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Reactive Distillation: An Attractive Alternative for the Synthesis of Unsaturated Polyester

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Summary: Unsaturated polyester is traditionally produced in a batch wise operating reaction vessel connected to a distillation unit. An attractive alternative for the synthesis of unsaturated polyester is a reactive distillation. To value such alternative synthesis route reliable process models need to be developed. In this paper, the strategy is described for the development of the reactive distillation model. Essential parts of the reactive distillation model are kinetic and thermodynamic which are subsequently validated with the experimental data of the traditional batch process such as acid value of the polyester, weight of the distillate and glycol concentration in the distillate. We find that the models predict these important variables reliably. Unsaturated polyester production time is around 12 hours in the traditional batch process. However, the simulation study of the reactive distillation process shows that the total production time of unsaturated polyester in a continuous reactive distillation system is between 1.5 hours to 2 hours for the same product quality as during batch production. The equilibrium conversion is raised by 7% compared to the traditional batch process. The model demonstrated that reactive distillation has the potential to intensify the process by factor of 6 to 8 in comparison to the batch reactor.

Keywords: equilibrium model; kinetic model; reactive distillation; thermodynamic model; unsaturated polyester synthesis

Introduction

The polyesterification of dicarboxylic acids with diols is a commonly applied process in the polymer industry.[1–3] Polyesterification reactions are usually equilibrium-controlled, and continuous removal of water is necessary to obtain high conversions. The polyester is produced in a batch reactor and usually a distillation column is directly coupled to the reactor vessel in order to avoid excessive loss of reactants during a batch, and nearly pure water is separated from the polymer mixture in the reactor. The total production time in such a batch process is around 12 hours and often leads to batch to batch inconsistency. [2–4] Process intensification is required for the unsaturated polyester process to reduce the production time and to achieve a better quality of the product. A promising alternative for the intensification of this process is reactive distillation. Reactive distillation may reduce capital and operating costs by replacing the chemical reactor and the distillation column with a single unit.[5] More importantly, it can drive equilibrium-limited reactions to completion by removing water upon formation through distillation.

The current scientific and industrial research in the area of reactive distillation is limited to a single product produced at relatively large capacities. Therefore application of these studies is not useful for multi-product production of relatively small capacities in the reactive distillation column. In the polyester industry, different

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grades of unsaturated polyesters are produced by changing either the reactants or by changing the reactant molar ratio. In order to be able to apply reactive distillation technology in the polyester industry, new concepts need to be developed which allow the combination of a significant increase in volumetric productivity with sharp product transitions while switching from one grade to other. To evaluate the concept of polyester synthesis by reactive distillation, a reactive distillation model should be developed. In this work, our objective is to develop this reactive distillation model for small capacities and to compare the model simulation results with the traditional batch process.

A reactive distillation model is composed of material balance, energy balance, kinetic model and thermodynamic model. The kinetic and thermodynamic model parameters are really crucial to describe the unsaturated polyester process reliably. In this work, we validated the kinetic and thermodynamic models and their parameters with the experimental data of a traditional batch process. The validated kinetic model, the thermodynamic model and their parameters are used in a reactive distillation model. The unsaturated polyester synthesis from maleic anhydride and propylene glycol is taken as a case study. Outline of this paper: the first part consists of a detailed discussion on the kinetic and thermodynamic models and validation of these models with experimental data. In the second part, the reactive distillation model is formulated and the reactive distillation process compared with the traditional batch process.

Kinetic Modelling

The synthesis of unsaturated polyester from maleic anhydride and propylene glycol involves four types of reactions.[2,3] Maleic anhydride (MAD) reacts with propylene glycol (PG) and produces a maleic acid end group (MA) and a propylene glycol end group (PG) with an ester (E) bridge. This is an exothermic and very fast reaction.

$$\begin{aligned}&\mathrm{MAD} + \mathrm{PG}\\&\quad \rightarrow \mathrm{COOH}\,(\mathrm{MA}) + \mathrm{E} + \mathrm{OH}(\mathrm{PG})\end{aligned} \tag{1}$$

The carboxylic acid end group reacts with the glycol end group to produce polyester (POLY) and water:

$$\begin{aligned}&\mathrm{COOH}(\mathrm{i}) + \mathrm{OH}(\mathrm{k})\\&\quad \leftrightarrows \mathrm{POLY}\,(\mathrm{p}) + \mathrm{WATER}(\mathrm{w})\end{aligned} \tag{2}$$

