three-dimensional structures of polymeric material obtained by sulfonation of a copolymer of polystyrene and divinyl benzene (DVB). It is in the form of opaque and dark gray-colored porous solid spherical beads of approximately 725 µm diameter. The resins used in this study were dried for two hours in an air oven at a temperature 90 °C to remove the moisture content.

Analysis by gas chromatography

The distillate and reboiler samples were analyzed using a gas chromatography instrument (GC-2014 ATF, Shimadzu, Japan.). It is equipped with a thermal conductivity detector (TCD). A packed column of Porapak-Q (2 m length and 3.17 mm id) was used to analyze the samples for composition. High-purity hydrogen gas was used as a carrier gas at a flow rate of 30.0 ml/min. The oven temperature was programmed to pre-heat it to 100 °C for 1 min and then raised to 170 °C at a ramp rate of 10 °C /min and a hold time of 4 min. The detector temperature was maintained at 200 °C. All the samples were injected by using a 10-microliter capacity syringe into the column and were analyzed by the GC. Constant sample volumes were taken for analysis. In the experimental analysis, a sample volume of 1 microliter is injected into the column to avoid the variation of the cumulative peak area in the chromatogram. It was found that the plot of GC area percentage versus mole percentage gives a good linear correlation. The composition of standard samples was correlated with both weight and mole%. Out of the two, the mole% correlation seemed to have a higher R-square value although both fit as a linear curve. Hence, such a correlation is used to quantify the mole fraction composition in the distillate and reboiler samples.

Experimental procedure

The schematic diagram of a simple distillation apparatus used for conducting the experiments is shown in Fig. 1. As per Fig.1, The specifications of the system are Heater – 2kW, Reboiler- 1L, Condenser type- Horizontal and Temperature sensor-PT 100. It consists of a round

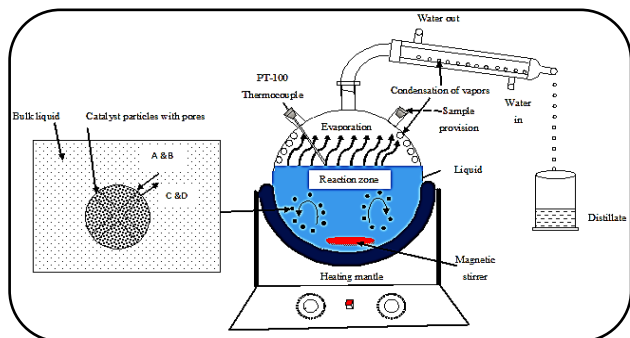


Fig. 1: Schematic diagram of the multi-scale phenomena of homogeneous and heterogeneous reaction occurring in a solid catalyzed batch reactive distillation apparatus.

bottom flask placed in a rota mantle with facility for magnetic stirring, electrical heating and temperature measurement by PT-100 thermocouple connected to a digital display with 0.1 °C resolution. The electrical supply to the rota mantle is routed through an ammeter in order to measure the current supplied. This measurement of current versus time would help in estimating the electrical energy supplied to the reboiler flask or the reaction mixture. The voltage applied is constant and current passing through the heating mantle is measured frequently. According to Ohm's law the product of voltage and current gives the input electrical power which is numerically integrated with respect to time to obtain a cumulative energy supplied as a function of time. It is done so, in order to fit a smooth continuous curve for energy supplied and when it is differentiated with respect time, it gives power supplied also as a continuous function. Thus the minute step changes caused by manual knob rotation are smoothed out for modeling purpose. Fig. 2 depicts the cumulative energy supplied versus time. There is a horizontal condenser connected to the top port of the reboiler flask. The coolant used in the condenser is water at room temperature (25 °C). A collection vessel is provided for collecting the distillate. Experiment begins by taking equal number of moles (2.5 gram moles each) of acetic acid and methanol and charging them to the round bottom flask making it a volume of 245 ml. Immediately, catalyst particles were added to the reactant mixture with a pre-calculated catalyst loading of 0.025 g/cc of reactant mixture. The glass flask or the reboiler is heated by supplying heat through an electric heater placed in the rota mantle, which surrounds the flask up to half way of its volume. The liquid level in the flask is found to be below the height of the electrical heating coil. Hence there would be uniform heating. Simultaneously

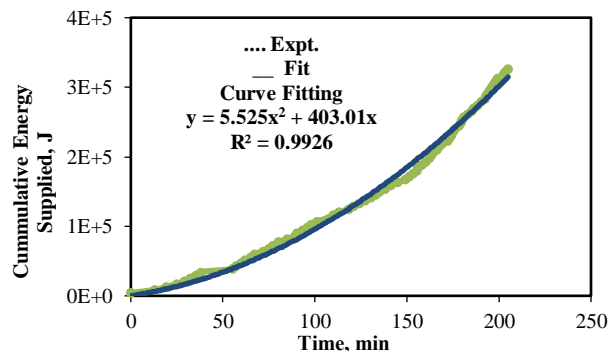


Fig. 2: Electrical energy supplied to the reboiler flask as a function of time.

