Modelling and simulation of an unsaturated polyester process.

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Abstract

This paper presents a model for the polyesterification of maleic- and phthalic anhydride with ethylene- and 1,2-propylene glycol. The reaction scheme is complex, and the proposed model takes four types of reactions into account: ring-opening, polyesterification, isomerization and saturation reactions. Laboratory measurements of acid number and water content have been used for validating the kinetic model, and the model predicts these important variables reasonable well.

Two different dynamic models of an industrial batch reactor including distillation column, condenser, condenser drum and heating- and cooling system are presented. The models are based on mass- and energy balances and simple vapor-liquid equilibrium calculations. The only difference between the two models is the calculation of vapor flow and composition from the reactor into the distillation column. One model uses the reactor energy balance to calculate flow and a flash calculation to predict composition, while the other uses simple mass transfer equations for the calculation of both vapor flow and composition. Industrial data is used for validation of the dynamic model.

1 Introduction

Most polyesters are produced by reacting different acid anhydrides or dicarboxylic acids with diols in semibatch reactors. Polyesterification reactions are usually equilibrium-controlled, and continuous removal of water is necessary to obtain high conversions.[1] A distillation column is usually directly coupled to the reactor vessel in order to avoid excessive loss of reactants during a batch, and nearly pure water can be separated from the polymer mixture in the reactor.

Processes involving simultaneous reaction and fractionation are referred to as reactive distillation. Most reactive distillation processes are treated as complex distillation units where reaction can take place in the entire column or in parts of the column. Emphasis is usually on the method of prediction of vapor-liquid equilibrium and advanced thermodynamic models are used. A comprehensive survey of modelling reactive distillation can be found in Taylor and Krishna.[2] The majority of literature on reactive distillation considers continuous systems.
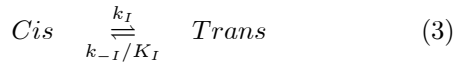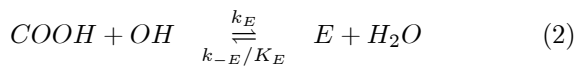
In unsaturated polyester processes, most of the reactions take place in the reactor and not in the column. This makes it possible to drastically simplify the modelling equations arising in reactive distillation. A detailed model involving complex thermodynamics is also difficult because of the growing polymer which makes it hard to estimate thermodynamic properties.

A typical unsaturated polyester is obtained by the polyesterification of maleic- and phthalic anhydride with ethylene- and 1,2-propylene glycol, and is used as a case study. The purpose is to develop a model of an industrial unsaturated polyester process including detailed kinetics, and the intended use is for simulation studies and advanced process control and estimation.

2 Kinetic model

The synthesis of unsaturated polyester from maleic and phthalic anhydride and glycols involves four types of reactions. First the anhydride (A) reacts with a glycol (G) to form an acid and alcohol end group (COOH and OH) together with a ester bridge (E) as shown in (1). This is the ring-opening reaction.

Esterification proceeds by the reaction of different acid and alcohol end groups to form new ester bridges and water (2), or by reaction of a glycol hydroxyl group with an acid end group to form an ester bridge and water. The double bond in maleic anhydride can be isomerized (3) or saturated (4). Saturation of the double bond causes crosslinking in the polymer, and approximately 10-20 % of the double bonds are saturated in the preparation of the polyester REF.

$$A + G \quad \overset{k_{ro}}{\rightarrow} \quad COOH + E + OH \quad (1)$$

$$COOH + OH \quad \underset{k_{-E}/K_E}{\overset{k_E}{\rightleftharpoons}} \quad E + H_2O \quad (2)$$

$$Cis \quad \underset{k_{-I}/K_I}{\overset{k_I}{\rightleftharpoons}} \quad Trans \quad (3)$$

$$Dbb + OH \quad \underset{k_{-S}/K_S}{\overset{k_S}{\rightleftharpoons}} \quad SatDbb \quad (4)$$

The rate expressions for the different types of reactions are given in (5)-(8). The ring-opening is assumed to be second order and irreversible. It is assumed that ethylene and 1,2-propylene glycol have the same reactivities towards ring-opening, but the anhydrides have different reactivities. This means the rate constants for the ring-opening of maleic anhydride with ethylene glycol and 1,2-propylene glycol are equal, and different form the rate constants involving phthalic anhydride.