Unsaturated dicarboxylic acids are used in the industrial production of polyesters. The presence of unsaturated carboxylic acids essentially leads to side reactions such as isomerization in which cis formed maleic acid produces trans formed fumaric acid:

$$\mathrm{MA}\,(\mathrm{Cis}) \leftrightarrows \mathrm{FA}\,(\mathrm{Trans}) \tag{3}$$

and a double bond saturation reaction in which double bond of maleic acid saturates with glycol end group and produce saturated acid (SACID):

$$\mathrm{MA} + \mathrm{OH} \leftrightarrows \mathrm{SACID} \tag{4}$$

The three types of carboxylic groups are involved in the esterification reaction. Fumaric acid groups are formed via isomerization of the maleic acid groups and the saturated acid group is generated through the double bond saturation reaction (Ordelt reaction). These three carboxylic groups produce three ester groups via an esterification reaction. The three reactions, esterification, isomerization and saturation form a network of nine reactions, which are listed in Table 1.

The isomerized fumaric acid (FA) and saturated acid (SACID) also esterify and produce isomerized polyester (POLY_{2D}) and saturated polyester (POLY_s), respectively. Polyester (POLY_{1D}) produces from maleic anhydride which also isomerizes and saturates to produce isomerized polyester (POLY_{2D}) and saturated polyester (POLY_s), respectively. The isomerized acid (FA) and isomerized polyester (POLY_{2D}) also saturates and produces saturated acid (SACID) and saturated polyester (POLY_s), respectively.

Table 1.
Reactions and rate equations.

Reactions	Rate equation	
Esterification reactions:		
$MA + PG \rightleftarrows POLY_{1D} + H_2O$	$r_1 = (k_1 C_{MA} C_{PG} C_{MA}^{n-1} - k'_1 C_{POLY1D} C_{H2O})$	(5)
$FA + PG \rightleftarrows POLY_{2D} + H_2O$	$r_2 = (k_2 C_{FA} C_{PG} C_{MA}^{n-1} - k'_2 C_{POLY_{2D}} C_{H2O})$	(6)
$SACID + 0.5\,PG \rightleftarrows POLY_S + H_2O$	$r_3 = (k_9 C_{SACID} C_{PG} C_{MA}^{n-1} - k'_9 C_{POLY_S} C_{H2O})$	(7)
Isomerization reactions:		
$MA \rightleftarrows FA$	$r_4 = (k_3 C_{MA} C_{MA}^{n-1} - k'_3 C_{FA})$	(8)
$POLY_{1D} \rightleftarrows POLY_{2D}$	$r_5 = (k_4 C_{POLY1D} C^{n-1} MA - k'_4 C_{POLY_{2D}})$	(9)
Saturation reactions:		
$MA + 0.5\,PG \rightleftarrows SACID$	$r_6 = (k_5 C_{MA} C_{PG} C^{n-1} MA - k'_5 C_{SACID})$	(10)
$FA + 0.5\,PG \rightleftarrows SACID$	$r_7 = (k_6 C_{FA} C_{PG} C_{MA}^{n-1} - k'_6 C_{SACID})$	(11)
$POLY_{1D} + 0.5\,PG \rightleftarrows POLYS$	$r_8 = (k_7 C_{POLY_{1D}} C_{PG} C_{MA}^{n-1} - k'_7 C_{POLY_S})$	(12)
$POLY_{2D} + 0.5\,PG \rightleftarrows POLYS$	$r_9 = (k_8 C_{POLY_{2D}} C_{PG} C_{MA}^{n-1} - k'_8 C_{POLY_S})$	(13)