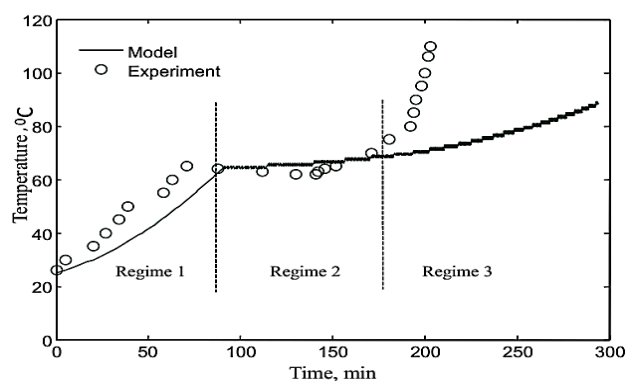


Fig. 3: Temperature in reboiler/heating flask versus time: comparison of experimental and predicted dynamics

the magnetic stirrer is switched on to maintain a high rpm. This feature ensures uniform heating and availability of catalyst to the reactant mixture. The initial electrical power supplied was calculated to be 400 W. It is gradually increased with time manually by turning a knob on the rota mantle.

The cumulative electrical energy supplied as a function of time is calculated from the time integral of product of voltage supplied, which is 220 V and current measured by the ammeter. It is plotted as shown in Fig. 2. A trend line is fitted to this cumulative energy supplied curve and it is found to be of quadratic in nature as given below in Eq. (2).

$$E_{\text{Elec}} = 400t + 5.525t^2 \quad \text{Joules} \quad (2)$$

where t is in min. The temperature recorded as a function of time in the reboiler solution is plotted in Fig. 3. The purpose of varying the thermal energy supplied to the reaction mixture or the solution is to obtain the drop by drop condensation in distillate so that the lighter component, which is methyl acetate, would be obtained in a maximum proportion. The temperature variation as shown in Fig. 3, shows distinctly three regimes of

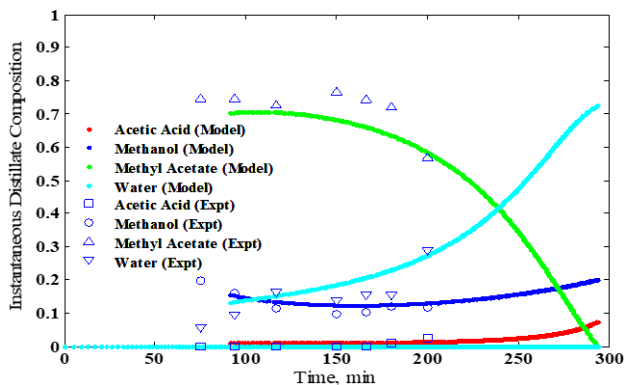


Fig. 4: Composition in terms of mole fraction of instantaneous distillate versus time: comparison of experimental data and model predicted dynamics.

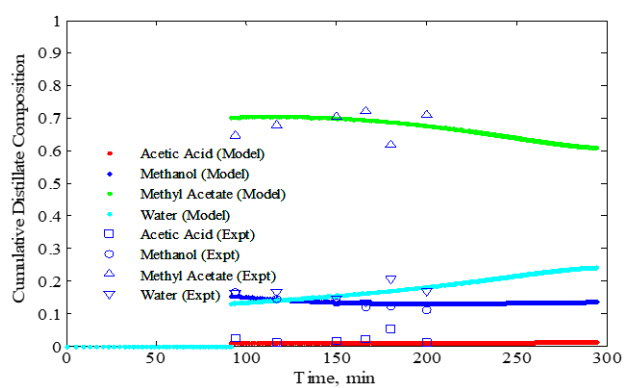


Fig. 5: Composition in terms of mole fraction of cumulative distillate versus time: comparison of experimental and predicted dynamics.

the thermal dependence of reactive distillation kinetics. During regime 1, no distillate was obtained. This is because the supplied heat is utilized in increasing the sensible heat of the solution. Simultaneously there would be an increase in temperature as well as reaction taking place in the reaction mixture. During regime 2, the temperature of the reactant mixture in the reboiler flask remained nearly constant, and drop-by-drop condensation was observed in the distillate. In the regime 3, a steep increase in temperature was noticed. The condensation rate was also faster than the drop by drop and therefore it could be that excess heat than required for differential distillation could have been supplied. Hence a deviation could be expected between the predicted and experimental temperature variation during regime 3. The prediction methodology will be delineated in the next section on mathematical modeling.