Esterification, isomerization and saturation reactions have been thoroughly discussed by Chen&Wu,[3] Paatero et al.,[4] Salmi et al.,[5] Jedlovčnik et al.,[6] Salmi et al.[7] and Zetterlund et al.[8] In this modelling and simulation study the rate expressions and rate constants have been adopted from literature.[4,5,7] The variable rate order as been removed in order to simplify the kinetic expressions (6)-(8), and slightly dif-

ferent definition of the functional groups has been used for the kinetic treatment. These changes can affect the predictive properties of the kinetic model, and the kinetic model has therefore been verified against laboratory measurements of acid number and water content. Maleic anhydride, phthalic anhydride and 1,2-propylene glycol was loaded into a laboratory reactor equipped with a distillation column before heating. A predefined temperature and pressure trajectory which resembled industrial practice was followed, and samples were collected from the reactor during the batch and analyzed for acid number and water content. Pressure, temperature and amount of water escaped from the reactor were also measured.

$$r_{ro} = k_{ro}c_A c_G \quad (5)$$

$$r_E = k_E c_{Acid}\left(c_{COOH}c_{OH} - \frac{1}{K_E}c_E c_{H_2O}\right) \quad (6)$$

$$r_I = k_I c_{Acid}\left(c_{Cis} - \frac{1}{K_I}c_{Trans}\right) \quad (7)$$

$$r_S = k_S c_{Acid}\left(c_{Dbb}c_{OH} - \frac{1}{K_S}c_{SatDbb}\right) \quad (8)$$

$$k_i = k_{0i}e^{-\frac{E_i}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \quad (9)$$

Figure (1) shows the measured and simulated acid number and water content in the reactor. The simulation is done by using the measured temperature and distillate flow as inputs in the simulation model, while acid number and water content are predicted by the model. The reactor model is a simple ideally stirred tank batch reactor model.

The prediction of acid number is still good after simplification of the kinetic model, whereas the prediction of water content (wt%/wt%) is fairly good. At the end of the batch the water content prediction is negative, which of course is impossible. The reason is that some heavy components vaporizes at the end of the batch, while only vaporization of water and 1,2-propylene glycol is included in the model. In addition, the measurement error for the mass of distillate is relatively large, because this is a volumetric measurement from which the mass has been calculated based on a refractive index measurement to estimate
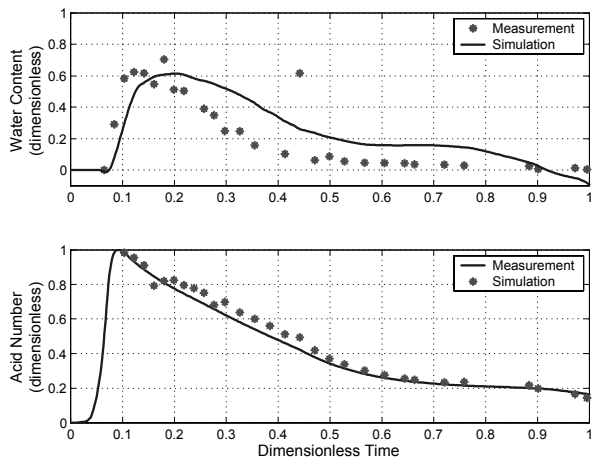
Figure 1: Comparison of simulated and measured acid number and water content in the reactor.

distillate composition. The simplified kinetic model is considered good enough for the intended purpose.

3 Modelling the industrial process

The production of unsaturated polyester in industrial scale usually takes place in a batch reactor system as shown in figure (2). The system consists of the reactor, heating and cooling circuit, a packed distillation column, condenser, condenser drum and accumulator. A typical batch cycle starts with feeding the reactants into the reactor. In the beginning the exothermic ring-opening reactions release heat and no heating is needed. When these reactions slow down, external heat is added trough the hot oil system. During esterification water is produced and starts evaporating into the column. Some of the water is used for cooling down the column, while excess water flows into the accumulator. At the end of the batch, the pressure is lowered to ease the removal of water. During the entire batch nitrogen is pumped into the reactor to prevent oxidation