The esterification, isomerization and saturation reactions have been thoroughly discussed by Chen et al., Paatero et al., Salmi et al., Jedlovcnik et al. and Zetterlund et al..[3–4,8–10] The esterification, isomerization and saturation reactions are acid catalyzed and the strongest carboxylic acid gives the dominant catalytic effect. The maleic acid is the strongest acid with respect to another acid in the system. Hence, the main contribution to the catalytic effect is from maleic acid. The kinetic model in this paper differs from the kinetic model presented in Salmi et al.[3] such that the autocatalytic effect of the strongest carboxylic acid is considered only in the forward reaction. Due to the autocatalytic effect of the reaction, the reaction follows first order with respect to the acid at the beginning and second order at the end of the reaction.[3] The variable rate order effect in the rate equation is represented by,

$$n = \left[1 - \left(1 - 2^{1-q}\right) X\right]^{\frac{1}{1-q}} \tag{14}$$

Where, X is the equilibrium conversion and q an adjustable parameter and n is the order of reaction. This parameter is fitted in the present work for the maleic anhydride and propylene glycol system. In this system the parameter q value is 7. This kinetic model has 18 rate constants. There are two rate constants in each of the reactions. In order to reduce the number of adjustable parameters, the rate constants are lumped in eq. (15) – (20).

$$k_E = k_1 = k_2 = k_9 \tag{15}$$

$$k_I = k_3 = k_4 \tag{16}$$

$$k_D = k_5 = k_6 = k_7 \tag{17}$$

$$k'_E = k'_1 = k'_2 = k'_9 \tag{18}$$

$$k'_I = k'_3 = k'_4 \tag{19}$$

$$k'_D = k'_5 = k'_6 = k'_7 = k_8 \tag{20}$$

The rate constants of esterification, isomerization and saturation reactions are calculated by Arrhenius law. The Arrhenius law parameters, pre exponential constant (k) and (k′) in Mol/kg/min/[ci$^{\alpha}$], where α is exponent of component i and activation energy (Ea) in J/mol recalculated from reaction rate data published in Salmi et al.[3] The Arrhenius law parameters are tabulated in Table 2..

Table 2.
Recalculated Arrhenius law parameters from Salmi et al. (1994).

Reaction	Forward reaction		Backward reaction	
	K	*E_a*	*k′*	*E_a*
Esterification	1200000	75000	620	59000
Isomerization	127000	56000	178	41700
Saturation	273	47000	176	49600

Thermodynamic Modelling

The current unsaturated polyester process is operated at low pressure (1 bar), and at the end of the process vacuum is applied to completely remove the water from the polymer mixture.[2] As the system is operating at low pressure, the activity coefficient approach is sufficient to predict vapour-liquid equilibrium. The vapour phase is ideal and the partial pressure of species i in the vapour phase, p_i equals

$$p_i = x_i \gamma_i(x_i, T) p_i^{sat}(T) = y_i P \tag{21}$$

where x_i is the liquid mole fraction of species i, $\gamma i(x_i, T)$ is the activity coefficient of species i as function of liquid composition x_i, temperature T (K) and P_i^{sat} is the vapour pressure of pure species i (bar). As the system is highly polar, the only suitable models are the polymer NRTL and UNIQUAC. The polymer NRTL model is selected as it includes an effect of the polymer mixture on the activity coefficient parameters. The polymer NRTL is available in Aspen property plus. The polymer NRTL model is an extension of the NRTL model for low molecular weight compounds. The interaction parameters are independent of the polymer concentration and the polymer molecular weight.[11,12] The model parameters estimation procedure is depicted in Figure 1.

There are total of 28 binary pairs are required to represent the 8 component mixture. The activity coefficients at infinite dilution are predicted for each binary pair with the help of modified UNIFAC model. The interaction parameters of the polymer NRTL model are predicted by using the activity coefficients at infinite dilution for each binary system. The interaction parameters for the polymer NRTL model are listed in Table 3. The interaction parameters for the maleate polyester species (POLY1D), isomerized polyester (POLY2D) and saturated polyester (POLYs) are taken equal and reported as polyester (POLY) in Table 2. The polymer NRTL model activity coefficients ($\gamma_i = f(b_{ij}, b_{ji}, \alpha), \alpha = 0.3$) are used in the vapour-liquid equilibrium correlation (21) to describe the vapour phase composition during the polyesterification reaction.

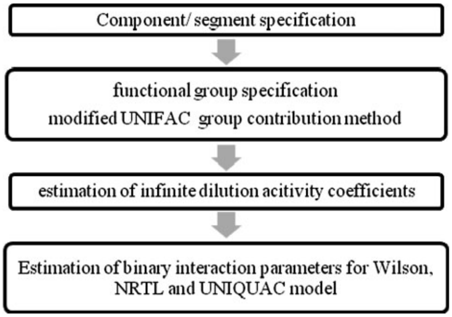

Figure 1.
A schematic view of binary interaction parameters estimation procedure.

