

IMPROVED DYNAMIC MODEL FOR AN UNSATURATED POLYESTER PROCESS BY NON-IDEAL THERMODYNAMICS

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Summary

An extended dynamic model is presented for a polyesterification reaction in a semi-batch wise operated vessel connected to a distillation column. The developed model describes the effect of polymerization on reactants. The model also contains kinetics describing the change of rate order during the reaction. To improve the predictive capabilities, the model has been extended with advanced thermodynamic POLYNRTL activities. The extended model is subsequently validated with experimental data from literature. It was found that the prediction of distilled mass (regression coefficient (R^2) = 0.995) and propylene glycol concentration (R^2 = 0.97) in distilled mass is significantly improved.

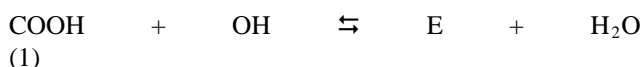
Keywords

Polyesterification, Unsaturated polyester, polymer thermodynamics, POLYNRTL

Introduction

Traditionally polyester production is done in two steps, first reaction, and then separation. A promising alternative for intensification of this process is by means of reactive distillation. To value such alternative production route reliable process models are required. In this paper we discussed the development of a dynamic model for the polyester process of our interest.

Carboxylic acids react with diols and form a polyester:



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:



and a double bond saturation reaction:



During the polyesterification reaction, a change of rate order occurs. Esterification reactions are usually equilibrium-controlled, and continuous removal of water is necessary to obtain high conversions. Esterification, isomerization and saturation reactions have been thoroughly discussed by number of authors. However, only Salmi et al.¹ have studied the unsaturated polyester kinetics including the change in rate order during the reaction. In earlier work², a dynamic model was developed that includes detailed kinetics describing the change of

rate order during the reaction. The ideal behaviour of polymer mixture in the liquid phase was also incorporated in the kinetic model. However, the ideal behaviour assumption prohibits a reliable prediction of the vapour liquid equilibrium and thus the concentration of components in the vapour and liquid phase. Non-ideal behaviour of the unsaturated polyester mixture and the effect of an unsaturated polyester mixture on the activity of the components have to our knowledge not been addressed yet in the scientific literature.

In this work we extended the previously developed reaction model with non-ideal behaviour thermodynamics to improve the description of the vapour liquid equilibrium. In our approach, we used a segment based activity coefficient model - polymer, non-random, two-liquid (POLYNRTL). The activity coefficient parameters were estimated by Aspen property plus. The polyesterification of maleic anhydride with 1, 2-propylene glycol was used as model reaction in this study. The dynamic model has been developed in Aspen custom modeller.

Thermodynamics Modelling

The current unsaturated polyester process is operated at low pressure (1 bar), and at the end of the process under vacuum to completely remove water from the polymer mixture. 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

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the partial pressure of species i in the vapour phase, p_i equals to

$$p_i = x_i \gamma_i(x_i, T) p_i^{\text{sat}}(T) = y_i P \quad (4)$$

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 POLYNRTL and UNIQUAC. The POLYNRTL model is selected as it is less complex compared to UNIQUAC. POLYNRTL is available in Aspen property plus. The POLYNRTL 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. The model parameters estimation procedure is described in figure 1. The activity coefficient parameters of the POLYNRTL model were estimated by ASPEN Property Plus.

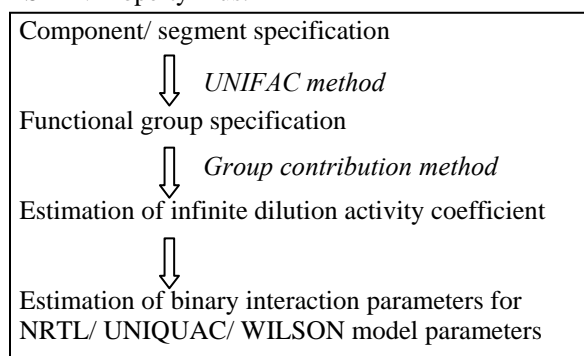


Figure 1: Model parameters estimation procedure

The POLYNRTL model activity coefficients ($\gamma_i = f(b_{ij}, b_{ji}, \alpha)$, $\alpha = 0.3$) were used in the vapour liquid equilibrium equation (4) to describe the non-ideal behaviour of the polymer during the polyesterification reaction.

Results

By extending the model with activity coefficients obtained from the POLYNRTL model, the predictive capabilities are improved significantly. The model is verified with the experimental data¹. The model improved the prediction of the dimensionless distilled mass ($\zeta = M_D/M_O$, where M_D is distilled mass and M_O is the initial total mass of the reactants) and the weight fraction of the propylene glycol compared to ideal behaviour modelling, shown in figures 2 and 3, respectively. The dimensionless distilled mass is under predicted in the case of ideal behaviour compared to non-ideal behaviour as shown in figure 2. The reason is that due to the non-ideal behaviour glycol, water, maleic and fumaric acid are present in the vapour phase instead of only glycol and water. The regression coefficient (R^2) for dimensionless distilled 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 using only ideal behaviour compared to experimental data as illustrated by figure 3. The regression coefficient (R^2) for weight fraction of propylene glycol is 0.97 in non-ideal behaviour

modelling, which shows that improved model reliably predicted the weight fraction of propylene glycol.

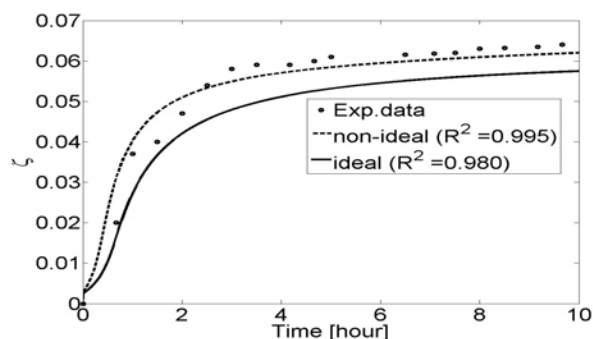


Figure 2: Dimensionless distilled mass

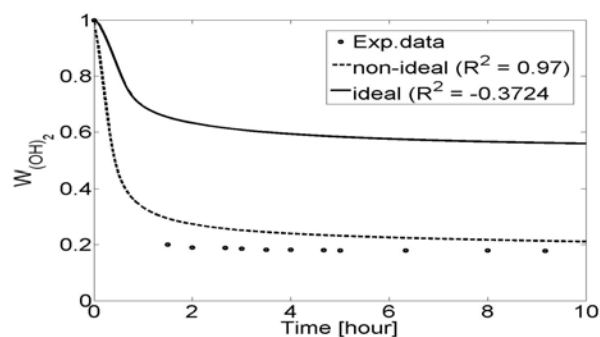


Figure 3: Weight fraction of propylene glycol in the distillate

Conclusion

In this work we have extended a dynamic model for a polyesterification reaction with the POLYNRTL non-ideal thermodynamics model. Validation of the improved model with the experimental data has demonstrated that the predictive capabilities improved significantly.

References

- (1) Salmi, T. and Paatero, E. 1994. Kinetics of melt polymerization of maleic and phthalic acids with propylene glycol. *Chemical Engineering Science* **1994**, 49, 5053-5070.
- (2) Shah, M.; Zondervan, E.; De haan, A. B. Modelling and simulation of an unsaturated polyester process. *The Proceeding of 3rd International Conference on Chemical & Bioprocess Engineering - Universiti Malaysia Sabah, Kota Kinabalu, Sabah 2009*, CPE-10, 334-339