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DEVELOPMENT OF A MODEL FOR THE SYNTHESIS OF UNSATURATED POLYESTER BY REACTIVE DISTILLATION

M. Shah[1], E. Zondervan[1], M.L. Oudshoorn[2], A.B de Haan[1]
[1]Process Systems Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands, m.shah@tue.nl
[2]DSM research, Geleen, 6160MD, The Netherlands

Abstract
Traditionally polyester production is done in a batch reactor equipped with a separation column for batch distillation. A promising alternative for the intensification of this process is reactive distillation. In this paper, a reactive distillation model is developed for the synthesis of an unsaturated polyester process. The simulation results are compared with the industrial batch reactor output data of the product. It is found that the model predicts the polymer attribute, isomerisation and saturation composition of the polymer in the range of industrial unsaturated polyester production. Industrial unsaturated polyester production time is around 12 hours. However, the simulation study 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 also raised by 7% compared to the conventional 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: Reactive distillation, Polyesterification, Unsaturated polyester, modelling

1. Introduction

Reactive distillation is a well-known technology for reactive-separation systems close to equilibrium[1]. The integration of reaction and separation holds clear advantages for many systems in comparison with subsequent reaction and separation[1-3]. The removal of reaction water in esterification systems is a good example and has already been extensively studied[1-3]. However, the current scientific and industrial research is often limited to the optimization of reactive distillation columns for a single product type produced at relatively large capacities. This makes the application of the outcome of these studies not useful for applying reactive distillation in a multi-product environment with relatively small capacities as encountered in the polyester industry. In order to be able to apply reactive distillation technology in multi-product environments, new concepts need to be developed which allow the combination of a significant increase in volumetric productivity with sharp product transitions. To evaluate the multi-product concept in the reactive distillation process, a dynamic reactive distillation model should be developed. Thus, in this work, our objective is to develop a dynamic reactive distillation model for small capacities and to compare the model simulation results with the conventional batch process.

For this study, we have taken the unsaturated polyester synthesis from maleic anhydride and propylene glycol as case study since this unsaturated polyester is synthesised in small capacity. Unsaturated polyesters are traditionally produced in a batch wise operated reaction vessel connected to a distillation unit[4-5]. The total production time is around 12 hours and batch to batch inconsistencies are frequently encountered. To evaluate the potential of reactive distillation a dynamic model has been developed in Aspen custom modeller (ACM). The reaction scheme is complex and the proposed model takes four types of reactions into account: ring opening, polyesterfication, isomerisation and saturation. The model includes mass and energy balances, kinetic rate equations including a change of rate order during the reaction and the polymer NRTL non-ideal thermodynamics model.

2. Dynamic Equilibrium Reactive Distillation Modelling

A schematic view of the reactive distillation column is shown in Figure 1.The column is operated as counter current vapour-liquid contactor. The 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.

