Journal of Applied Sciences

ISSN 1812-5654
Modelling and Simulation of an Unsaturated Polyester Process

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Abstract: This study presents a dynamic model for a polyesterification reaction in a system containing a semi-batch wise operating reaction vessel connected to a distillation unit. This model can be used for multi-product batch production. The reaction between maleic anhydride and 1, 2-propylene glycol has been taken as a case study. The model has been developed in Aspen custom modeller. The reaction scheme is complex and the proposed model takes four types of reactions into account, ring opening, polyesterification, isomerisation and saturation reactions. The model includes kinetics, describing the change of rate order during the reaction, simple thermodynamics and mass balances. The parameter describing the changing rate order during the reaction is fitted. The acid value and water content have been used to validate the model and the model predicts these important variables reliably.

Key words: Unsaturated polyester, polyesterification, reaction and separation, kinetics

INTRODUCTION

The American chemist Wallace Carothers discovered in the late 1920's that reactions between dibasic acids and diols produce molecules with a high molecular weight (Carothers, 1929). These molecules contain multiple ester linkages and were therefore named polyesters. The arise and steady growth of the petro-chemical industry after World War II provided an extensive range of raw materials for the production of polyesters. The use of these new raw materials led to polyesters with superior physical characteristics, resulting in a steady growth in the production of polyesters. The polyesterification kinetics of dicarboxylic acids and diols has been studied initially by Flory (1939).

The polyesterification of dicarboxylic acids with diols is a commonly applied process in polymer industry. Polyesterification reactions are usually equilibrium-controlled and continuous removal of water is necessary to obtain high conversions. Thus most polyesters are produced in semi-batch reactors 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 separated from the polymer mixture in the reactor. The production of polyester has been carried out with a combination of different reagents for varying physical and chemical properties (Parker, 1966).

The presence of unsaturated carboxylic acids essentially leads to a complex reaction mechanism. The double-bond of the acid undergoes cis-trans isomerisation (Vaneso-Szmerosanyi et al., 1966) and the double-bond saturation takes place through the Ordelt reaction (Franglet and Marechal, 1982). Polyesterification also includes change of rate order during the reaction. The reaction follows first order with respect to the acid at the beginning and second order at the end of the reaction (Salmi et al., 1994). Although, the reactions appearing in this kind of polyesterification are well known, detailed kinetics studies of esterification reaction and side reactions of different carboxylic acids and diols mixtures are limited (Salmi et al., 2001).

The aim of the present study is to develop a model for multi-product batch production and the intended use is for simulation studies. The polyesterification of maleic anhydride with 1, 2-propylene glycol was used as model reaction in this study. The model includes detailed kinetics, describing the change of rate order during the reaction, simple thermodynamics and mass balances. The parameter describing the changing rate order during the reaction is fitted.

KINETIC MODELLING

The synthesis of unsaturated polyester from maleic anhydride and 1, 2-propylene glycol involves four types of reactions. First the reactants, anhydride (A) and Glycol (G) are mixed and heated to temperatures higher than 60-80°C. A very fast exothermic reaction ($\Delta H = -40 \text{ KJ mol}^{-1}$)
occurs and the acid and alcohol end group (COOH and OH) together with an ester bridge (E) as shown in Eq. 1.

\[ A + G = \text{COOH} + E + \text{OH} \]  

Esterification proceeds by the reaction of different acid and alcohol end groups to form new ester bridges and water, or by reaction of a glycol hydroxyl group with an acid end group to form an ester bridge and water as shown in Eq. 2.

\[ \text{COOH} + \text{OH} = E + \text{H}_2\text{O} \]  

Half mole of the water is consumed in the ring opening reaction as the ring of anhydride opens by reacting with water. The reaction order increases during the reaction because the change of the physical properties of liquid phase during the reaction and by the shift of the monomer-dimer equilibrium during the esterification reaction (Frandet and Marechal, 1982).

The double bond in maleic acid is isomerized at the higher reaction temperatures according to Eq. 3.

\[ \text{Cis} = \text{Trans} \]  

When the reaction temperature exceeds 180°C they effectively relieve the strain by transforming to the more planar trans-fumarate isomer, which reduces the steric congestion (Mark et al., 1985; Feuer et al., 1954). The corresponding fumarate polymers are subject to less steric interference as the Trans form and are able to assume a planar configuration, displaying reactivity almost 20 times of the maleate reaction products in subsequent copolymerization reaction with styrene (Melville and Burnett, 1954). The isomerization of maleate esters and oligomers to the corresponding fumarate derivatives during the polyesterification process is of fundamental importance in development of optimum physical characteristics (Parker, 1966). Hence, the side reaction is not regarded as loss.

