Predicting Kinetics of the PET Glycolysis Reaction using an electrolyte thermodynamics-based framework.

Accounting for the thermodynamic activity of the Zn^{2+}-catalyst on reaction kinetics of PET depolymerisation.

Maria Schlüter, Christoph Held

The optimization of the reaction conditions of a chemical reaction usually requires extensive experimental efforts to maximize kinetics. This is caused by the fact that reaction kinetics typically depend on reactant concentration(s), catalyst concentration, temperature, and co-solvents that might be present in the reaction mixture. One of the most important depolymerization reactions is the polyethyleneterephthalate (PET) glycolysis reaction. Currently, only empirical methods are available for modeling PET glycolysis kinetics. Such models do not have any predictive power and thus, these rely heavily on experimental data and are limited to defined operation conditions. In this work, a predictive model was developed aiming at predicting the impact of reactant ratio, catalyst concentration, and co-solvent effects on the equilibrium + kinetics of the PET glycolysis. To this end, the electrolyte equation of state ePC-SAFT was used in an activity-based kinetic framework. The thermodynamic activity of the catalyst zinc acetate was included, enabling the incorporation of catalyst interactions with the liquid environment in the reaction phase. The results showed very promising results, meaning that thermodynamics is highly useful to screen the most promising reaction conditions that allow fast reaction kinetics and maintain the high equilibrium yield of PET glycolysis.

In the present study, we developed an activity-based model to predict the kinetics of the PET glycolysis reaction, given by the following expression for the rate *r*:

$$r \cdot \bar{a}_{ZnAc_2} = k^{int} \cdot x_{PETru} \cdot \gamma_{PETru} \cdot x_{EG} \cdot \gamma_{EG} - \frac{k^{int}}{K_{th}} \cdot x_{BHET} \cdot \gamma_{BHET} \qquad (1)$$

Here, *x* and *γ* denote the mole fraction and the activity coefficient of the reaction partners PETru (ru=repeating unit), EG (ethylene glycol) and BHET. k^{int} and K_{th} are the intrinsic kinetic constant and the thermodynamic equilibrium constant. An electrolyte theory was necessary to model the activity of the catalyst ($ZnAc_2$) as well as *γ* of the reaction partners PETru, EG and BHET. In this work, ePC-SAFT was used to model the interactions of Zn^{2+} with the solvent and with the reactants as well as among the reaction partners. The pure-component parameters and binary interaction parameters were obtained from reaction-independent data (e.g., solubility data). We used the hetero-segmented approach to retrieve PC-SAFT parameters for the PET repeating unit to reduce the number of parameters (strength of PC-SAFT for polymer systems).

In a first step, new experimental data were provided in this work tackling the influence of different reactant ratios and of the catalyst concentration on the kinetics of the PET glycolysis reaction. One experimental kinetic curve was used to determine the experimental kinetic constant, which was then used as input data to enable the development and validation of the predictive ePC-SAFT-based kinetic model in Eq. (1) including k^{int}, which is <u>not</u> a function of catalyst or concentration. The latter is included in the catalyst activity coefficient and thus, in a_{ZnAc2} in Eq. (1). This approach allows predicting reaction kinetics as a function of reactant ratio and of catalyst concentration (cf. Fig. 1 (upper)) as well as of the green co-solvent *γ*-valerolactone (GVL), cf. Fig 1 (lower), which is an outstanding result. This big advancement not only contributes to the theoretical understanding of PET glycolysis but also reduces the need for extensive experimental work in the future.

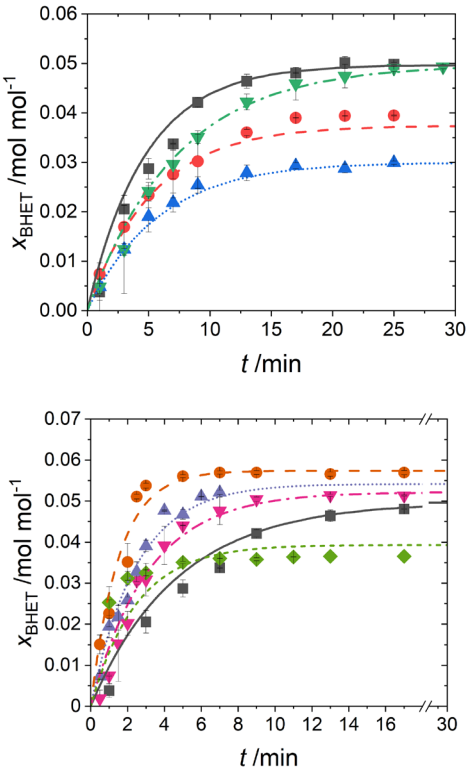

Figure 1. BHET mole fraction x_{BHET} over reaction time *t* for different GVL ratios and catalyst concentrations at 190°C and 1 bar. Experimental data (symbols) vs. ePC-SAFT modeling (lines). Black: co-solvent free reaction with PETru:catalyst ratio of 50. **Upper**: Red, blue: Same as black but with higher EG excess over PETru (30%,60%). Green: Same as black but halved catalyst concentration. **Lower**: Pink, violet, orange: Same conditions as black but with GVL addition (12%,24%,48%). Green: Same conditions as black but with GVL addition (48%) and halved catalyst concentration.

christoph.held@tu-dortmund.de (C. Held)

Publications:
Schlüter, M.; Bhutani, S.; Wohlgemuth, K.; Held, C., Predicting Kinetics of the PET Glycolysis Reaction Using an Activity-Based Model and Experimental Validation. Industrial & Engineering Chemistry Research 63 (2024), 15458-15465.
https://doi.org/10.1021/acs.iecr.4c02382