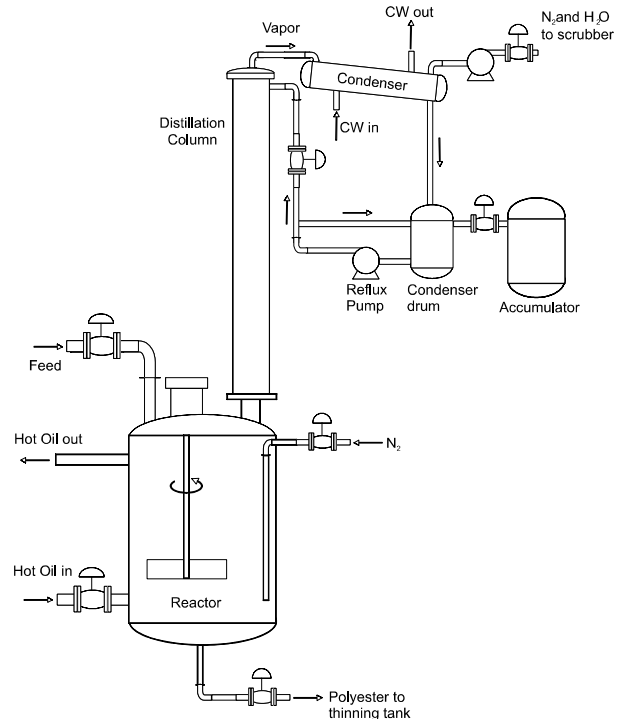and improve mixing in the reactor.

Figure 2: Overview of the unsaturated polyester process at industrial scale.

The idea of the modelling is to make as simple model as possible, but still having a model capable of representing important dynamic behavior of the process. Focus is on the reactor and the prediction of polymerization progress and properties such as acid number, water content, saturation fraction and molecular weight. Two models have been proposed and tested. Both models have the same description of the reactor mass balances, distillation column model, condenser and condenser drum model and accumulator model. The reactor total mass balance and component balances are given by (10)-(11).

$$\frac{dm_{tot}}{dt} = \dot{m}_{in} - \dot{m}_{out} \qquad (10)$$

$$\frac{dn_i}{dt} = r_i \cdot m_{tot} + l_i - v_i \qquad (11)$$

3

The total mass flow out of the reactor, $\dot{m}_{out}$, is trivially modelled as the sum of component molar flows multiplied by molecular weight. It is assumed that only the maleic anhydride, phthalic anhydride, ethylene glycol, 1,2-propylene glycol and water are volatile, and that reactions take place in the reactor vessel only. 25 different reactions among the 28 defined functional groups, reactants and products are used to describe the kinetics.

A standard equilibrium stage model is used for the packed distillation column where the number of stages is determined from packing data i.e. the number of ideal trays per meter packing height. The column model is based on the following assumptions: vapor-liquid equilibrium, negligible vapor holdup and constant molar holdup (liquid dynamics neglected). In the model $i = 1 : NC$, $NC = 5$, defines the components and $j = 1 : NT$, $NT = 12$, defines the equilibrium trays.

The internal vapor flow is equal the calculated vapor flow from the reactor into the column, while the internal liquid flow is equal the reflux flow multiplied by the factor q_D which accounts for subcooling of the reflux flow.

$$\frac{dx_{i,j}}{dt} = L\left(x_{i,j+1} - x_{i,j}\right) + V\left(y_{i,j-1} - y_{i,j}\right) \quad (12)$$

$$y_{i,j} = \gamma_{i,j} \cdot x_{i,j} \frac{P_{i,j}^{sat}(T_j)}{P_j} \quad (13)$$

$$0 = \sum_{i=1}^{NC} y_{i,j} - 1 \quad (14)$$

$$L_j = q_D \cdot L_D \quad (15)$$

$$V_j = V_R \quad (16)$$

$$V_{NT} = (1 - q_D) \cdot V_R \quad (17)$$

$$q_D = \frac{h_{sat}^V - h_D}{\Delta H^{vap}} \quad (18)$$

The condenser and condenser drum model (19)-(21) assumes that the condenser is total, and all components in the gas, except nitrogen, leaving the column top tray is condensed to liquid in the condenser drum.

$$\frac{dN_c}{dt} = V_{NT} - L_D - D \quad (19)$$

$$\frac{dN_c x_{i,c}}{dt} = V_{NT} y_{i,NT} - (L_D + D) x_{i,c} \quad (20)$$

$$\frac{dx_{i,c}}{dt} = \frac{1}{N_c}\left(\frac{dN_c x_{i,c}}{dt} - x_{c,i}\frac{dN_c}{dt}\right) \quad (21)$$