The double bond in maleic anhydride is saturated by reacting with glycol, Eq. 4.

\[ \text{Dbb} + \text{OH} = \text{SatDbb} \]  

The saturation of the double bond causes cross-linking in the polymer and approximately 10-20% of the double bonds are saturated in the preparation of the polyester (Parker, 1966; Frandet and Marechal, 1982). This side reaction occurs in the first reaction stage and the destruction of unsaturation is favoured by higher initial temperatures. The thermal polymerization of maleic anhydride double bonds can also occur at elevated temperature, it follows that there is an optimum temperature for polyester production. The optimal temperature of the polyester process to avoid destruction of unsaturation and found optimal temperature is between 210 and 220°C (Parker, 1966).

**Rate equation:** 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 acids group are generated through the double bond saturation reaction (Orndt reaction).

The three carboxylic groups form three ester groups. The overall six basic functional groups of the carboxylic acids and esters and hydroxyl group are shown in Table 1. The three reactions, esterification, isomerization and saturation form network of nine reactions.

\[ \text{RCOOH}_{1d} + R'\text{OH} \rightarrow \text{RCOOR'}_{1d} + \text{H}_2\text{O} \]  

\[ \text{RCOOH}_{2d} + R'\text{OH} \rightarrow \text{RCOOR'}_{2d} + \text{H}_2\text{O} \]  

\[ \text{RCOOH}_{3d} + 0.5 R'\text{OH} \rightarrow \text{RCOOR'}_{3d} + \text{H}_2\text{O} \]  

**Isomerization reactions:**

\[ \text{RCOOH}_{1d} \rightarrow \text{RCOOH}_{2d} \]  

\[ \text{RCOOR'}_{1d} \rightarrow \text{RCOOR'}_{2d} \]  

**Saturation reactions:**

\[ \text{RCOOH}_{1d} + 0.5 R'\text{OH} \rightarrow \text{RCOOH}_{2} \]  

\[ \text{RCOOH}_{2d} + 0.5 R'\text{OH} \rightarrow \text{RCOOH}_{3} \]  

\[ \text{RCOOR'}_{1d} + 0.5 R'\text{OH} \rightarrow \text{RCOOR'}_{2} \]  

\[ \text{RCOOR'}_{2d} + 0.5 R'\text{OH} \rightarrow \text{RCOOR'}_{3} \]

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Abbreviations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl group</td>
<td>OH</td>
</tr>
<tr>
<td>Maleic acid end</td>
<td>COOH₁₀</td>
</tr>
<tr>
<td>Fumaric acid end</td>
<td>COOH₂₀</td>
</tr>
<tr>
<td>Saturated acid end</td>
<td>COOH₃₀</td>
</tr>
<tr>
<td>Maleate ester monomer (cis)</td>
<td>COOR₁₀</td>
</tr>
<tr>
<td>Fumarate ester monomer (trans)</td>
<td>COOR₂₀</td>
</tr>
<tr>
<td>Saturated ester monomer</td>
<td>COOR₃₀</td>
</tr>
<tr>
<td>Ester group</td>
<td>COOR'</td>
</tr>
</tbody>
</table>

Table 1: The functional groups in the polyesterification of maleic anhydride and 1, 2-propylene glycol
The esterification, isomerization and saturation reactions have been thoroughly discussed by Chen and Wu (1982), Pastor et al. (1994), Salmi et al. (1994, 2001), Jedlovec et al. (1995) and Zetterlund et al. (2002). In this modelling and simulation study the rate expressions and rate constants have been adopted from literature (Pastor et al., 1994; Salmi et al., 1994, 2001). The variable rate order expression from Salmi et al. (1994) has been changed by setting different definition of chemical equilibrium concentration and based on that new rate expression derived. (Salmi et al., 1994, 2001) has obtained rate order (n) expression according to Eq. 14 and 15 from semi-empirical differential equation \( dn = - an dc_{\text{COOH}} \).

\[
n = \left[1 - (1 - 2^{1-q}) C_{C} - C_{\text{COOH}} \right]^{q (1 - q)} \quad (14)
\]

\[
n = \left[1 - (1 - 2^{1-q}) \right]^{1/(1-q)} \quad (15)
\]

where, q is an adjustable exponent. This parameter is fitted in the present work for maleic anhydride and 1, 2-propylene glycol system. In this system the parameter q value is 7. The value for factor a is determined by integration of differential equation using the limits n = 1, \( c_{\text{COOH}} \) - \( C_{C} \) and n = 2, \( c_{\text{COOH}} \) - \( C_{eq} \). \( C_{eq} \) is the initial concentration of maleic anhydride and \( C_{C} \) is the equilibrium concentration. Salmi et al. (1994) has considered water and glycol vaporization effect to define an equilibrium concentration of carboxylic acid. In this study, an equilibrium concentration of carboxylic acid defined as Eq. 16 and water and glycol vaporization effect is counted in the dynamic batch reactor model. The conversion of carboxylic acid is given by Eq. 17.

