AUTO-CATALYTIC EFFECT OF ACETIC ACID ON THE KINETICS OF THE METHANOL / ACETIC ANHYDRIDE ESTERIFICATION

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1. Introduction

The exothermic esterification reaction of acetic anhydride with methanol is a widely used test process for safety-oriented investigations in the field of chemical engineering. For the modelling and simulation of dynamic processes during fault scenarios caused by runaway reactions, a reaction kinetic model is needed to describe the thermal reaction course over a wide temperature range. At the Institute of Safety Research the esterification reaction is used as a test process to model and simulate pressure relief processes and safety-relevant fault scenarios caused by local exothermicities (i.e. hot spots due to stirrer faults) in stirred tank reactors as well as to simulate reacting flows using CFD codes in general. These research tasks make great demands on the kinetic models to reproduce the thermal and chemical reaction courses over a wide range of the temperature and the concentration. This includes the consideration of special reaction mechanisms like autocatalytic effects. To develop a kinetic model that fulfils these requirements, extensive calorimetric investigations using on-line FTIR analyses were carried out and special evaluation methods have been developed. From these investigations, a two-step kinetic model results in fulfilling the requirements mentioned above.

2. Applicability of existing reaction kinetic models

The exothermic esterification reaction of acetic anhydride with methanol proceeds according to the following reaction equation:

$$\underset{\substack{\textit{acetic anhydride}\\ AAH}}{(CH_3CO)_2O} + \underset{\substack{\textit{methanol}\\ ME}}{CH_3OH} \rightarrow \underset{\substack{\textit{methyl acetate}\\ MA}}{CH_3COOCH_3} + \underset{\substack{\textit{acetic acid}\\ AA}}{CH_3COOH} \qquad \Delta H_R = -66\ \text{kJ/mol}$$

A basic kinetic model requirement for the use in safety-oriented investigations is the validity of the model in respect of the reproduction of the thermal reaction course over a wide temperature range. For this purpose, in the past the kinetic models were usually developed by means of experiments using adiabatic calorimetry. From the literature, there are some kinetic models available obtained by experiments in adiabatic calorimeters using a fixed initial molar ratio of the educts [1,2]. These so called overall kinetics approaches, describing the reaction rate r as a function of the reaction temperature T and the concentrations of the educts [AAH] and [ME], have the following model structure:

$$r = k_0 \cdot e^{\left(\frac{-E_A}{R \cdot T}\right)} \cdot [AAH]^m \cdot [ME]^n \qquad (1)$$

In equation (1), E_A is the activation energy and k_0 is the frequency factor. The exponents m and n are the reaction orders with respect to the reactants acetic anhydride and methanol. The overall reaction order is given by the sum of the exponents m and n.

To model and simulate different safety-relevant fault scenarios from the start of the reaction via the fault event to subsequent chemical processes, the kinetic models have to reproduce the thermal reaction course and the concentration courses over wide ranges of the temperature and the concentration. Furthermore, the models should also reproduce the reaction courses in the adiabatic, isothermal and isoperibolic process control. To check the applicability of the existing kinetic models, isothermal and adiabatic esterification reactions at several initial molar ratios of educts were carried out using the RC1 calorimeter (isothermal experiments) and the calorimeter PhiTecII (adiabatic operation). Figure 1 shows the thermal reaction course of an isothermal esterification in comparison to simulation results using kinetic models taken from the literature [1,2]. Both the kinetics are based on adiabatic experiments using an initial molar ratio of [ME] : [AAH] = 2 : 1. The course of the reaction temperature of an adiabatic experiment compared to simulations using the same kinetic models is shown in Fig. 2.