The flow D over the weir of the condenser drum is expressed as $D = 0$ if $h_c < H$ where $h_c = \frac{m_c}{A \cdot \rho_c} = h_c(T_c, x_c)$ is the height of liquid calculated from given temperature and composition in the condenser drum, and H is the height from the bottom to the weir. If $h_c \geq H$ the flow is calculated as $D = V \cdot \frac{M_{V_{NT}}}{M_c} \cdot \frac{\rho_c}{\rho_{V_{NT}}} - L_D + k \cdot (n_h - n_H)$. This equation comes from a volume balance if $h_c = H$, and the term $k \cdot (n_h - n_H)$ is a correction if $h_c > H$ in the calculations. This equation implicitly assume that the flow D is not restricted, e.g. from a small pipe diameter. The accumulator model is the simple mass balance (22).

$$\frac{dm_{acc}}{dt} = D \cdot M_c \quad (22)$$

The two proposed models differ in the way the molar fluxes v_i in the reactor model equations is calculated. *Model 1* uses the simplified reactor energy balance (23) to calculate the total molar flow V_R from reactor into the column. Specific heat is assumed constant, and the flow of nitrogen is neglected in the equations. Reactor temperature T_R is assumed known and is used as input in the simulations.

$$m_{tot} c_p \frac{dT_R}{dt} = Q_{oil} + Q_{rx} + L_1 \cdot h_1^L - V_R \cdot \Delta H_{vap} \quad (23)$$

$$Q_{oil} = UA \cdot \left(\overline{T}_{oil} - T_R\right) \quad (24)$$

$$Q_{rx} = \sum_{j=1}^{NR} r_j \cdot m_{tot} \cdot \Delta H_{rx,j} \quad (25)$$

The composition of the vapor flow $y_{i,R}$ is calculated from performing a PT-flash based on the liquid pressure, temperature and composition if the mixture is two-phase. The molar fluxes are calculated as $v_i = y_{i,R} \cdot V_R$.

Model 2 is based on calculating v_i from simple mass transfer equations (26) with constant mass transfer coefficients $k_g a_i$. This model also includes the flow of nitrogen in the calculations.

$$v_i = k_g a_i \cdot (P_i^* - P_i) \tag{26}$$

$$P_i^* = \gamma_{i,R} \cdot x_{i,R} \cdot P_i^{sat}(T_R) \tag{27}$$

$$P = \sum_i P_i + P_{N_2} \tag{28}$$

$$V_R = \sum_i v_i + \dot{N}_{N_2} \tag{29}$$

$$y_i = \frac{v_i}{V_R} = \frac{P_i}{P} \tag{30}$$

The total model of the system consists of 29 differential equations for the reactor, 60 for the column, and 7 for the condenser and accumulator giving a total of 96 differential equations. The number of algebraic equations for *Model 1* is 75, 72 from vapor-liquid equilibrium and summation equations in the column, 1 from the PT-flash equation and 2 from the calculation of q_D. *Model 2* has a total of 85 algebraic equation, 10 equations more than *Model 1* due to the mass transfer equations. The dynamic simulations are performed using a stiff differential-algebraic solver (*ode15s*) in MATLAB (The MathWorks Inc).

4 Results and discussion

During an industrial batch extra samples were taken from the reactor and analyzed for acid number and water content. In addition, the accumulated mass of distilled water from the reactor was measured together with temperatures in the column and reactor.

Focus in the model development was the reaction rates and the interaction between the reactor and column. The dynamic model was used to simulate the industrial process using measured reactor temperature, pressure and reflux temperature and estimated reflux flow as inputs to the model. A variety of outputs can be extracted from the model. Figures (3)-(5) show the measured and simulated acid number, water content and accumulated distillate mass, respectively.
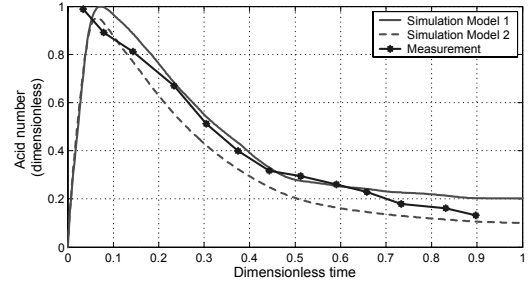

Figure 3: Comparison of measured and simulated acid number using the two different models.
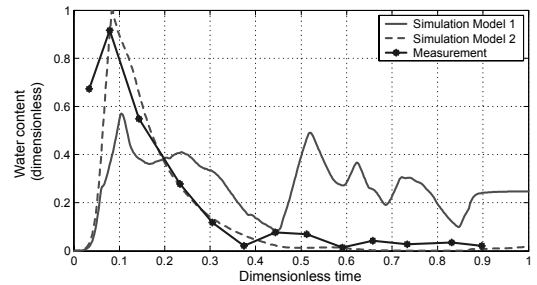

Figure 4: Comparison of measured and simulated water content using the two different models.