Batch Reactor Model

A batch reactor model is developed in Aspen custom modeller (ACM) to validate the kinetic and the thermodynamic model. The idea of the modeling is to make the model as simple as possible, but still having dynamic behavior of the process. Focus is on the reactor and the prediction of the polymerization progress and properties

Table 3.
Activity coefficient parameters of the binary system for the polymer NRTL model.

Component i and j	b_{ij}	b_{ji}	Component i and j	b_{ij}	b_{ji}
MAD- PG	247.89	6.99	PG – SACID	1259.05	−648.34
MAD - WATER	−240.72	922.82	WATER – FA	761.89	−354.33
MAD – FA	446.42	−334.48	WATER - POLY	1374.87	−266.50
MAD – POLY	425.18	−321.70	WATER - SACID	1217.47	−370.09
MAD – SACID	−202.03	−52.15	FA – POLY	−631.65	1126.21
PG – WATER	−248.24	790.26	FA – SACID	−553.33	890.65
PG – FA	303.67	−229.10	POLY - SACID	1823.81	−796.03
PG – POLY	540.32	−129.88			

such as acid value, water content, isomerization fraction, saturation fraction and molecular weight. The model presented here accounts for a reactor-separation system which consist of a reactor, distillation column and a distillate accumulator as shown in Figure 2. The distillation column was considered as one theoretical plate. A separation unit is important to remove water from the reaction system to shift the equilibrium of the main reaction to the product side.

The reaction takes place in the liquid phase. The liquid phase mass balance for component i in the reaction vessel can be written according to,

$$\frac{dc_i}{dt} = r_i - \frac{v_i}{M_0} \tag{22}$$

Where, c is concentration of component i in mol/kg, r is reaction rate in mol/kg/hr, v_i is vapour phase flow rate in mol/hr and M_0 is initial total mass of the reactant. The vapour-liquid interphase can be considered as a double film without reaction, where the mass transfer is mainly limited by the highly viscous liquid phase. Thus, the following equation with the overall mass transfer coefficient $K_l\ a$ (360 hr^{-1}) and the vapour-liquid equilibrium ratio K_i can be written as equation (23).

$$v_i = K_l a\left(x_i - \frac{y_i}{K_i}\right) \tag{23}$$

The vapour phase mass balance according to eq. (24) includes the mass transfer from liquid phase and the flow out from the vapour phase of the reactor.

$$\frac{dy_i}{dt} = \frac{-F_{out}y_i + v_i}{v_{vap}} \tag{24}$$

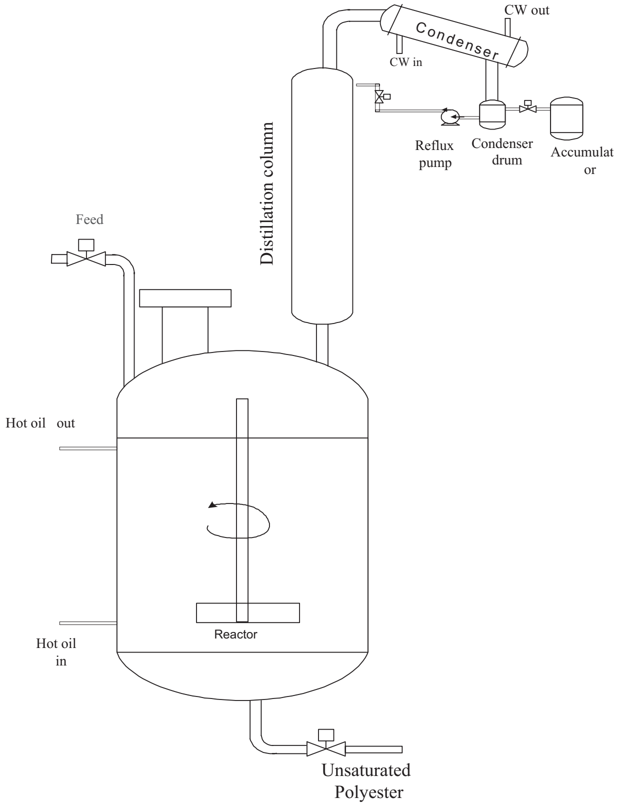

Figure 2.
Industrial unsaturated polyester process.