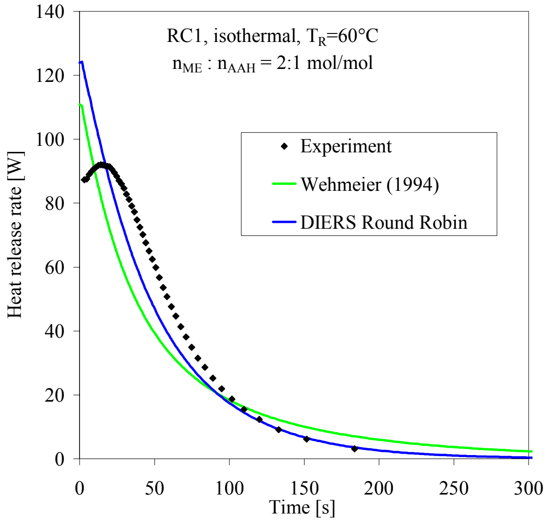

Fig.1: Thermal reaction course of the isothermal esterification

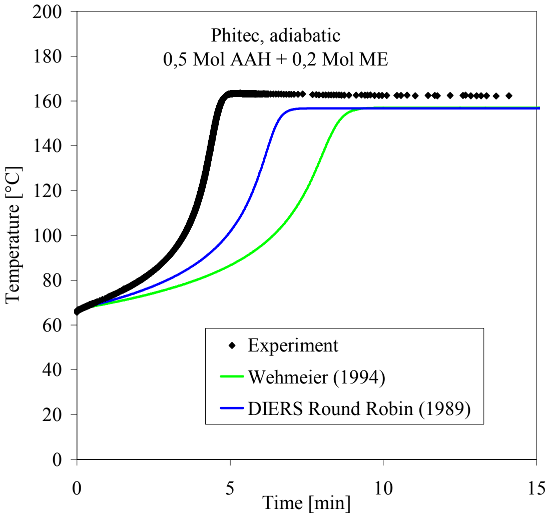

Fig.2: Course of the reactor temperature during the adiabatic esterification

Especially, the thermal process behaviour at the start phase of the isothermal reaction is not describable by the structure of the models. Furthermore, the thermal reaction course in the adiabatic operation is not reproduced if the educt concentrations differ from the initial molar ratio of [ME] : [AAH] = 2 : 1. Thus, the following conclusions were drawn in terms of the model validity in case of this particular reaction:

- The validity of the existing 2^{nd} and pseudo 1^{st} order overall kinetics is confined to the adiabatic operation.
- The validity of the existing kinetics is confined to the educt concentrations used in the experiments to develop the models.

Therefore, the development of advanced reaction kinetic models was necessary to fulfil the model demands mentioned above.

3. Setting up a new model structure

It is assumed that the increasing reaction rate at the beginning of the isothermal esterification (Fig.1) is caused by the autocatalytic effect of the acetic acid formed during the reaction. The autocatalytic behaviour was proven by isothermal esterification using the RC1 calorimeter. For this purpose, different amounts of acetic acid were added to the reaction mixtures before the reactions were started. Figure 3 shows the thermal reaction courses of the related experiments.

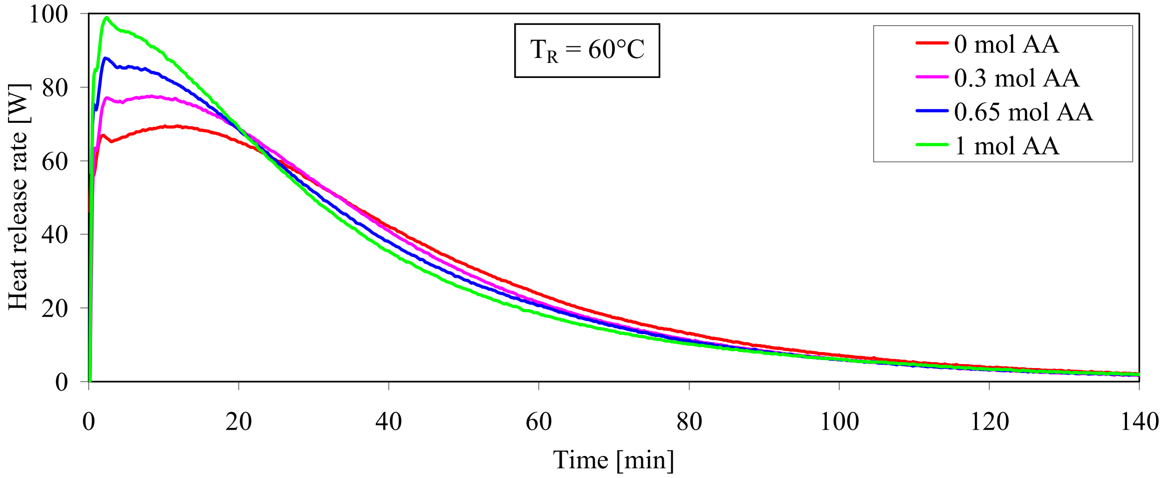

Fig. 3: Thermal reaction courses of isothermal esterification with addition of acetic acid

As can be seen from Fig. 3, the reaction rate at the beginning of the esterification increases with the increasing amount of the added acetic acid. Therefore, the time-dependent acetic acid concentration has to be inserted into the kinetic model as a new model parameter. To maintain the usual structure of the overall kinetic models, the autocatalytic reaction was modelled as two simultaneous reaction steps – the uncatalysed esterification of acetic anhydride according to equation (2) and the esterification catalysed by acetic acid according to equation (3).

$$r_1 = k_{0_1} \cdot e^{\left(\frac{-E_{A_1}}{R \cdot T}\right)} \cdot [AAH]^{m_1} \cdot [ME]^{n_1} \tag{2}$$

$$r_2 = k_{0_2} \cdot e^{\left(\frac{-E_{A_2}}{R \cdot T}\right)} \cdot [AAH]^{m_2} \cdot [ME]^{n_2} \cdot [AA]^{p_2} \tag{3}$$

With $$r = r_1 + r_2 \tag{4}$$

By using the standard overall kinetics structure, most of the commercially available simulation tools can be used to model and simulate the autocatalytic esterification process.

