Safety Challenges on Runaway Reactions: the Esterification of Acetic Anhydride with Methanol

Federico Florit[a], Sabrina Copelli*[,b]

[a]Politecnico di Milano, Dip. di Chimica, Materiali e Ingegneria Chimica "G. Natta", Via Mancinelli 7 - 20131 Milano – Italy
[b]Università degli Studi dell'Insubria, Dip. di Scienza e Alta Tecnologia, Via Valleggio 9 – 22100 Como - Italy
sabrina.copelli@uninsubria.it

Esterification reactions are commonly used in industrial practice. These reactions are fast and moderately exothermic thus they are prone to exhibit a runaway behavior, that is a thermal loss of control of the synthesis reactor. This scenario may lead to either quality issues, such as formation of undesired side products, or safety concerns, as pressurization and rupture of the reactor itself.

To mitigate the risk, proper recipes should be designed and optimized for a safe conduction of the reaction at the full-plant scale. This can be done by knowing the kinetics of the involved reactions, both desired and undesired.

The aim of this work is to determine the kinetic parameters of the esterification of acetic anhydride with methanol (forming methyl acetate) in the presence of sulfuric acid as a catalyst to be used in a cost-effective safe optimization protocol. This reaction has been analyzed in the past because of its exothermicity, but without fully describing the involved reactions (both desired and side).

In this work, calorimetric measurements are used to observe both the thermic and quality characteristics of the overall synthesis run in a semi-batch, lab-scale reactor. Both a detailed kinetic scheme and the associated parameters are determined to provide safe and productive operating conditions for the process, properly considering all the side reactions than could emerge during the synthesis. The study also required the implementation of a dedicated mathematical model for the simulation of the lab-scale semi-continuous reactor.

1. Introduction

Runaway phenomena in chemical reactors have been extensively analyzed in the process safety literature of the last thirty-five years (e.g., Maestri et al., 2009; Copelli et al., 2010, 2013; Casson et al., 2012, 2016). Particularly, a runaway reaction can be described as the consequence of the thermal loss of control of a reacting system, triggered by a number of different upset operating conditions: e.g., anomalies in the dosing line, cooling system failures, temperature controller breakdown or external fires. This type of phenomenon, also referred to as thermal explosion, always results in a huge increase of the desired reaction rate that, increasing the system temperature, could trigger unwanted decomposition reactions of the reacting mixture. Whenever a decomposition occurs within a reactor, it is not possible to protect the vessel against overpressures because the rate of incoercible gases generation is so high to make impossible a realistic vent sizing. This means that the reactor will unavoidably explode releasing high amounts of toxic and/or flammable gases into the atmosphere. Terrible examples of runaway scenarios were Seveso (1976) and Bhopal (1984) accidents that implied disastrous consequences for both workers and inhabitants of the neighboring of the damaged factories. As a good practice, to either evaluate the consequences or prevent the triggering of a thermal runaway in a chemical reactor, a series of thermochemical and kinetic data are usually required. Particularly, it is necessary to know reaction enthalpy and heat capacity of the reacting mixture, boiling point of the reacting mixture (if boiling phenomena can be triggered in the temperature range of interest), maximum allowable temperatures above which dangerous decomposition reactions can be triggered and their reaction enthalpy, amount and rate of gas evolution, and last, but not least, the detailed kinetics of all the involved reactions. Moreover, it is also important to take into account all features related to either the reactants feeding procedures (linear, ramp, etc..) and the reactor temperature control (isothermal, isoperibolic, etc..).

All these information are then used to write a suitable system of ordinary differential equations (ODEs) where mixing rules for volumes determination, global and components material balance equations, reactor and jacket energy balance equations, dosing strategies and reactor temperature control equations must be inserted to describe completely the analyzed process dynamics under whatever operating conditions.

In this work, the relevant case study of the esterification of acetic anhydride and methanol catalyzed by sulfuric acid was studied to determine, using a "pure" calorimetric approach (that is, using only reaction calorimeters of Peltier-cells type), the kinetics of all the reactions involved within the synthesis path of this process.

The results showed that, for moderately exothermic and fast reactions (as that one selected in the present study), it is possible to employ a pure calorimetric approach to completely characterize the dynamic of the process avoiding loss of accuracy in the reaction kinetics determination. All data obtained in the present analysis, also including the kinetics, could be therefore used to either optimized the proposed synthesis or simulate the system dynamics under both desired (e.g. using either an isothermal or an isoperibolic temperature control mode) and upset operating conditions (such as those originated by cooling system failures or the presence of an external fire).