Where, y_i is vapour mole fraction, F_{out} is out flow from vapour phase and v_{vap} is vapour hold up in the reactor. The flow out from the vapour phase is separated to an outgoing vapour flow, V and a liquid flow, L from the flash condenser. The liquid flow is collected in the accumulator. The mole fraction is calculated by an isothermal flash calculation [13] as,

$$Z_i F_{out} = L x_i + V y_i \tag{25}$$

$$y_i = K_i x_i \; K_i = \gamma_i \frac{p_i}{P} \tag{26}$$

Where, K_i is the vapour-liquid equilibrium ratio for component i which is function of temperature, pressure, liquid mole fraction and vapour mole fraction. In this work, K_i is calculated from the activity coefficients predicted by the polymer NRTL model. p_i is the vapour pressure of the pure component i and P is the total pressure of the system.

This dynamic model can be used for the unsaturated polyester production from the different reagents. The simulation results presented in this paper are for the reaction of maleic anhydride with propylene glycol. The simulation has been performed at temperature of 160 °C, 180 °C and 200 °C, and at atmospheric pressure. The molar ratio of the anhydride and glycol is 1.0:1.1. The initial amounts of maleic anhydride and propylene glycol are 5.0 mol and 5.5 mol, respectively. The simulation has been performed in Aspen Custom Modeller. The simulated acid values of the polyester in the dynamic batch reactor model are used to validate the kinetic model. The thermodynamic model is validated by comparing simulation results of the distillate fraction with experimental data. The experimental data for the acid values of the polyester, weight of the distillate and the glycol concentration in the distillate are taken from Salmi et al.[3] The acid value presented here is in terms of the total carboxylic acid concentration ($C_{MA} + C_{FA} + C_{SACID}$) in mol/kg as shown in Figure 3. The model predicts reliably the concentration profile of carboxylic acid at the different temperature.

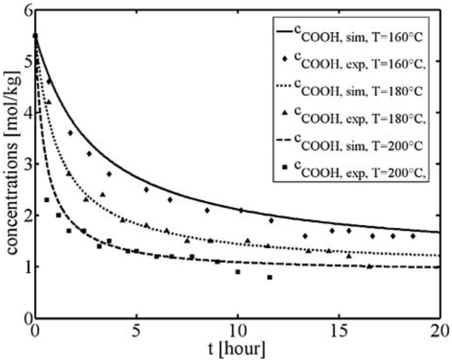

Figure 3.
Comparison of simulated concentration profile of carboxylic acid with experiments.[3]

In the dynamic model to represent the vapour liquid equilibrium two thermodynamic models are compared. One is ideal solution thermodynamic model which obeys Raoult's law and the second is the polymer NRTL non-ideal thermodynamic model. For the ideal behaviour modelling, the activity coefficient γ_i is equal to 1 and for the non-ideal behaviour modelling, the polymer NRTL activity coefficients are used. The activity coefficients of the polymer NRTL model for the synthesis of unsaturated polyester are depicted in Table 3. The accumulation of the distillate ($\varsigma = M_D / M_O$, where M_D is the distilled mass and M_O is the initial total mass of the reactants) in the accumulator during the synthesis of unsaturated polyester is plotted in Figure 4 and the weight fraction of propylene glycol in the distillate is plotted in Figure 5.

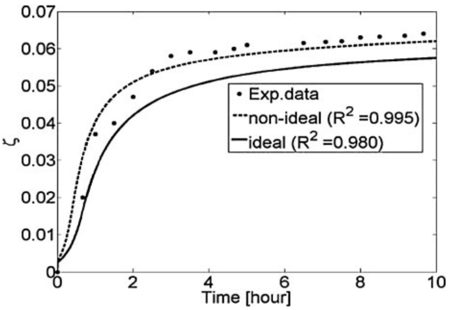

Figure 4.
Dimensionless distilled mass.