Model 1 and *Model 2* have different predictive characteristics. The acid number prediction of *Model 1* is better than *Model 2* in the middle of the batch, while *Model 2* gives the best prediction at the end of the batch. The acid number at the end of the batch is most important, and both models are quite inaccurate. *Model 2* is superior when it comes to prediction of water content, even though the model is not perfect. The accumulated distillate mass increases continuously until the dimensionless time is approximately 0.6, where the total pressure is decreased below 1 atm. During this vacuum period the amount of distillate flow can not be measured, and the measured accumulated distillate mass is constant even though more water is removed. *Model 1* uses the energy balance to calculate total vapor flow from the reactor, which makes this model able to predict
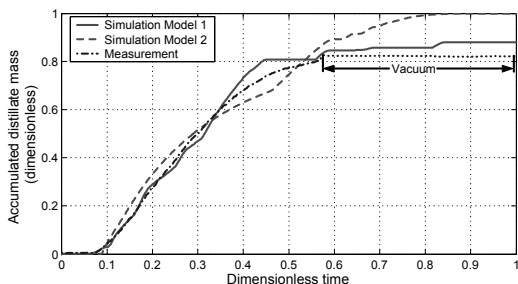
Figure 5: Comparison of measured and simulated accumulated distillate mass using the two different models.

variation in vapor flow caused by varying added heat. However, this model is insensitive to changes in total pressure since the influence of changing pressure is neglected in the energy balance, which makes *Model 1* incapable of predicting an increased vapor flow under the vacuum period. The mass transfer equations in *Model 2* are directly affected by the change in pressure through the equilibrium pressure P_i^*, and can predict an increase in vapor flow when the pressure is lowered. However, this model is decoupled from the energy balance and is not affected by changes is added heat except indirectly through the increase in reactor temperature.

There is a substantial coupling between these measured variables through the reversible reactions and the vapor flow. This means that prediction errors in one of the variables are likely to cause errors in the other two. The total model is sensitive to the calculation of vapor flow and composition from the reactor into the column. From the simulation results it can be concluded that *Model 2* is the best of the two models.

The column model and the thermodynamic properties calculation are simplified, and will probably contribute considerably to the deviations between simulated and measured values. It is a known fact in reactive distillation that the need for accurate thermodynamic models are essential for good performance of the models. In ordinary reactive distillation it has been shown that the kinetic model and the model of the column periphery have the most significant influence on the simulation results.[9]

5   Conclusions

The focus in this work was to develop a dynamic model of an industrial unsaturated polyester process suitable for simulation studies and advanced process control and estimation. An important feature of the combined reactor and separator system is the strong interactions between column and reactor. A detailed kinetic model was developed and verified against laboratory measurements, and the kinetic model showed good agreement with important measured variables.

Two different models were proposed for the industrial process. Both models are built from mass balances in the reactor, column and condenser. The models differs in the way component molar flows from reactor into the column are calculated. *Model 1* calculates these from the reactor energy balance and a flash calculation, while *Model 2* calculates these fluxes from mass transfer equations. Validation of the simulation results against industrial data has been done, and the results show that *Model 2* is best overall. The two models have different strengths and weaknesses, and the purpose of the model will determine which is best.