\[
c_n = \frac{k_{i} \times c_{\text{COOH}} \times c_{H_{2}O}}{k_{i} \times c_{H_{2}O}} \quad (16)
\]

\[
x = \frac{C_{C} - c_{\text{COOH}}}{C_{C} - C_{eq}} \quad (17)
\]

The esterification, isomerization and saturation reactions are acid catalyzed and the strongest carboxylic acid gives dominant catalytic effect. The maleic acid is the strongest acid with respect to another acid in the system. Hence, the main contribution to catalytic effect is from maleic acid. The kinetic model in this paper differs from the kinetic model presented in Salmi et al. (1994) in way that the autocatalytic effect of the strongest carboxylic acid is considered only in the forward reaction. The rate expression for reactions (5-13) is given by (18-26), respectively.

**Esterification:**

\[
R_{1} = (k_{i} c_{\text{COOH}} c_{OH} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}} c_{eq}) \quad (18)
\]

\[
R_{2} = (k_{i} c_{\text{COOH}} c_{OH} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}} c_{eq}) \quad (19)
\]

\[
R_{3} = (k_{i} c_{\text{COOH}} c_{OH} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (20)
\]

**Isomerization:**

\[
R_{d} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (21)
\]

\[
R_{s} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (22)
\]

**Saturation:**

\[
R_{g} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (23)
\]

\[
R_{s} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (24)
\]

\[
R_{g} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (25)
\]

\[
R_{s} = (k_{i} c_{\text{COOH}} c_{eq}^{1-\alpha} \times k_{j} c_{\text{COOH}}) \quad (26)
\]

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 were lumped as follow:

\[
k_{i} = k_{i} = k_{i} = k_{s} \quad (27)
\]

\[
k_{j} = k_{j} = k_{j} \quad (28)
\]

\[
k_{i} = k_{i} = k_{i} = k_{s} \quad (29)
\]

\[
k_{i} = k_{i} = k_{i} = k_{s} \quad (30)
\]

\[
k_{i} = k_{i} = k_{i} = k_{s} \quad (31)
\]

\[
k_{i} = k_{i} = k_{i} = k_{s} \quad (32)
\]

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/(c^1), where (x) is exponent of component I and activation energy (E_0) in KJ mol^-1.
Table 2: Recalculated Arrhenius law parameters from Salmi et al. (1994).

<table>
<thead>
<tr>
<th>Reactions</th>
<th>k</th>
<th>E_k</th>
<th>k'</th>
<th>E_k'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Esterification</td>
<td>120000</td>
<td>75000</td>
<td>620</td>
<td>59000</td>
</tr>
<tr>
<td>Isomerization</td>
<td>127000</td>
<td>56000</td>
<td>178</td>
<td>41700</td>
</tr>
<tr>
<td>Saturation</td>
<td>273</td>
<td>47000</td>
<td>176</td>
<td>40600</td>
</tr>
</tbody>
</table>

Recalculated from reaction rate data published in (Salmi et al., 1994). The Arrhenius law parameters are tabulated in Table 2.

The kinetic model is validated against laboratory measurement of acid value from Salmi et al. (1994). The total concentration of the carboxylic group (acid value), the concentration of trans-isomer as well as the saturation concentration are related to the functional groups as:

\[ C_{COOH} = C_{COOH} + C_{COOH} + C_{COOH} \]
\[ C_i = C_{COOH} + C_{COOH} \]
\[ C_f = C_{COOH} + C_{COOH} \]

**REACTOR 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 polymerization progress and properties such as acid value, water content, fraction isomerization, fraction saturation and molecular weight. The model presented here accounts for a reactor-separation system which consist of reactor, distillation column and a distillate accumulator. 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:

\[ \frac{dC_i}{dt} = r - \frac{V_{i}}{M_i} \]

where, c is concentration of component I in mol kg\(^{-1}\), r is reaction rate in mol/kg/hr, V\(_i\) is vapour phase flow rate in mol/hr and M\(_i\) is initial total mass of the reactant. The only glycol and water are assumed to be volatile in the system. 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\(_{in}\) and the vapour-liquid equilibrium ratio K\(_i\) can be written as Eq. 37.

\[ V_i = K_{in} \left( x_i - \frac{Y_i}{K_i} \right) \]

The total vapour in the reaction vessel is given by Eq. 38.

\[ V_i = V_{fg} + V_{water} \]

The vapour phase mass balance according to Eq. 39 includes the mass transfer from liquid phase and the flow out from the vapour phase of the reactor.

\[ \frac{dy_i}{dt} = -F_{out} y_i + V_i \]

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 calculated by an isothermal flash calculation as, (Seader and Henley, 2006):

\[ Z F_{out} = L x_i + V y_i \]
\[ y_i = K_i x_i, \quad K_i = \frac{P}{P} \]