4. Estimation of the model parameters

Since the autocatalytic effect on the reaction course plainest appears under isothermal conditions, the activation energies and the frequency factors have to be estimated by means of isothermal experiments. For the fitting of the isothermal reaction rate constants, the simulation programs ProSim Batch and BatchCAD were used. However, the Arrhenius Plots as a result of the isothermal experiments at different temperatures and educt concentrations to calculate the model parameter $E_{A,i}$ and $k_{0,i}$ based on the isothermal rate constants show different activation energies and frequency factors depending on the initial batch concentration. These dependencies could not be avoided by changing the reaction orders. Therefore, it was decided to set the reaction orders with respect to each substance in the equations (2) and (3) to 1 and to introduce the initial batch concentration, defined as the start molar fraction of acetic anhydride x_0 according to equation (5), as a new parameter into the kinetic model.

$$x_0 = \frac{n_{0,AAH}}{n_{0,AAH} + n_{0,ME}} \tag{5}$$

In equation (5), $n_{0,AAH}$ and $n_{0,ME}$ are the initial amounts of substances of the acetic anhydride and of the methanol, respectively.

The activation energies and the frequency factors depending on the start molar fractions are shown in Fig. 4 and Fig. 5, respectively.

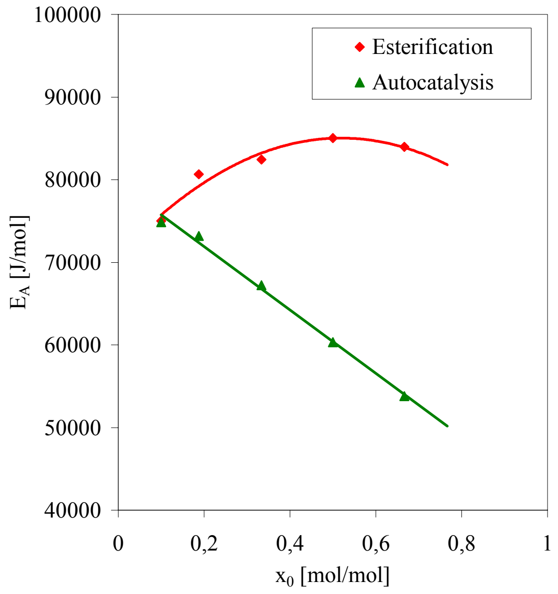

Fig. 4: Activation energies depending on the start molar fraction

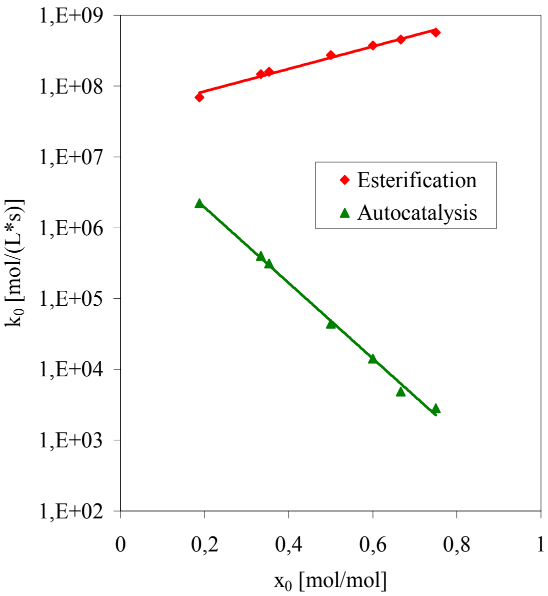

Fig. 5: Frequency factors depending on the start molar fraction

The equations to calculate the model parameters depending on the start molar fraction were obtained by fitting the parameters based on the isothermal experiments and subsequent adjustment by means of adiabatic esterification. As a result, the following reaction kinetic model was obtained [4]:

$$r_1 = k_{0_1} \cdot e^{\left(\frac{-E_{A_1}}{R \cdot T}\right)} \cdot [AAH] \cdot [ME] \tag{6}$$