6   Acknowledgement

7   Symbols

a_i = interfacial area $[m^2]$

A = area of condenser drum $[m^2]$

c_i = concentration of component i $\left[\frac{mol}{kg}\right]$

c_p = specific heat capacity $\left[\frac{kJ}{kg \cdot K}\right]$

D = molar flow of distillate to accumulator $\left[\frac{mol}{min}\right]$

E = activation energy $\left[\frac{kJ}{mol}\right]$

6

h = height $[m]$

h_D = reflux enthalpy $\left[\frac{kJ}{mol}\right]$

h^L = liquid enthalpy $\left[\frac{kJ}{mol}\right]$

h_{sat}^V = saturated vapor enthalpy $\left[\frac{kJ}{mol}\right]$

H_c = height to weir in condenser drum $[m]$

ΔH_{rx} = heat of reaction $\left[\frac{kJ}{mol}\right]$

ΔH^{vap} = heat of vaporization $\left[\frac{kJ}{mol}\right]$

k = reaction rate constant

k_g = mass transfer coefficient

K = equilibrium constant

l_i = molar liquid flow of component i $\left[\frac{mol}{min}\right]$

L = total molar liquid flow $\left[\frac{mol}{min}\right]$

L_D = molar reflux flow $\left[\frac{mol}{min}\right]$

m = mass $[kg]$

$\dot{m}$ = mass flow $\left[\frac{kg}{min}\right]$

M = molecular weight $\left[\frac{kg}{mol}\right]$

n_i = number of moles of component i $[mol]$

n_h = number of moles in $h \cdot A$ (condenser) $[mol]$

n_H = number of moles in $H \cdot A$ (condenser) $[mol]$

N = total number of moles $[mol]$

$\dot{N}_{N_2}$ = molar flow of nitrogen $\left[\frac{mol}{min}\right]$

NC = number of components

NT = number of ideal trays

P = total pressure $[Pa]$

P_i = partial pressure of component i $[Pa]$

P^{vap} = vapor pressure $[Pa]$

P^* = equilibrium pressure $[Pa]$

q_D = fraction

Q_{oil} = heat added from oil $\left[\frac{kJ}{min}\right]$

Q_{rx} = heat added from reactions $\left[\frac{kJ}{min}\right]$

r = reaction rate $\left[\frac{mol}{kg \cdot min}\right]$

R = universal gas constant

T = temperature $[K]$

UA = overall heat transfer coefficient $\left[\frac{kJ}{K \cdot min}\right]$

v_i = molar vapor flow of component i $\left[\frac{mol}{min}\right]$

V = total molar vapor flow $\left[\frac{mol}{min}\right]$

$x_{i,j}$ = liquid mole fraction of component i at tray j

$y_{i,j}$ = vapor mole fraction of component i at tray j

Subscripts and superscripts

c = condenser

D = reflux

E = esterification

i = component i

I = isomerization

j = tray j

R = reactor

ro = ring-opening

S = saturation

V = vapor

Abbreviations

A = anhydride

$Acid$ = total amount of acid end groups

Cis = cis maleate ester or acid

$COOH$ = acid end group

Dbb = double bond

E = ester bridge

G = glycol

OH = alcohol end group

$SatDbb$ = saturated double bond

$Trans$ = trans fumarate ester or acid

References

1. Odian, G. *Principles of polymerization*, Wiley: New York, 1991.

2. Taylor, R.; Krishna, R. Modelling reactive distillation. *Chem. Eng. Sci.* **2000**, 55, 5183.

3. Chen, S.-A.; Wu, K.-C. Kinetics of polyesterification. II. Foreign acid-catalyzed dibasic acid and glycol systems. *Journal of Polymer Science* **1982**, 20, 1819.'

4. Paatero, E.; Närhi, K.; Salmi, T.; Still, M.; Nyholm, P; Immonen, K. Kinetic model for main and side reactions in the polyesterification of dicarboxilic acids with diols. *Chem. Eng. Sci.* **1994**, 49, 3601.

5. Salmi, T.; Paatero, E.; Nyholm, P; Still, M.; Närhi, K. Kinetics of melt polymerization of maleic and phtalic acids with propylene glycol. *Chem. Eng. Sci.* **1994**, 49, 5053.

6. Jedlovčnik, R.; Šebenik, A.; Golob, J; Korbar, J. Step-growth polymerization of maleic anhydride and 1,2-propylene glycol. Pol. Eng. Sci. **1995**, 35, 1413.

7. Salmi, T.; Paatero, E.; Lehtonen, J.; Nyholm, P; Harju, T.; Immonen, K.; Haario, H. Polyesterification kinetics of complex mixtures in semibatch reactors. *Chem. Eng. Sci.* **2001**, 56, 1293.

8. Zetterlund, P.B.; Weaver, W.; Johnson, A.F. Kinetics of polyesterification: modelling of the condensation of maleic anhydride, phtalic anhydride and 1,2-propylene glycol. *Poly. Reac. Eng.* **2002**, 10, 41.

9. Schneider, R.; Noeres, C.; Kreul, L.U.; Górak, A. Dynamic modeling and simulation of reactive batch distillation. *Comp. Chem. Eng.* **2001**, 25, 169.