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 Raoult’s law. P is the vapour pressure of the pure component I and P is the total pressure of the system. The mole fraction is calculated by:

\[ x_i = \frac{x_i}{\sum x_i}, \quad y_i = \frac{y_i}{\sum y_i} \]

The properties of the liquid melt polymerized polyester in the Flory (1939), the degree of polymerization, the molecular weight number and molecular weight is calculated as, respectively:

\[ DP = \frac{1}{(1 - X)} \]
\[ MWN = \frac{188}{(1 - X)} \]
\[ MWW = 158(1 + X) \]

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where, $X$ is conversion and 188 is molecular weight of repeated unit in the polymer chain.

**RESULTS**

The dynamic model can be used for unsaturated polyester production from different reagents. The simulation results presented in this paper for the reaction of maleic anhydride with 1,2 propylene glycol. The simulation has been performed at the temperature 160, 180 and 200°C and at 1 atm pressure. The molar ratio of the anhydride and glycol is 1:1.1. The initial amounts of maleic anhydride and 1, 2-propylene glycol were 5 mol and 5.5 mol, respectively. The simulation has been performed in Aspen Custom Modeller. The dynamic model is validated against experimental results for acid value and water content from Salmi et al. (1994). The acid value presented here is in terms of total carboxylic acid concentration (33) in mol kg$^{-1}$ as shown in Fig. 1. The model predicts reliably the concentration profile at the different temperature.

The dimensionless water content, $\lambda$ of the distillate as calculated by Eq. 46 is compared with the result of Salmi et al. (1994) in Fig. 2. The water content of the distillate is in good agreement with experimental results from Salmi et al. (1994).

$$\lambda = \frac{M_D}{M_S + M_D}$$  \hspace{1cm} (46)

where, $M_D$ is the accumulated distilled mass. The changing rate order during the reaction and the strong autocalytic effect of maleic acid is illustrated in Fig. 3. The isomerisation concentration (Eq. 34) and saturation concentration (Eq. 35) increases at higher temperature as shown in Fig. 4 and 5, respectively. The isomerisation and double bond saturation are fast at the beginning and, they will reach equilibrium at the end. The saturation effect of the double bond of an unsaturated acid can be lowered by setting process at low beginning temperature. The simulated results of isomerisation and saturation concentration profile could not be verified due to the lacking of the experimental data.

The concentration of each functional group and H$_2$O concentration are shown in Fig. 6. The product distribution in maleate esters, fumarate ester and saturated ester of melt polymerized polyester has been shown in Fig. 7. It is noticeable from the product distribution that percentage of maleate ester is 15-25%, percentage of fumarate ester is 50-60% and saturated ester is 20-30%. The fraction of saturation is higher than the reported

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**Fig. 1:** Comparison of simulated concentration profile of carboxylic acid with experiments (Salmi et al., 1994)

**Fig. 2:** Comparison of simulated dimensionless water content with experiments (Salmi et al., 1994) at 180°C

**Fig. 3:** Order of reaction at different temperature
Fig. 4: Isomerization fraction at the different temperature

Fig. 5: Saturation concentration at the different temperature

1: C_{COOH}, 2: C_{COO}, 3: C_{CON}, 4: C_{CON},
5: C_{OSO}, 6: C_{OS}, 7: C_{OH}, 8: C_{HO}

T = 180°C

Fig. 6: Simulated liquid-phase concentration profile of functional groups and H₂O

T = 180°C

Fig. 7: Simulate product distribution of melt polymerized polyester

Fig. 8: Comparison of simulated molecular weight number profile with experimental result of (Jedlovenik et al., 1995)

by Parker (1966) and Frandet and Marechal (1982) because simulation performed isothermally at 180°C. In the practice polyesterification reaction temperature in the second half of the process is higher than 180°C and at higher temperature fraction of saturation is lower as shown in Fig. 5. The degree of polymerization, molecular weight number and molecular weight derived from conversion and molecular weight of repeated unit according to Eq. 43-45, respectively. The degree of polymerization is between 12 and 14. The molecular weight number profile is shown in Fig. 8. The molecular weight number at the end of the polymerization is in good agreement with the industrial data from Jedlovenik et al. (1995).
CONCLUSION

The focus in this study was to develop a dynamic model of an industrial unsaturated polyester process suitable for simulation studies. An important feature of the combined reactor and separation system is the strong interaction between column and reactor. A detailed kinetic model was developed and verified against laboratory measurements. The behavior of the model system, the polyesterification of the unsaturated carboxylic acid and two side reactions, isomerisation and double bond saturation was predicted well.

ACKNOWLEDGMENT

The authors would like to thank Dutch Separation Technology Institute (DSTI) for funding the project.

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