$$r_2 = k_{0_2} \cdot e^{\left(\frac{-E_{A_2}}{R \cdot T}\right)} \cdot [AAH] \cdot [ME] \cdot [AA] \tag{7}$$

$$E_{A_1} = 15924\,(x_0)^2 + 20568\,x_0 + 77337 \tag{8}$$

$$E_{A_2} = -40472\,x_0 + 80750 \tag{9}$$

$$k_{0_1} = -1.36 \cdot 10^8 + 1.36 \cdot 10^8 \cdot e^{(2.2\,x_0)} \tag{10}$$

$$k_{0_2} = 2 \cdot 10^7 \cdot e^{(-12.28\,x_0)} \tag{11}$$

5. Verification of the reaction kinetics

The verification of the kinetics was carried out by isothermal and isoperibolic experiments using the RC1 calorimeter in conjunction with an on-line FTIR spectrometer as well as by adiabatic esterification using the PhiTecII calorimeter. Figures 6 and 7 show the thermal reaction courses of isothermal experiments in comparison to simulation results for different temperatures and molar fractions of the educts, respectively.

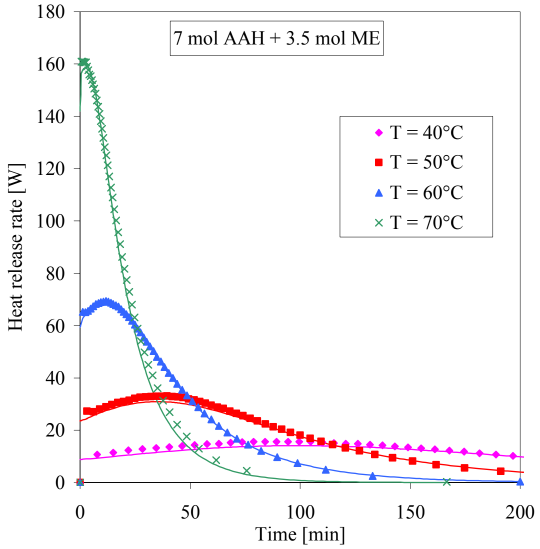

Fig. 6: Thermal reaction courses of isothermal esterification at different temperatures

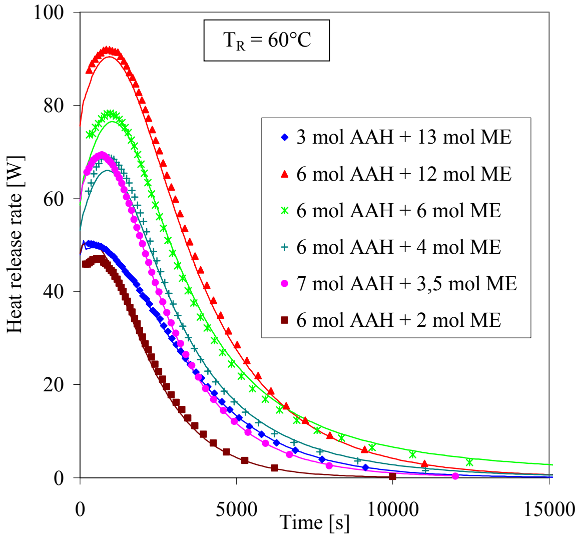

Fig. 7: Thermal reaction courses of isothermal esterification at different start molar fractions

The results of the simulations are in good accordance with the experimental data. Furthermore, the autocatalytic startup behaviour of the reaction is reproduced correctly. To estimate the model accuracy in case of the isoperibolic and the adiabatic process control, results of RC1 and PhiTecII experiments were compared to the related simulations.