Samples were taken from the instantaneous distillate drops, the cumulative distillate and the reboiler. These samples

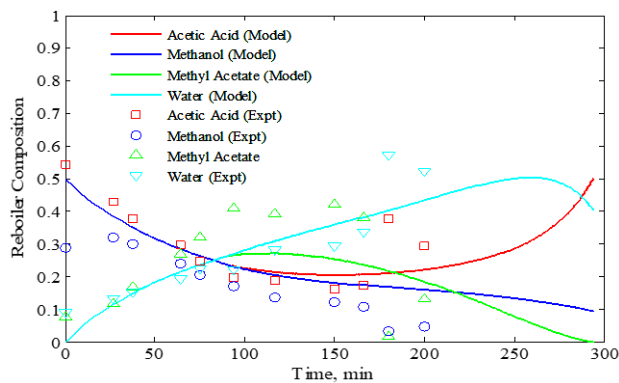


Fig. 6: Composition of reboiler/heating flask versus time: comparison of experimental and predicted dynamics.

were analyzed using GC to measure the composition by the procedure as mentioned in analysis by gas chromatography the section. This data along with the cumulative volume of distillate versus time are presented in Fig. 4 to Fig. 7 later comparing with the model predictions as well.

MATHEMATICAL MODELING

The following assumptions are made in order to develop a dynamic model to predict the reaction rate in the reboiler as well as that of distillate composition.

- Only the reaction in Eq. (1) takes place in the reactant mixture of reboiler and no side reactions take place. This aspect is supported by the GC analysis of all samples which showed only four peaks corresponding to the two reactants and two products.

- The reaction rate is modeled as two parts: one is the homogeneous reaction rate in bulk fluid and the second is the heterogeneous reaction occurring inside the pores of the catalyst [7]. The equation in the pseudo-homogeneous form is given as

$$dC_A/dt = -k_f[C_A^2 - (1 - C_A/C_{A0})^2/K_c]$$

- The rate constants, diffusion constants and other properties are adopted from our earlier publication [7].

- The vapor pressures exerted by each component are calculated using Raoult's law assuming an ideal solution. The saturation pressure of each component is calculated using the Antoine equations.

- In the model, the vapors are allowed to condense and form distillate only when the total vapor pressure of the solution in the reboiler exceeds the certain threshold value.

- For total vapor pressure below the threshold value, it is assumed that the vapors re-condense back to the reboiler

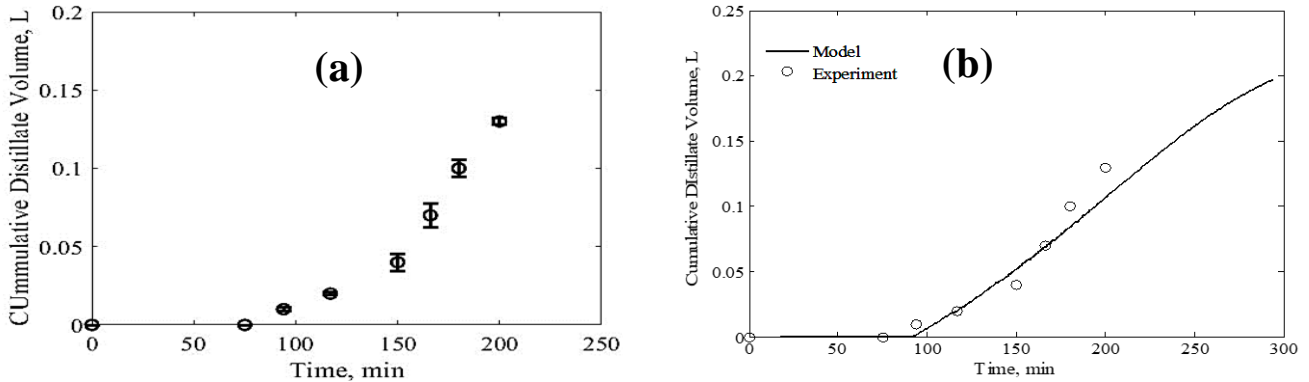


Fig. 7: Volume of cumulative distillate collected versus time (a) experimental data with error bar from two experiments. (b) comparison of experimental and predicted dynamics.

but the reboiler solution loses the latent heat due to evaporation process.

- Heat is supplied to the reboiler solution only when total vapor pressure is less than the threshold value. As the total vapor crosses the threshold value, high evaporation and condensation occur which does not ensure drop by drop condensation. Hence, by withdrawing the heat supply, the solution cools down a little and the total vapor pressure drops below the threshold value. Again, heat is supplied. This scheme is included in the algorithm of model ensures that the total vapor pressure hovers around a threshold value.

- The evaporation rate of every component is based on Himus type of equation [19] with an assumption that the concentrations of component vapors in the bulk vapor phase inside condenser are zero as immediate condensation occurs. It implies that the remaining portion of the gas phase in reboiler and condenser consists of air. The threshold vapor pressure of the solution is proposed as an adjustable parameter in the model only and it is not an experimentally measured variable. The gas phase is assumed to be occupied by the vapors of the four components and air. The gas phase pressure is one atmosphere but fraction of it is occupied by air. This is because the vapors are condensed in condenser as soon as they enter it. As per the model, the threshold pressure is defined as the value which when exceeded by the sum total of the products of mole fractions and saturation vapour pressures of all the components in gas phase results in condensation and distillate is collected. This is implemented in the numerical simulation of the proposed model.

- It is assumed that the evaporation rate constant is same whether the component evaporates from a pure liquid or from the reboiler mixture. Only methyl acetate is

assumed to have a higher evaporation rate constant since the mixture in reboiler is at a higher temperature than methyl acetate's boiling point.