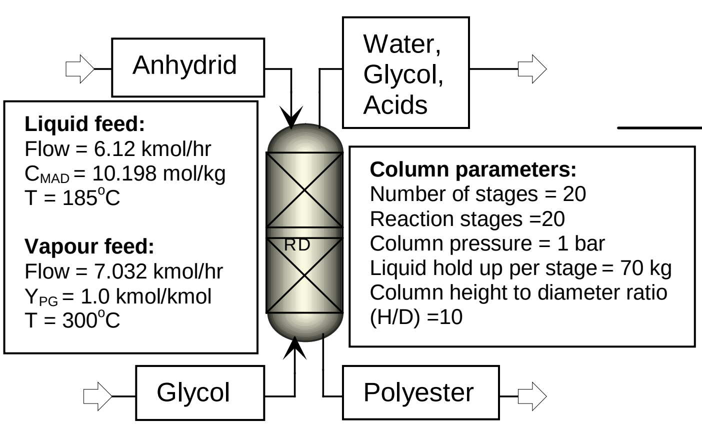

Figure 1: Reactive stripping column

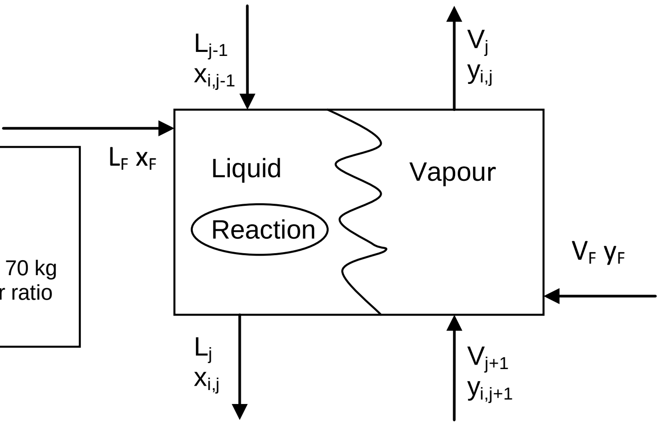

Figure 2: Equilibrium stage balance

The reactive distillation model consists of *J* (j = 1,..., J) stages. A schematic view of the equilibrium stage balance is shown in figure 2. 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} (kmol/hr). The composition of component *i* 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,..., J) is:

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

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,..., J) is:

$$\frac{dM_j}{dt} = L_{j-1} - L_j + V_{j+1} - V_j + \sum_{m=1}^{r} \sum_{i=1}^{C} \nu_{i,m} r_{m,j} \varepsilon_j \tag{2}$$

The steady state energy balance for stages (j+1,…, j-1) is:

$$L_{j-1}CP_L(T_{j-1} - T_j) + V_{j+1}CP_V(T_{j+1} - T_j) = \sum_{i=1}^{C} V_{j+1} y_{i,j+1} H^V_{i,j+1} \tag{3}$$

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 as the temperature transition is not an important parameter. However, the product transition is an important parameter for grade switching. Thus, the dynamic material balance is considered in this work. 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 mixture contains 8 components in which maleic anhydride and propylene glycol are pure reactants. The reaction scheme is complex and the proposed model takes four types of reactions into account; ring opening, polyesterfication, isomerisation and saturation. These four reactions form a network of nine reactions. The order of reaction is changing during the reaction from 1 to 2 with respect to carboxylic acid due to the autocatalytic effect of the carboxylic acid. The main four reactions are as follows; maleic anhydride (MAD) reacts with propylene glycol (PG) and produces an acid (COOH) and alcohol (OH) end group with an ester (E) bridge. This is an exothermic and very fast reaction.

$$\text{MAD + PG} \rightarrow \text{COOH + E + OH} \tag{4}$$

Carboxylic acids react with diols and form a polyester (POLY) and water:

$$\text{COOH (i) + OH (k)} \leftrightarrows \text{POLY (p) + WATER (w)} \tag{5}$$

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:

$$\text{Cis (MAD)} \leftrightarrows \text{Trans (FA)} \tag{6}$$

and a double bond saturation reaction:

$$\text{Dbb (MAD) + OH} \leftrightarrows \text{SatDbb (SAT ACID)} \tag{7}$$

The isomerized acid (FA) and saturated acid (SAT ACID) also esterify and produce polyester ($POLY_{2D}$) and saturated polyester ($POLY_S$), respectively. Polyester ($POLY_{1D}$) formed from maleic anhydride 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 (SAT ACID) and saturated polyester ($POLY_S$), respectively. The detailed kinetic model can be found in earlier work[4]. The reaction rate on each stage is given by,

$$r_{m,j} = kf0_m \exp\left[-\frac{Ea_m}{RT_j}\right]\left[C_{i,j}C_{k,j}C_{MA,j}^{n-1} - \frac{C_{w,j}C_{p,j}}{KE_m}\right] \quad KE_m = \frac{kf0_m}{kb0_m} \tag{8}$$

The rate constants of the esterification, isomerization and saturation reactions are calculated by the Arrhenius law. The Arrhenius law parameters, pre exponential constant *kf0* and *kb0* in Mol/kg/min/[c_i^{α}], where α is the exponent of component *i* and activation energy E_a in KJ/mol are taken from Shah et al.[4]. The variable rate order is represented by,

$$n = \left[1 - \left(1 - 2^{1-q}\right)X\right]^{\frac{1}{1-q}} \tag{9}$$

Where, X is equilibrium conversion and q an adjustable parameter. 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. The Arrhenius parameters are tabulated in table 1.