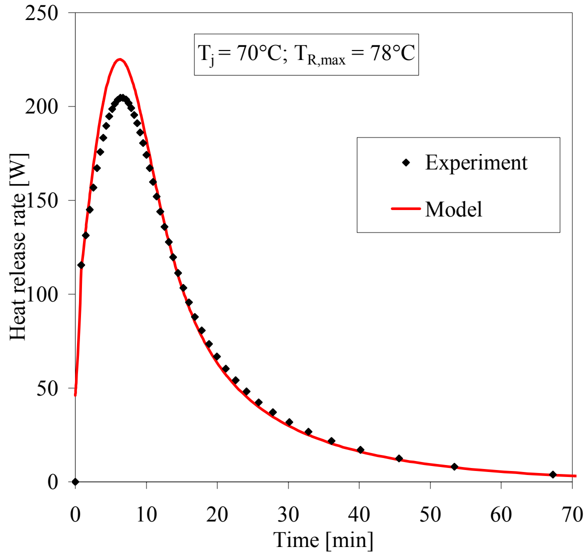

Fig. 8: Thermal reaction course of the isoperibolic esterification

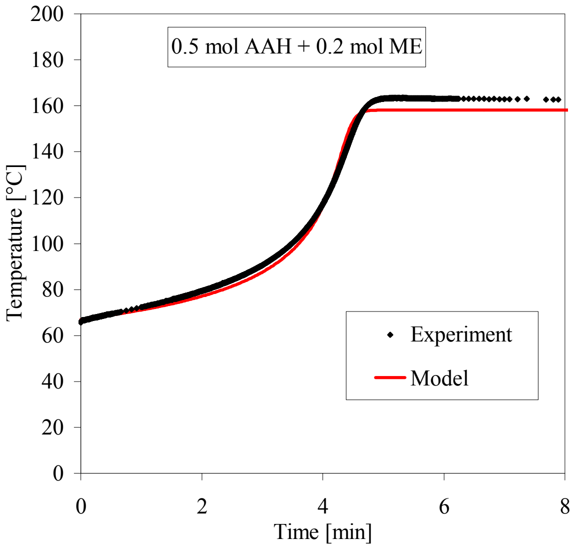

Fig. 9: Course of the reaction temperature during the adiabatic esterification

The thermal reaction courses of selected esterification at isoperibolic and adiabatic conditions are diagrammed in Fig. 8 and 9, respectively. The runs of the curves are reproduced correctly in case of both the isoperibolic and the adiabatic process mode. Solely, in using the kinetics to simulate the isoperibolic process, the maximum heat release rate oversteps the experimental value slightly. However, the relative model inaccuracy never exceeds a value of 10% during the whole process course. As a result of the model verification, it was found that the new reaction kinetic model is able to reproduce the process behaviour correctly within an educt molar fraction in the range of $x_0 = 0.1875 \ldots 0.75$.

6. Summary and outlook

A new two-step reaction kinetic model was developed for the esterification reaction of acetic anhydride with methanol by using calorimetric investigations and analytical methods. The main advantage of the new model over previously existing overall kinetics is the adaptability on wide educt concentration ranges. By taking into account the autocatalytic effects of the acetic acid, the model now can be used to simulate the process in the isothermal, isoperibolic and adiabatic operation. This wide field of applications is achieved by modelling the process as two simultaneous reaction steps and fitting the activation energies as well as the frequency factors depending on the initial molar fraction of acetic anhydride. For final conclusions on the model performance in terms of the applicability for simulations of safety-relevant fault scenarios like pressure relief processes, the new kinetic model has to be tested using appropriate simulation software (i.e. BRICK [3]).

A problem for the application of the new reaction kinetics to simulate reacting flows results from using empirical functions to estimate the model coefficients depending on the initial molar fraction. Thus, the actual process state described by the model depends on the initial process state. Therefore, it is difficult to simulate processes where the variations of the concentrations are not caused by the chemical reactions exclusively (i.e. semibatch processes, effects of mass transfer). Consequently, an alternative reaction kinetic model having the following structure is developed presently:

$$r = k_0([AA]) \cdot e^{\left(\frac{-E_A([AA])}{R \cdot T}\right)} \cdot [AAH]^m \cdot [ME]^n \tag{12}$$

In this model, both the activation energy and the frequency factor are inserted as functions of the actual acetic acid concentration [AA] to consider the autocatalytic effects. Thus, the alternative model structure has a stronger theoretical background and comprises model parameters, which depend on the actual process state exclusively. To estimate the functional dependencies $k_0([AA]$ and $E_A([AA])$, a new differential evaluation method was developed. The evaluation of the experiments according to the new method is still in progress but first results show the practicability of the model structure in general.

References

[1] G. Wehmeier (1994), Theoretische und experimentelle Untersuchung der Vorgänge bei der Druckentlastung von Chemiereaktoren, Fortschr.-Ber. VDI Reihe 3, 373, VDI-Verlag Düsseldorf

[2] J. C. Leung, M. J. Creed and H. G. Fisher (1989), Round-robin “Vent sizing package” results, Int. Symp. Runaway React., 264-280

[3] D. Lucas (2000), BRICK - a one-dimensional simulation tool for multiphase flow in vessels, Chemical Engineering and Technology, 23, 845-849

[4] S. Bohm (2004), Erarbeitung eines reaktionskinetischen Modells der Veresterung von Essigsäureanhydrid mit Methanol zur Einbindung in Druckentlastungs-Simulationsprogramme und CFD-Codes, Diploma thesis, TFH Berlin