The mathematical representation of the process is as follows. Let n_i be the number of gram moles of the component i in the reboiler flask at a given time t . Since there are four components it is assigned that $i=1$ for the acetic acid, $i=2$ for methanol, $i=3$ for methyl acetate and $i=4$ for water. The rate of homogeneous reaction of each of the reactant component is given as

$$\left. \frac{dn_i}{dt} \right|_{\text{rxn}_h} = -\frac{k_f}{V_t} \left[n_1 n_2 - \frac{n_3 n_4}{K_e} \right] \quad (3)$$

Here t is the time, V_t is the volume of reactant mixture in liters at time t , k_f is forward reaction rate constant, $l/\text{mol}\cdot\text{min}$ and K_e the equilibrium constant of the reaction which is a dimensionless value. The negative sign on RHS of Eq. (3) will be positive while evaluating the homogeneous reaction rate for the product components. The reaction rate constant k_f is given by Arrhenius equation as below [7].

$$k_f = k_{f0} \exp\left(-\frac{E}{R(T+273)}\right) \quad (4a)$$

$$K_e = \frac{X_{Ae}^2}{(1-X_{Ae})^2} \quad (4b)$$

Where X_{Ae} is equilibrium conversion of acetic acid and T is in $^{\circ}\text{C}$. The values of the parameters k_{f0} and E are $k_{f0} = 4536 l/\text{mol}\cdot\text{min}$, $E = 43507 J/\text{mol}$ in Eq.(4a) [7]. The value of K_e is nearly obtained as 4.95 using Eq. (4b) for a wide range of temperatures $25-70^{\circ}\text{C}$. One reason for constancy of the equilibrium constant is because the esterification reaction is reported as mildly endothermic as well as mildly exothermic in some literature [2, 5].

The heterogeneous reaction rate due to reaction occurring inside the pores of the catalyst is adopted from literature [7]. Since the boiling point of methanol is less compared to that of acetic acid, it is assumed that methanol is limiting reactant in the perspective of the reaction occurring inside the porous catalyst at later stages of reactive distillation as more of methanol would evaporate than acetic acid.

The reaction rate of methanol or the consumption rate of the methanol in the reboiler solution due to pore diffusion effect inside catalyst particles [7] is given by

$$\left. \frac{dn_2}{dt} \right|_{\text{rxn}_p} = N_p 4\pi R_p^2 J_2 \quad (5)$$

Where N_p is the number of catalyst particles, R_p is the average radius of the catalyst particle and J_2 is the inward surface molar flux into the catalyst particle. Here J_2 is given as

$$J_2 = D_{2m} \left. \frac{\partial C_2}{\partial r} \right|_{r=R_p} \quad (6)$$

Where D_{2m} is the effective diffusivity of methanol in the pores which takes into account the porosity of catalyst particle, $C_2(r)$ is concentration profile of methanol in each of the catalyst particle and r is the radial position measured from the centre of a catalyst particle. The diffusion-reaction equation is solved for inside the catalyst particle at every instance of time assuming a quasi-steady state and the details may be found in our earlier publication [7].

The molar reaction rates of other three components due to heterogeneous reaction are calculated in stoichiometric ratio to that of methanol as per Eq. (1). Hence we have

$$\left. \frac{dn_1}{dt} \right|_{\text{rxn}_p} = \left. \frac{dn_2}{dt} \right|_{\text{rxn}_p} = - \left. \frac{dn_3}{dt} \right|_{\text{rxn}_p} = - \left. \frac{dn_4}{dt} \right|_{\text{rxn}_p} \quad (7)$$

The number of particles N_p is related to the catalyst loading W_C as described in reference [7]. Since the volume of the reactant solution decreases with time the effective catalyst loading increases with time according to

$$W_C = W_{C0} \frac{V_0}{V_t} \quad (8)$$

where W_{C0} is the initial catalyst loading, V_0 is the initial volume of the reactant mixture and V_t is the instantaneous volume of the reactant mixture remaining in the reboiler. The volume of the solution in the reboiler is calculated as

$$V_t = \sum_i^4 \frac{n_i MW_i}{\rho_i} \quad (9)$$

Where MW_i is the molecular weight of the component i , ρ_i is the liquid density of the respective component i .