Table1. Arrhenius parameters from Shah et al. (2009)

Reaction	Forward reaction		Backward reaction	
	Kf0	Ea	Kb0	Ea
Esterification	1200000	75000	620	59000
Isomerization	127000	56000	178	41700
Saturation	273	47000	176	49600

As the system is operating at low pressure (1 bar), the activity coefficient approach is sufficient to represent the vapour-liquid equilibrium. The vapour phase is considered ideal and the partial pressure of species *i* in the vapour phase, $p_{i,j}$ equals

$$p_{i,j} = x_{i,j}\gamma_{i,j}(x_{i,j},T_j)p_{i,j}^{sat}(T_j) = y_{i,j}P_j \tag{10}$$

Where $x_{i,j}$ is the liquid mole fraction of species *i* on stage *j*, $\gamma_{i,j}(x_{i,j}, T)$ is the activity coefficient of species *i* as function of liquid composition $x_{i,j}$ and temperature *T* (K) and $P_{i,j}^{sat}$ (bar) is the vapour pressure of pure species *i.*

Table 2: 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 – SAT ACID	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 - SAT ACID	1217.47	-370.09
MAD - SAT ACID	-202.03	-52.15	FA - POLY	-631.65	1126.21
PG - WATER	-248.24	790.26	FA - SAT ACID	-553.33	890.65
PG - FA	303.67	-229.10	POLY - SAT ACID	1823.81	-796.03
PG - POLY	540.32	-129.88			

The vapour phase compositions are calculated by the polymer NRTL non-ideal thermodynamics model. The interaction parameters for the polymer NRTL model are listed in table 2. 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 (10) to describe the non-ideal behaviour of the polymer during the polyesterification reaction. The interaction parameters for the maleate polyester species ($POLY_{1D}$), isomerized polyester ($POLY_{2D}$) and saturated polyester ($POLY_s$) are taken equal and reported as polyester (POLY) in table 2. 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,

$$\tau = \sum_{j=1}^{j} \frac{M_j}{L_j} \tag{11}$$

3. Results

3.1 Reactive distillation process versus industrial batch process

The developed reactive distillation model can be used for unsaturated polyester synthesis from different reagents. The simulation results presented in this paper are for the reaction of maleic anhydride with propylene glycol. The model is developed in Aspen custom modeler (ACM). The components, properties, thermodynamics 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 1.

Table 3: Operating conditions for the reactive distillation process and the batch process

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

The reactive distillation model simulation results are compared with the industrial batch reactor output data of the product[5]. The operating conditions of the reactive distillation process and batch process are compared in table 3. The optimum reaction temperature of the polyester process in batch production is between 210°C and 220°C to avoid destruction 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 3 top 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 4. 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 batch reactor.

Table 4: Comparison of the product specifications

Product specifications	RD process	Batch reactor process (industrial production)[4-5]
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

The benefits of the reactive distillation process over the conventional batch reactor process are shown in figure 3. 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 liquid phase and shifting the equilibrium to the product side. 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^{o}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.

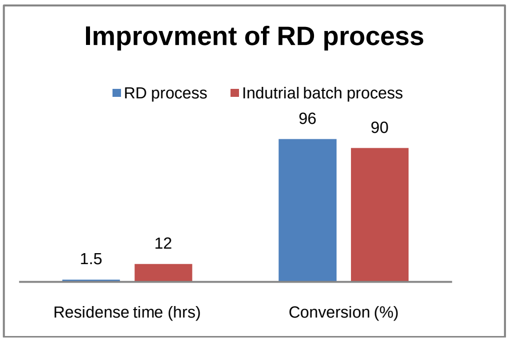

Figure 3: Advantages of the Reactive distillation (RD) process over the industrial batch reactor process