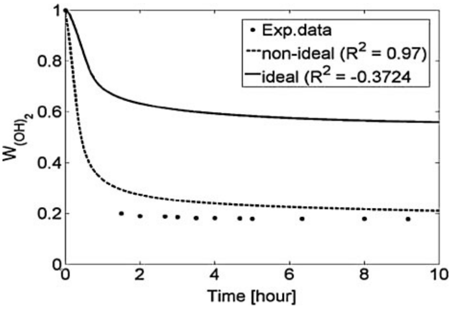

Figure 5.
Weight fraction of glycol in distillate.

By extending the model with activity coefficients obtained from the polymer NRTL model, the capabilities to predict the compositions of vapour phase are improved significantly. The model improves the prediction of the distillate mass and the weight fraction of the propylene glycol compared to ideal behaviour modelling, as shown in Figures 4 and 5, respectively. The distillate mass is under predicted in the case of ideal behaviour compared to non-ideal behaviour as illustrated in Figure 4. The reason is that fumaric and maleic acid are present in the vapour phase but they are not considered in the ideal calculation. The regression coefficient (R^2) for the distillate mass is 0.980 in the ideal behaviour modeling and 0.995 in the non-ideal behavior modelling, which shows an improvement in predictive capabilities. The propylene glycol weight fraction in the distillate is significantly over-predicted in ideal behavior thermodynamic modelling compared to experimental data as illustrated by Figure 5. The regression coefficient (R^2) for weight fraction of propylene glycol is 0.97 in the non-ideal thermodynamic modelling, which shows that the polymer NRTL model reliably predicts the weight fraction of propylene glycol.

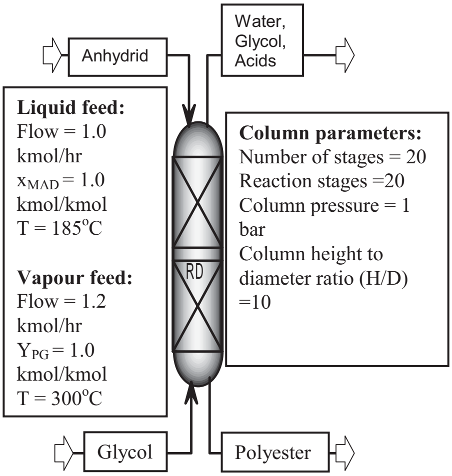

Figure 6.
Reactive distillation column.

Dynamic Equilibrium Reactive Distillation Modelling

A schematic view of the reactive distillation column is shown in Figure 6. The column is operated as counter current vapour-liquid contactor. The maleic anhydride is fed as liquid at the top of the column and propylene glycol is fed at the bottom of the column as vapour. The polyester product leaves from the bottom of the column and water, glycol and acids leave at the top of the column.

The reactive distillation model consists of J $(j = 1,..., J)$ stages. A schematic view of the equilibrium stage balance is shown in Figure 7. The first stage $(j = 1)$ is the top stage, where the anhydride is fed with flow L_F (kmol/hr) to the column and the vapour comes out from the top stage with flow V_{out} (kmol/hr). The last stage $(j = 20)$ is the bottom stage, where the glycol is fed with flow V_F (kmol/hr) to the column and the bottom product flows out with flow L_{out}

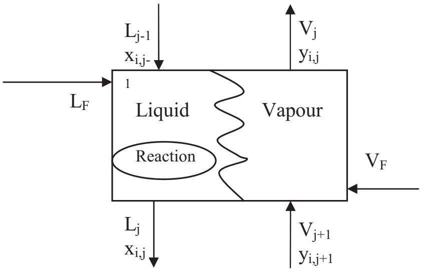

Figure 7.
Equilibrium stage balance.

(kmol/hr). The composition of component *i* on stage *j* in the liquid phase is $x_{i,j}$ and in the vapour phase is $y_{i,j}$. The total molar holdup per stage is denoted by M_j (kmol) and $\nu_{i,m}$ represents the stoichiometric coefficient of component *i* in reaction *m* and ε_j represents the reaction volume. The vapour flows between the stages are expressed as V_j (kmol/hr) and liquid flows between the stages are expressed as L_j (kmol/hr).The component material balance for each of the stages J ($j = 1,\ldots, J$) is:

$$
\begin{aligned}
M_j \frac{dx_{i,j}}{dt} = {} & L_{j-1}x_{i,j-1} - L_j x_{i,j} \\
& + V_{j+1}y_{j+1} - V_j y_{i,j} \\
& + \sum_{m=1}^{r} \nu_{i,m} r_{m,j} \varepsilon_j
\end{aligned}
\tag{27}
$$