The evaporation rate of each of the component is calculated as

$$\left. \frac{dn_i}{dt} \right|_{\text{evap}} = -A_c k_i (x_i p_i^{\text{sat}} - y_i P_{\text{atm}}) \quad (10)$$

Where x_i is the mole fraction of a component in liquid phase, P_{atm} is the atmospheric pressure and y_i in bulk gas phase which is assumed to be zero. This is a popularly used non-equilibrium rate based model for the evaporation rate in a batch distillation [3]. This is similar to Himus type of expression used for calculating pure water evaporation [19]. Here, A_c is the surface area of the evaporating liquid. It is assumed to vary with time starting with 0.0113 m^2 as the liquid evaporates from the partially filled round bottom flask. Based on the volume of liquid V_t and radius of the round bottom flask, a formula for calculating the instantaneous surface area based on geometry is incorporated into the computer program. The evaporation rate constants k_i (mol/min m^2 atm) are determined experimentally based on pure component evaporation at around 65°C since most of the distillation or the condensation of components seems to occur around this temperature as observed from the temperature data in Fig. 3. The evaporation rate constants k_i (mol/min m^2 atm) were estimated based on pure component evaporation. Pure liquid was taken in a 100 ml beaker of diameter 6.5 cm and placed on a heater so that the temperature reaches 65°C which is the plateau temperature observed during the reactive distillation. At 65°C , the beaker was placed on a weighing balance and the time required for loss of 1 g of liquid was measured. These observations were used to calculate the evaporation rate constants k_i from $N_{ei} = k_i (P_i^{\text{sat}} - P_{i,\text{bulk}})$. Here, N_{ei} is the evaporation rate per unit surface area mol/min m^2 , $P_{i,\text{bulk}}$ in air is assumed zero and P_i^{sat} is the saturation vapor pressure of that component in atm units. Thus k_i were estimated experimentally. The evaporation rate constants are found to be $k_1=3.07$, $k_2=6.69$, $k_3=2.97$ and $k_4=20.73$ in units of mol/min- m^2 -atm.

In order to predict distillation rate accurately it is assumed that k_3 the evaporation rate constant of methyl acetate is an adjustable parameter which is higher than its pure component value. The justification for such assumption is that the methyl acetate boiling point is 56°C where as the bubble point of the mixture seems to be 65°C .

Table 1. Antoine constants.

Component	A	B	C
Acetic acid	22.1	-3654.62	-45.39
Methanol	23.5	-3643.3	-33.43
Methyl acetate	21.15	-2662.78	-53.46
Water	23.2256	-3835.18	-45.343

Hence there is evaporation of methyl acetate occurring at a super heated condition and it needs to be modeled accordingly with an adjustable evaporation rate constant

Generally, the total vapor pressure of the reboiler solution is equal to one atmosphere as in a column distillation where only the liquid components are present in the vapor. In the present simple distillation, the vapors are condensed as soon as they enter the horizontal condenser. Since there is condensation of the vapor, the gas phase in the condenser and the gas phase in reboiler contain air in addition to the vapors of the four components. Therefore, it is assumed that condensation of vapors occurs only when the total vapor pressure P_t exceeds the certain threshold value of P_0 . This P_0 could be anywhere between 0 to 1 atmospheres which will be optimized statistically so that the dynamics of distillate generation matches with the experimental data.

In general, the total pressure exerted by the vapor P_t is calculated as below by applying Raoult's law.

$$P_t = \sum_{i=1}^4 x_i p_i^{\text{sat}} \quad (11)$$

The mole fractions x_i are calculated from instantaneous values as $n_i/\Sigma n_i$. The saturation vapor pressure of each component is calculated using Antoine equation as given below [15].

$$\ln(p_i^{\text{sat}}) = A + \frac{B}{C + T} \quad (12)$$

The constants A, B and C are given in Table 1.

Here, T is the instantaneous temperature of the reboiler solution. The condensation will occur based on the temperature of the coolant fluid. In the present experiment the coolant fluid is water at a temperature of 25 °C. Hence condensation may occur when the total vapor pressure of reboiler solution exceeds certain threshold value and it need not be one atmospheric pressure as explained earlier.

Another parameter which needs to be optimized is the efficiency factor for conversion of the electrical to

thermal energy of the heating mantle. Generally, its value could be anywhere between 0 to 1. This factor η_e is also obtained statistically by reducing the error between model predicted dynamics and experimental data of cumulative distillate volume versus time and distillate concentration of methyl acetate versus time.

The composition of each component in the reboiler is updated as below provided the total vapor pressure P_t is greater than the threshold value of P_0 .

$$\left. \frac{dn_i}{dt} \right|_{\text{total}} = \left. \frac{dn_i}{dt} \right|_{\text{rxn}_h} + \left. \frac{dn_i}{dt} \right|_{\text{rxn}_p} + \left. \frac{dn_i}{dt} \right|_{\text{evap}} \quad (13)$$

Here, all the contributions of homogeneous reaction, heterogeneous reaction inside particles and evaporation are taken into consideration. If P_t is less than P_0 then the reaction terms are only considered for updating the composition in the reboiler solution.

If $P_t > P_0$ then the composition of the instantaneous distillate (ID) is determined as

$$x_{ID,i} = \frac{\left. \frac{dn_i}{dt} \right|_{\text{evap}}}{\sum_i^n \left. \frac{dn_i}{dt} \right|_{\text{evap}}} \quad (14)$$

The composition or the mole fraction in the cumulative distillate (CD) is estimated as

$$x_{CD,i} = \frac{\int_0^t \left. \frac{dn_i}{dt} \right|_{\text{evaporation}}}{\sum_i^n \int_0^t \left. \frac{dn_i}{dt} \right|_{\text{evaporation}}} \quad (15)$$

The cumulative distillate volume is calculated as

$$V_{CD} = V_0 - V_t \quad (16)$$

where V_t is calculated from the Eq. (9). Here, it is assumed that there are no vapor losses from the condenser.