2. Materials and methods

2.1 Case study

The esterification of acetic anhydride with methanol can be described by the following chemical reactions, all catalyzed by sulfuric acid:

$$A + B \xrightarrow{r_1} C + D \tag{1}$$

$$D + B \xrightleftharpoons[r_{2-}]{r_{2+}} C + W \tag{2}$$

$$A + W \xrightarrow{r_3} 2D \tag{3}$$

where A is acetic anhydride, B methanol, C methyl acetate (the product of interest), D acetic acid, W water. Therefore, the main esterification reaction (Eq (1)) is complemented with the esterification of acetic acid (Eq (2)), and the hydrolysis of acetic anhydride (Eq (3)). As written, the reactions are all exothermic and contribute to the exothermicity of the process. Eq (1) and Eq (3) are considered to be irreversible due to the large (negative) Gibbs free energy of reaction at common temperatures for the process (-10 – 25 °C). Instead, Eq (2) is considered to be reversible as the reaction Gibbs energy is small and positive (NIST). The catalytic effect of weak acids (*i.e.*, acetic acid) will be neglected and only the catalysis of sulfuric acid will be considered. All reactions rates are modelled using a power law, where the reaction order is unitary for reagents and sulfuric acid, while it is null for products; each reaction rate, r_j, is characterized by a kinetic constant k_j described by an Arrhenius' law. Consequently, all reactions are overall third order or they can be considered first order with respect to the reagents (overall second order) but with a kinetic constant that is dependent on the concentration of sulfuric acid. The uncatalyzed reactions happening in the system are neglected.

The kinetic constants (pre-exponential factor and activation energies) of the four reactions can be found via fitting of experimental data. Given the formation enthalpies, the Gibbs free energy of formation (NIST), and the specific heat capacities (described via polynomial functions of temperature as detailed in Green et. al (2019)) of the species involved, it is possible to establish a relationship between the forward and backward reactions (2) using the Van't Hoff and Kirchhoff's laws.

In particular, the ratio between the two kinetic constants can be found as a function of temperature: $k_{2+}/k_{2-} = 1.36 \cdot 10^{-2} \exp(959/T[K])$, which shows that the backward reaction is always thermodynamically favored with respect to the forward reaction (2) for all standard process temperatures. This relationship will be used as a constrain on the experimental data fitting for the determination of the unknown kinetic parameters.

Experimental data were collected using three recipes, attempting to decouple the reactions, as Eq (1) triggers Eq (2) and (3), but Eq (2) alone does not trigger Eq (1) and (3). The reactions were run both under isoperibolic and isothermal conditions in reactors having volumes of 500 mL and 1 L.

Table 1 reports the recipes of the three experiments, indicating which species were fed and the temperature mode of operation (isoperibolic/isothermal).

Such tests will be used to fit the kinetic expressions of Eq (1), Eq (2) and Eq (3).

Acetic anhydride (> 99%), methanol (> 99.9 %), acetic acid (> 99 %), and concentrated sulfuric acid (97%) were purchased from Sigma Aldrich and used without further purification.

*Table 1: Parameters of the experimental tests. The symbol * on the mass indicates that the species was fed; (J) beside the temperature indicates isoperibolic conditions, while (R) indicates isothermal conditions.*

Exp	Acetic anhydride [g]	Methanol [g]	Acetic acid [g]	Sulfuric acid [g]	Temperature [°C]	Feed time [s]
1	55.0 *	150.0	0	0.47	20 (J)	9
2	81.3 *	222.3	0	1.00	20 (J)	10
3	0	192.2	90.1	5.0 *	20 (R)	14

2.2 Calorimetric Reactors

All the tests carried out within the present work were conducted within Peltier-cells calorimeters, namely Easymax 102™ and Optimax 1001™ from Mettler Toledo. Such workstations are widely used for studying reactions under a calorimetric point of view (Zogg et al., 2004).

The main concept behind their functioning consists in exploiting a Peltier element to control the temperature of either the reacting mixture or the reactor walls. A Peltier cell is an element made of a coupling of semiconductors which can heat or cool the reactor jacket (that is, the reactor wall) according to a supplied electrical power.

In short, a temperature controller evaluates the electrical power that should be supplied to the Peltier element in order to compensate the required heat flow.

They can be operated within a wide range of temperatures, that is -40 °C/180 °C, therefore allowing for studying different groups of chemical reactions (from esterifications to nitrations, sulfonations, polymerizations, oxidations, etc..).