For the top stage ($j = 1$), $L_{j-1} = L_F$, $x_{i,j} = x_F$, $V_j = V_{out}$, $y_j = y_{out}$ and for the bottom stage (j), $V_{j+1} = V_F$, $y_{j+1} = y_F$, $L_j = L_{out}$, $x_{i,j} = x_{out}$. The total material balance for stages J ($j = 1,\ldots, J$)

$$
\begin{aligned}
\frac{dM_j}{dt} = {} & L_{j-1} - L_j + V_{j+1} - V_j \\
& + \sum_{m=1}^{r} \sum_{i=1}^{C} \nu_{i,m} r_{m,j} \varepsilon_j
\end{aligned}
\tag{28}
$$

The steady state energy balance for stages J ($j + 1,\ldots, j-1$) is:

$$
\begin{aligned}
& L_{j-1} CP_L (T_{j-1} - T_j) \\
& + V_{j+1} CP_V (T_{j+1} - T_j) \\
& = \sum_{i=1}^{C} V_{j+1} y_{i,j+1} H^V_{i,j+1}
\end{aligned}
\tag{29}
$$

Where, T_j (°C) is the temperature at stage *j*, CP_L is the liquid mixture heat capacity and CP_V is the vapour mixture heat capacity, $H^{v}_{i,j+1}$ is the heat of vaporization of component *i* on stage $j + 1$. For the top stage ($j = 1$), $T_{j-1} = T_{lf}$ (°C) is the liquid feed temperature, $T_j = T_{tout}$ (°C) is the temperature of the vapour outlet stream at the top of the column and for the bottom stage ($j = 20$), $T_{j+1} = T_{vf}$ (°C) is the vapour feed temperature, $T_j = T_{bout}$ (°C) is the temperature of the liquid outlet stream at the bottom of the column, H^{v}_F is the heat of vaporization of the vapour feed. In the present work, a dynamic model for the energy balance is not used to simplify the model. However, the product transition is an important parameter for grade switching. Thus, only the dynamic material balance is considered in this work. The polyester synthesis in the batch reactor is mass transfer limited due to limited interfacial area between vapour and liquid but in reactive distillation high interfacial area between vapour and liquid can be achieved and thus the polyester synthesis in reactive distillation is not mass transfer limited. Therefore, the vapour and liquid are assumed to be in equilibrium (VLE) on all stages; both liquid and vapour phase are assumed to be perfectly mixed on each stage. The pressure drop is neglected. There is negligible vapour holdup on each stage. The model accounts for reaction on each stage and the number of stages is 20. From a sensitivity analysis we have determined that at least 20 stages are required to obtain sufficient conversion. The reaction rate on each stage is given by,

$$
\begin{aligned}
r_{m,j} = {} & kf0_m \exp\left[-\frac{Ea_m}{RT_j}\right] \\
& \left[C_{i,j} C_{k,j} C^{n-1}_{MA,j} - \frac{C_{w,j} C_{p,j}}{KE_m}\right] \\
KE_m = {} & \frac{kf0_m}{kb0_m}
\end{aligned}
\tag{30}
$$

The vapour phase compositions are calculated by the polymer NRTL non-ideal thermodynamic model. The polymer NRTL model activity coefficients ($\gamma_{i,j} = f(b_{ij}, b_{ji}, \alpha)$, $\alpha=0.3$) are used in the vapour-liquid equilibrium correlation

$$
p_{i,j} = x_{i,j} \gamma_{i,j}(x_{i,j}, T_j) p^{sat}_{i,j}(T_j) = y_{i,j} P_j \tag{31}
$$

to describe the vapour phase compositions during the polyesterification reaction. As the reaction is kinetically controlled (slow reaction), the residence time requirement is large to achieve sufficient conversion. The residence time required in the reactive distillation column is estimated by,

$$
\tau = \sum_{j=1}^{j} \frac{M_j}{L_j} \tag{32}
$$

Reactive Distillation Process Versus Industrial Batch Process

The reactive distillation model is developed in Aspen custom modeler (ACM). The components, properties and thermodynamic are defined by the problem definition file of Aspen plus/property plus. The non conventional component properties are estimated by Aspen property plus. The operating conditions of the reactive distillation column are depicted in Figure 6. The reactive distillation model simulation results are compared with the industrial batch reactor output data of the product and also with the simulation results of batch reactor model. The operating conditions of the reactive distillation process and batch process are compared in Table 4.