After the above calculations the temperature of the solution in the reboiler flask is updated as

$$\frac{dT}{dt} = \frac{1}{\sum_{i=1}^4 n_i C_{Pi}} \left[\dot{Q} - \sum_{i=1}^4 \lambda_i \left. \frac{dn_i}{dt} \right|_{\text{evap}} \right] \quad (17)$$

The heat supply \dot{Q} is applied only when the total vapor pressure P_t is less than P_0 . This ensures that only drop wise condensation occurs. Fig. 3 could be referred to notice that the rate of energy supplied to the reboiler solution increases gradually. Although the rate of heat supply

Table 2. Coefficients for specific heat capacity.

Component	α_1	α_2	α_3	α_4
Acetic acid	139640	-320.8	0.8985	0
Methanol	105800	-362.23	0.9379	0
Methyl acetate	61260	270.9	0	0
Water	276370	-2090	8.125	-0.014116

Table 3. Coefficients for latent heat of vaporization.

Component	$\beta_1 \times 10^{-7}$	β_2	β_3	β_4	T_c
Acetic acid	4.0179	2.6037	-5.0031	2.7069	591.95
Methanol	5.04519	0.33594	0	0	512.5
Methyl acetate	4.492	0.3685	0	0	506.55
Water	5.2053	0.3199	-0.212	0.25795	647.1

is increased manually it is obtained from the time derivative of Eq. (2) and multiplying it with an efficiency factor η_e as

$$Q = \eta_e(400 + 11.05t) \quad \text{Watts} \quad (18)$$

where η_e is the thermal efficiency of the electrical heating mantle. All other properties such as $C_{p,i}$ and λ_i are taken from the literature [20] as dependent on temperature as shown below and the constants are presented in Table 2 and Table 3 for all the four components.

$$C_{p,i}(T) = \alpha_1 + \alpha_2(T + 273) + \alpha_3(T + 273)^2 + \alpha_4(T + 273)^3 \quad (19)$$

$$\lambda_i(T) = \beta_1 \left(1 - \frac{T+273}{T_c} \right)^{\beta_2 + \beta_3((T+273)/T_c) + \beta_4((T+273)/T_c)^2} \quad (20)$$

Here T_c is the critical temperature of the pure components.

An algorithm for implementing the above modeling scheme is presented as a flow chart in Fig. 8.

SIMULATION RESULTS

Initially the amounts of reactants are taken as $n_1=2.5$ moles, $n_2=2.5$ moles and that of products are $n_3=0$ and $n_4=0$. The initial temperature of the reactant solution is taken as 25 °C. An Euler explicit method with an adaptive time step is utilized for updating the temperature and composition of reboiler solution as well as that of the distillate composition and volume using the kinetic equation of Eqs. (13-17). The adaptive time step is such that there is only a 1 °C change in the temperature of the reboiler solution for each iteration. The numerical code is implemented using MATLAB. When above algorithm is