3.2 Steady state analysis

The steady state simulation is performed for the operating conditions of the reactive distillation column in figure 1. Polyester (POLY = $POLY_{1D}$ + $POLY_{2D+}$ $POLY_s$) and saturated acid (SAT ACID) are not present in the vapour phase which can be seen in figure 4. This is due to the non volatile nature and high molecular weight of the polyester and the saturated acid. The glycol concentration in the vapour phase decreases slowly in the bottom stages and decreases steeply in the top stages as depicted in figure 4. This is because of the effect of the temperature change in the column and that there is free anhydride and acid to form monoesters at the top stages. The reaction rate between glycol and anhydride (or acid) to form monoesters is faster than the polyesterification reaction. Thus the glycol concentration decreases steeply in the top stages. Water is stripped out throughout the column with propylene glycol, which acts as stripping agent for the water. Hence, the water concentration is very low in the bottom stages while the glycol concentration is higher in the bottom stages. As the water formation rate is higher due to the reaction between glycol and free acid at the top stages, the water concentration is high at the top stages. Water compositions in the vapour and liquid phase have been depicted in figure 4 and 5 (a), respectively.

The degree of isomerization (CI = FA + $POLY_{2D}$) in the vapour and liquid phase has been shown in figure 4 and 5 (b), respectively. The isomerization concentration increases steeply in the top stages and after that reaches a peak and then the isomerization concentration decreases throughout the column towards the bottom stages. Because there is free maleic anhydride and maleic acid available, they effectively relieve the strain by transforming to the more planar trans-fumarate isomer when the reaction temperature exceeds 180^oC. The polyesterification reaction rate also increases with temperature and when the temperature exceeds 210^oC, isomerized acids also esterify with the glycol and produce isomerized ester ($POLY_{2D}$). However, certain isomerized ($POLY_{1D}$) and maleate ester ($POLY_{2D}$) saturate by breaking the double bond with glycol. Thus, the saturation concentration (CS = SAT ACID + $POLY_s$) increases throughout the column and reaches equilibrium as shown in figure 5 (a). The temperature profile is plotted in figure 6.

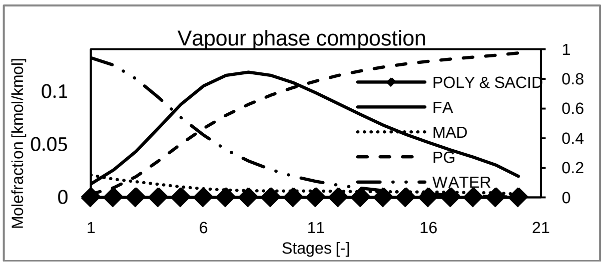

Figure 4: Vapour phase

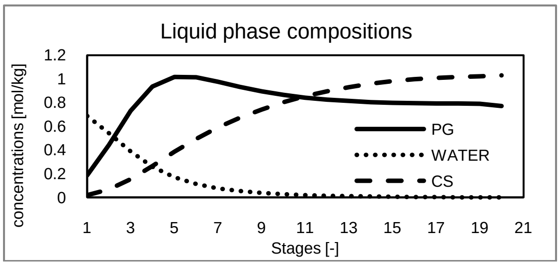

Figure 5 (a): Liquid phase

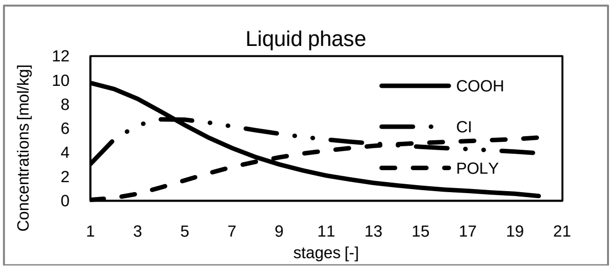

Figure 5 (b): Liquid phase compositions and temperature profile

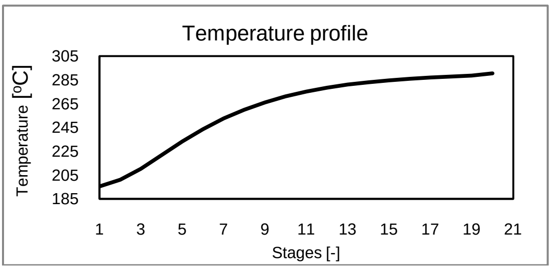

Figure 6: Temperature Profile

4. Conclusion

In this paper, a reactive distillation model for unsaturated polyester process is formulated. It is found that the reactive distillation process has distinct advantages over the conventional batch reactor process. The unsaturated polyester synthesis by reactive distillation is intensified 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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