The temperature control (either isoperibolic or isothermal) is achieved by the means of a Proportional-Integral controller, which can be tuned according to the reactive mixture type (organic or aqueous) and reactor nominal volume (from 100 mL to 1L).

These devices can provide different outputs such as: the overall heat flow exchanged between reactor and its walls, jacket and reactor temperature vs. time trend (from which it is possible to retrieve reaction kinetics), volumes variations, viscosity trends (through the monitoring of the power absorbed by the stirring unit; such a function is very useful to investigate the effects of the use of different agitator types, that is anchor, propeller, etc..). In addition, with the use of a dedicated calibration probe, it is possible to evaluate both the global heat transfer coefficient and the specific heat of either the reacting mixture or all the involved substances (system calibration when a reaction is running can be done but taking into account a certain loss of accuracy; the same holds true whenever a boiling phenomenon is occurring).

The system is also provided with a dedicated software (iControl) that can be used to automatically integrate heat flow curves (both online and offline) to easily retrieve values such as reaction heat, calorimetric conversion, and adiabatic temperature rise.

One of the main concerns related to the use of these systems, and in general to the use of calorimetry, to study reaction kinetics of complex reacting systems (that is, where more than one exothermic reaction occurs) is related to their limitations in uncoupling the contributions of the different reactions to the overall heat flux released during the synthesis. This is particularly true when very fast reactions, such as esterifications (either catalyzed or not), must be characterized.

Anyway, in principle, it is always possible to search for operating conditions where the exothermicity of all reactions, but one, is negligible, therefore permitting to study the kinetics of the "thermally active" reaction (with a good degree of accuracy for a use in either safety or optimization purposes) using a pure calorimetric approach.

2.3 Mathematical model

The experimental apparatus can be modelled as a non-isothermal semi-batch reactor where temperature (of either the reactor or the jacket) is controlled through a proportional-integral control action.

Experimentally, the addition of acetic anhydride in methanol leads to a very slight cooling due to endothermic mixing. Only this non ideality (mixing enthalpy) will be considered, while all other properties will be computed under the assumption of ideal mixtures.

From a species material balance equation, the evolution over time, t, of the number of moles of each species i can be described by the following equation:

$$\frac{dn_i}{dt} = F_i(t) + \sum_j^{NR} \nu_{ij} r_j V \tag{4}$$

where F_i is the (constant) molar feed flowrate of species i, NR is the number of reactions, ν_{ij} is the stoichiometric coefficient of species i in reaction j, and V the reaction volume.

The thermal inertia of the impeller and measuring instruments, together with the cooling effect of the head of the reactor, were considered in an energy balance equation to describe the evolution of temperature, T, over time:

$$\left(m_L c_p^L + C_p^S\right)\frac{dT}{dt} = -\sum_j^{NR} \Delta H_{R,j} r_j V - \sum_i^{NC}\left(F_i(t)\int_{T_F}^{T} c_{p,i}(\tau)\, d\tau\right) - F_{dos}(t)\Delta h_{mix} - \dot{Q} \tag{5}$$

where m_L is the liquid mass, c_p^L is the liquid mixture specific heat capacity, C_p^S the heat capacity of the inserts (impeller and instruments, given by the experimental apparatus), $\Delta H_{R,j}$ the j-th reaction enthalpy, NC the number of species involved in the system, $c_{p,i}$ the specific heat capacity of species i, $F_{dos} = \sum_i^{NC} F_i$ the total feed flowrate, Δh_{mix} the mixing enthalpy, and $\dot{Q}$ the thermal power exchanged with the jacket and the external environment. The mixture specific heat capacity is computed as a mass-average of the pure species heat capacities (polynomial functions of temperature).
The mixture enthalpy is obtained via fitting of the experimental data.
The thermal power is computed as:

$$\dot{Q} = UA\left(T - T_j\right) + (UA)_{ext}(T - T_{ext}) \tag{6}$$

where U is the global heat exchange coefficient, A the wetted surface, T_j the jacket temperature (controlled variable in the control loop), and $(UA)_{ext} = 0.1\,W/K$ a term considering the heat exchange at the top of the reaction vessel due to the external temperature $T_{ext} = 19\,°C$. U considers the resistances given by the vessel glass wall (roughly 130 W/m²/K) and the internal convection. The latter is computed with a correlation for agitated vessels equipped with propellers (using Nienow correlation (Green et al., 2019)), taking into account the effect of the impeller speed and the fluid properties. The Nusselt number for internal convection is evaluated as:

$$Nu = 0.46\,Re^{2/3} Pr^{1/3} \tag{7}$$

where Re is the Reynolds number and Pr is the Prandtl number of the mixture. Re is evaluated as $ND^2\rho/\eta$, being N the propeller rotation speed (200 rpm in this work), D the propeller diameter, ρ the mixture density (computed as an ideal mixture), and η the dynamic viscosity of the mixture (computed as a weight average of the pure species viscosities). Pure liquid densities and viscosities were expressed as a function of temperature (Green et al., 2019) while constant thermal conductivities were used.
The jacket temperature is controlled using Peltier cells and the control action is described by:

$$T_j = K_p\left(\varepsilon + \frac{1}{\tau_I}\int_0^t \varepsilon(\tau)\, d\tau\right) \tag{6}$$

where the proportional action, K_p, is equal to 4 and the integral time, τ_I, is equal to 500 s for the 500 mL reactor and 60 s for the 1 L reactor.
The aforementioned equations were numerically solved and the results fitted to the experimental data to obtain the unknown kinetic parameters (namely, the kinetic constants and the activation energies for the three forward reactions 1-3). The objective function selected was the sum of square errors of the reactor temperature.

3. Results

Experimental tests #1, #2 and #3, whose recipes are detailed in Table 1, were used to fit the kinetics of Eq (1) to Eq (3). Particulalry, Figure 1 reports the comparison of experimental reactor temperature vs model predictions, showing a good agreement. Figures 1a and 1b denote the endothermic effect of mixing, accounted for by a mixing enthalpy of about 4 kJ/mol (in good agreement with the value of 5 kJ/mol reported in Casson et al. (2012)). The slight overestimation of the peak temperature can be due to a minor evaporation of the solvent (neglected in the model) which was observed in the experiments, as droplets formed on the vessel ceiling. Figure 1c shows that reaction (2) is almost thermally neutral and that the integral action of the temperature controller becomes relevant leading to oscillations.
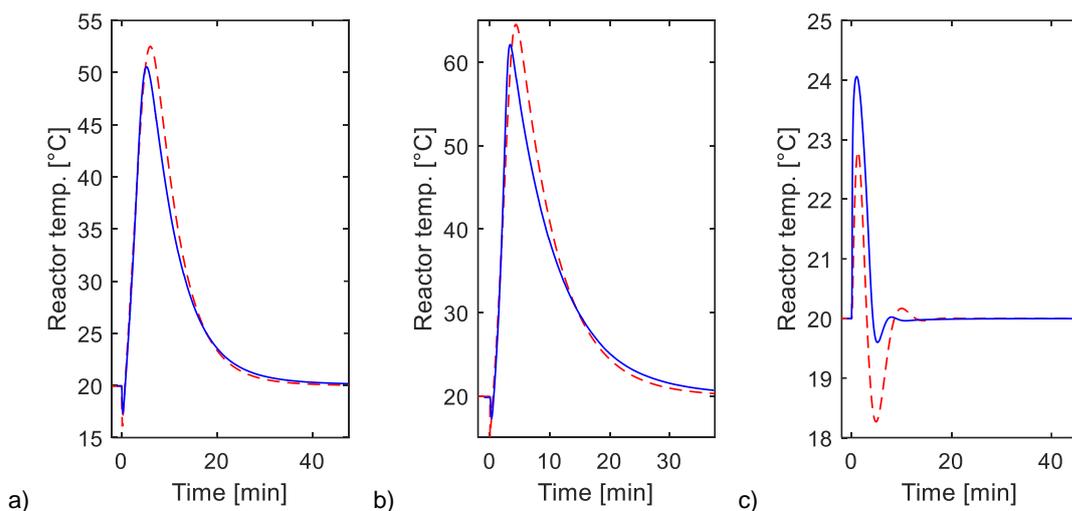
Figure 1: Comparison of the experimental data (solid blue line) and model predictions (dashed red line) for experiment 1 (a), 2 (b), and 3 (c).

The fitted kinetic parameters and the reaction enthalpies at 25 °C are reported in Table 2. The reaction enthalpies considered in the model were derived from the reactants and products formation enthalpies (NIST) and their comparison with the experimental values obtained from Tests #1, #2 and #3 was good. Moreover, for Eq (1), the modeled value well agrees with the experimental one determined by Casson et al. (2012).

Table 2: Obtained kinetic parameters and reaction enthalpy at 25 °C.