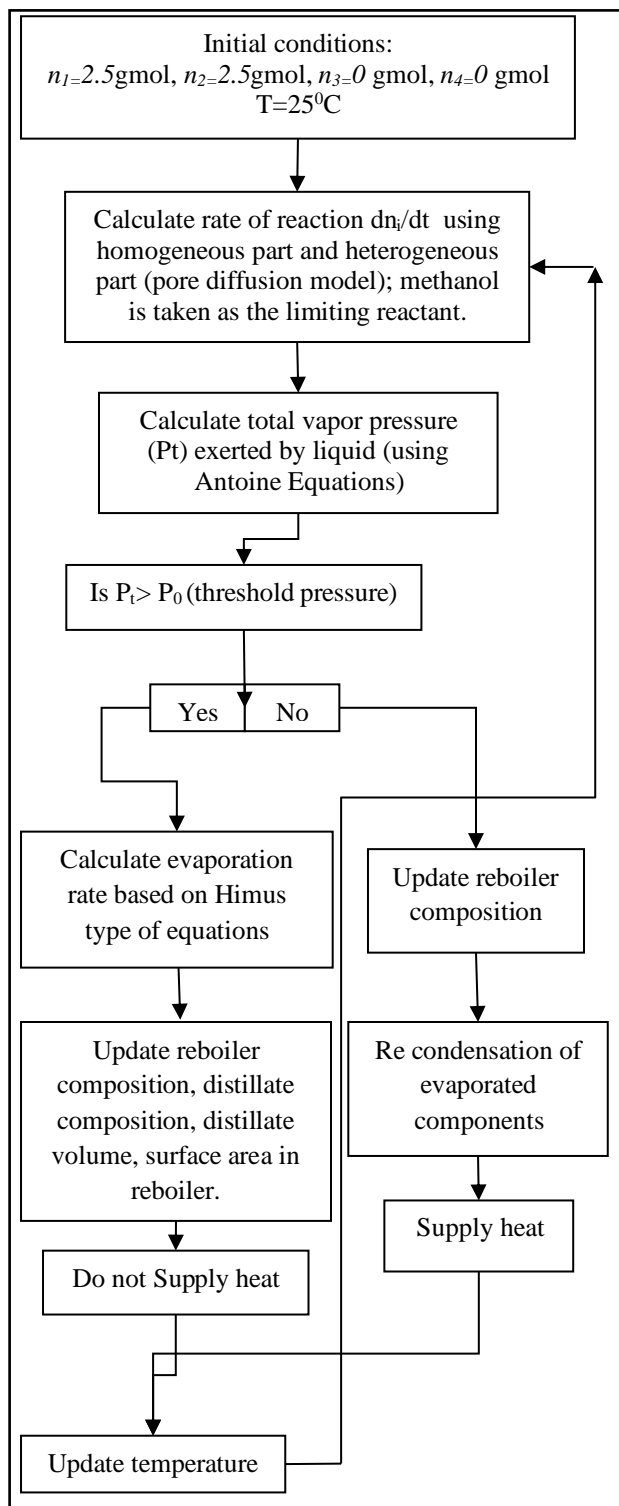


Fig. 8: Algorithm for simulation of batch reactive distillation process in a simple distillation apparatus.

implemented it is found by trial and error method that optimum values of parameters are $P_0=0.68$ atm, $\eta_e=0.26$ and $k_3 = 20.79$ mol/min·m²·atm in order to minimize the overall

Table 4. Estimate of standard deviation between predicted and experimental profile of cumulative volume of distillate for various input parameters to the model with $k_3=20.79$ mol/min m^2 atm.

	$\eta_e = 0.24$	$\eta_e = 0.26$	$\eta_e = 0.28$
$P_o=0.66$	0.0087	0.0075	0.0077
$P_o=0.68$	0.0088	0.0076	0.0076
$P_o=0.70$	0.0089	0.0074	0.0077
$P_o=0.72$	0.0093	0.0078	0.0075

Table 5. Estimate of standard deviation between predicted and experimental profile of Methyl acetate mole fraction in instantaneous distillate for various input parameters to the model for $k_3=20.79$ mol/min m^2 atm.

	$\eta_e = 0.24$	$\eta_e = 0.26$	$\eta_e = 0.28$
$P_o=0.66$	0.3577	0.2664	0.2618
$P_o=0.68$	0.3592	0.0167	0.3293
$P_o=0.70$	0.2772	0.3527	0.3507
$P_o=0.72$	0.3459	0.3707	0.3511

standard deviation or error between model prediction and experimental data of cumulative distillate volume versus time and mole fraction of methyl acetate in instantaneous distillate versus time. These errors are tabulated for various trial values of parameters in Table 4 and Table 5.

The obtained model predictions are compared with the experimental data for temperature of the reboiler solution, instantaneous distillate composition, cumulative distillate composition, composition of the reboiler solution and cumulative distillate volume as shown in Fig. 3 to Fig. 7. A good fit is found especially for predicting the methyl acetate composition in instantaneous distillate and cumulative distillate as well as other variables. A deviation is found only in the temperature prediction during the regime 3 as shown in Fig. 3. The reason for this is that the experimentally provided heat could be more than that is required for drop wise condensation.

Although the model is a simple representation incorporating pore diffusion model for reaction kinetics at catalyst scale, the Raoult's law based evaporation rate model has nearly predicted the experimental trends of the four components in distillate. In the regime 3, the liquid content in the still or the reactor reduces due to evaporation. Whereas the supplied heat is increased slowly as can be obtained from the derivative of energy versus time in Eq. (2). Also, the lighter components such as Methyl Acetate and Methanol

distill out first whereas the heavier components like Water and Acetic acid remain in the still and their boiling points are much above. Therefore, the bubble point of the mixture in still increases steeply in regime 3.

In Fig.4, as the reaction proceeds, the products methyl acetate and water are formed. When the temperature reaches near to the boiling points of components, it will vaporize and collected as distillate. So methyl acetate is collected first owing to its least boiling point (56 °C). Water comes into distillate much later owing to its high boiling point (100 °C). Actually, when the catalyst is mixed with reactants initially, the reaction also begins but with no distillate formation. Fig. 4 shows the instantaneous distillate composition and it indicates that distillate starts to come only after 90 min.

Fig. 5 shows the cumulative distillate composition. So if we wait for longer time all four components come into distillate and their composition reaches a steady value. Also, there is no catalyst in distillate therefore, it shows no variation of cumulative distillate composition implying that esterification reaction is very slow or does not occur at room temperature.

The developed model is able to predict the trend of experimental data in all three regimes of Fig. 3 to 7. The deviation observed in regime 1 seems to be due to delay of distillate and in regime 3 due to removal of lighter components from the reaction mixture. In key assumption in model Eq. (10) is that the evaporation rate coefficients k_i are assumed constant. But in reality they may depend on the multi-component composition of the mixture. Hence a deviation between model and experimental data is observed.