The optimum reaction temperature of the polyester process in batch production is between 210 °C and 220 °C to avoid loss of double bonds of the unsaturated acid. Due to the short residence time requirement in the reactive distillation process, the reaction temperature is kept between 185 °C and 300 °C. The free acid (or anhydride) is present only in the top three stages of the reactive distillation column and the reaction temperature on these stages is between 185 °C and 210 °C. Thus, there is no possibility of destruction of unsaturated acid in the reactive distillation process. The product specifications that are achieved in the reactive distillation process are compared with the batch reactor process in Table 5. The reactive distillation process model predicts acid value, hydroxyl value, maleate, fumarate, saturation compositions and polymer attributes of the polymer in the range of industrial unsaturated polyester production in a batch reactor.

The benefits of the reactive distillation process over the traditional batch reactor process are shown in Figure 8. The industrial unsaturated polyester production time is around 12 hours. However, the reactive distillation process simulation study shows that the total production time of unsaturated polyester in a continuous reactive distillation system is between 1.5 and 2 hours for the same product quality as during 12 hours of batch production. Reactive distillation will intensify the process by a factor of 6 to 8 in comparison to the batch reactor process. The equilibrium conversion in a batch reactor process is around 88-90%. However, in the reactive distillation process the equilibrium conversion is significantly higher compared to the batch reactor and can be up to 97%. The limiting factor for equilibrium conversion is water evaporation from the liquid phase and shifting the equilibrium to the product side.

Table 4.
Operating conditions for the reactive distillation process and the batch process.

Operating conditions	RD process	Industrial batch process[4]
Temperature range (°C)	185-300	40-210
Pressure (bar)	1	1
Process	Continuous	Batch

Table 5.
Comparison of the product specifications.

Product specifications	RD process	Batch reactor process and industrial production data[4,6]
Acid value	20-25	20-25
Hydroxyl value	70-90	80-100
Maleate ester (%)	20-40	20-40
Fumarate ester (%)	50-65	50-65
Saturated ester (%)	10-15	10-15
Molecular weight number	1000-4000	800-1600
Degree of polymerization	8-27	8-15

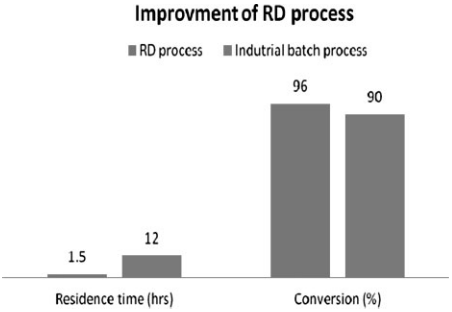

Figure 8.
Advantages of the Reactive distillation (RD) process over the industrial batch reactor process.

In the reactive distillation process, glycol acts as a stripping agent to remove water from the liquid phase while nitrogen or xylene are used as stripping agent in a batch reactor process. Due to the high temperature (250-300 °C) and the high concentration of glycol in the vapour phase at the bottom stages, water evaporation is much more efficient in the reactive distillation process compared to the batch reactor process.

Conclusion

In this paper, the essential parts of reactive distillation, kinetic and thermodynamic models are validated with experimental data of the batch reactor process and a dynamic equilibrium reactive distillation model is formulated and simulation results are compared with the industrial batch reactor process data. We find that the changing rate order kinetic model and the polymer NRTL non-ideal thermodynamic model represent the system reliably. The polymer NRTL non-ideal thermodynamic model improves significantly the predictive capability of the vapour phase compositions in the batch reactor.

From the simulation study we conclude that the reactive distillation process has distinct advantages over the traditional batch reactor process. The unsaturated polyester synthesis in the reactive distillation column is improved in all domains of structure, energy, synergy and time. A 7% higher equilibrium conversion is achieved in the reactive distillation process compared to the batch reactor process. The required residence time is only 1.5-2 hours compared to 12 hours of batch time in the conventional process. Reactive distillation has the potential to intensify the process by factor of 6 to 8 in comparison to the batch reactor.

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