Fig. 9. depicts the variation of the total vapor pressure with respect to time as obtained from simulation. This is an immeasurable variable and hence the characteristic of it is obtained through simulation. It shows that the total vapor pressure P_t gradually increases till the set threshold value of P_0 and hovers over it owing to the model implementation that heat is withdrawn for $P_t > P_0$. As the solution cools due to evaporation heat loss when heat supply is withdrawn, the temperature falls and subsequently the total vapor pressure also drops below the threshold set value. Again heat is supplied to the reactant mixture since the P_t is less than P_0 . This cycle repeats for certain number iterations and it is observed from the Fig. 9 that P_t hovers around the threshold value of P_0 . The total

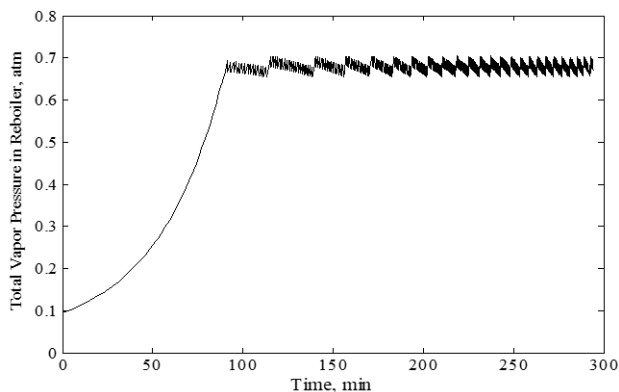


Fig. 9: Total pressure (P_t) exerted by the vapor emanating from the reboiler as a function of time.

vapor pressure is controlled at a threshold value to incorporate a quasi-steady state heat supply. If the total vapor pressure crosses the threshold, then heat supply is cut-off leading to reduction in vapor generation as well as total vapor pressure and vice versa. Thus, the model is robust in predicting the dynamics of a batch catalytic reactive distillation process.

CONCLUSIONS

The non-equilibrium evaporation rate based model in conjunction with pore diffusion model as a multi-scale approach for reactive distillation predicts the experimental kinetics of esterification of acetic acid and methanol to produce methyl acetate to a good accuracy. From the results it is observed that the maximum purity of the methyl acetate in initial distillate is obtained as 0.75 mole fraction. This value is more than the conversion obtained in just a reaction mode experiment which gives 0.345 mole fraction of methyl acetate in product mixture. For obtaining pure methyl acetate, starting with the later method requires higher energy for distillation. Hence, the present study and model has proven that reactive distillation is a energy efficient method for production of high purity methyl acetate by heterogeneous catalytic esterification. The assumption that condensation starts in a simple distillation apparatus after the total vapor pressure exceeds the certain threshold value is justified. The evaporation rate model may be adopted for process scale up and simulation of column reactive distillation which otherwise is not possible accurately with the stage-wise equilibrium model. Reaction kinetics are also modeled by a pore diffusion model rather than by pseudo homogeneous model. Some of the applications of the

insights are that a first cut could be obtained from a simple reactive distillation and it would be suitable for further distillation or molecular sieve separation to obtain a very high purity methyl acetate.

Nomenclature

Surface area of evaporation (m^2)	A_c
Concentration of methanol in the porous catalyst (mol/m^3)	C_2
Coefficient of specific heat capacity of i^{th} component ($J/mol\ ^\circ C$)	$C_{p,i}$
Effective diffusivity of methanol in porous catalyst (m^2/min)	D_{2m}
Activation energy of homogeneous forward reaction (J/mol)	E
Electrical Energy (J)	E_{Elec}
Molar flux of methanol into catalyst surface ($mol/m^2\ min$)	J_2
Forward reaction rate constant for homogeneous part ($l/mol\ min$)	k_f
Pre-factor in reaction rate constant ($L/mol\ min$)	k_{f0}
Equilibrium rate constant, dimensionless	K_e
Evaporation rate constant of i^{th} component ($mol/min\ m^2\ atm$)	k_i
Molecular weight of i^{th} component	MW_i
No. of gmols of i^{th} component (moles)	n_i
No. of catalyst particles	N_p
Saturation vapor pressure of i^{th} component (atm)	p_i^{sat}
Total vapor pressure exerted by the mixture (atm)	P_t
Rate of heat supply (W)	\dot{Q}
Radial position from center of a catalyst (m)	r
Universal gas constant ($J/mol\ K$)	R
Radius of catalyst particle (m)	R_p
Time (min)	t
Temperature ($^\circ C$)	T
Critical temperature of a pure component (K)	T_c
Volume of reactant mixture initially (l)	V_0
Volume of the reboiler solution at time t (l)	V_t
Initial catalyst loading (g/cc)	W_{c0}
Catalyst loading (g/cc)	W_c
Mole fraction of i^{th} component	x_i
Coefficients in specific heat capacity correlation	α_i
Coefficients in latent heat of vaporization	β_i
Latent heat of vaporization of i^{th} component (J/mol)	λ_i
Efficiency of electrical to heat energy conversion	η_e
Density of liquid component i (g/L)	ρ_i

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