	Reaction 1	Reaction 2+	Reaction 2-	Reaction 3
Pre-exponential factor [L^2 mol^{-2} s^{-1}]	$1.28 \cdot 10^5$	$2.87 \cdot 10^3$	$1.69 \cdot 10^{10}$	$2.15 \cdot 10^5$
Activation energy [kJ mol^{-1}]	41.6	34.8	66.9	42.8
$\Delta H_R(25°C)$ [kJ mol^{-1}]	−64.0	−8.2	−57.8	+8.2

The predictions of the global heat exchange coefficient and the specific heat capacity estimated through correlations were compared to the values measured at the end of the reaction and the agreement was satisfactory with errors below 10 % for the specific heat capacity and below 6 % for the exchange coefficient.
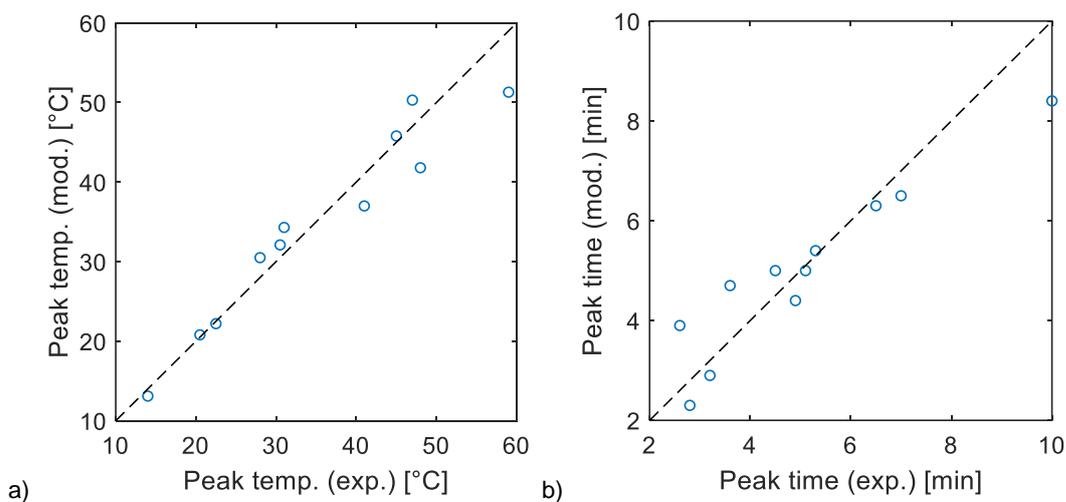

Figure 2: Comparison of peak temperature value (a) and time location (b) between the model predictions and the experimental data from Casson et al. (2012). The experiments are run with different sulfuric acid concentrations and various jacket temperatures. The value of UA was set to the measured value of 4.2 W/K.

The model predictions were also compared to the experimental results given in Casson et al. (2012), where the esterification of acetic anhydride is conducted with a large methanol excess, using different concentrations of sulfuric acid and various jacket temperatures under isoperibolic conditions. The peak temperature value and location (over time) is compared to the predictions of the proposed model in Figure 2.

The agreement is satisfactory both for the value of the peak (Figure 2a) and its location (Figure 2b), showing that the proposed model can be used under very different reaction conditions.

4. Conclusions

This work aimed at demonstrating that it is possible to study the kinetics of a series of fast and moderately exothermic reactions using a simple calorimetric approach.

The relevant case study of the acid catalyzed (by concentrated sulfuric acid) esterification between acetic anhydride and methanol was selected to demonstrate that, in most cases, it is always possible to uncouple the contributions of the different reactions to the overall heat flux released during the synthesis by selecting different operating conditions where all reactions, but one, are "thermally inactive". The kinetics of the "thermally active" reaction can be therefore studied, with a good degree of accuracy for a quick and easy application for either optimization or safety purposes, using reaction calorimetry.

Particularly, the following kinetic parameters were estimated through the fitting procedure:

- Reaction 1: Pre-exponential factor [$L^2 mol^{-2} s^{-1}$]= $1.28 \cdot 10^5$, Activation energy [kJ mol^{-1}] = 41.6;
- Reaction 2+: Pre-exponential factor [$L^2 mol^{-2} s^{-1}$]=$2.87 \cdot 10^3$, Activation energy [kJ mol^{-1}] = 34.8;
- Reaction 2-: Pre-exponential factor [$L^2 mol^{-2} s^{-1}$]=$1.69 \cdot 10^{10}$, Activation energy [kJ mol^{-1}] = 66.9;
- Reaction 3: Pre-exponential factor [$L^2 mol^{-2} s^{-1}$]=$2.15 \cdot 10^5$, Activation energy [kJ mol^{-1}] = 42.8.

Moreover, the use of Peltier cells calorimeters instead of reaction calorimeters (equipped with a flowing coolant within the reactor jacket) was found to be sufficiently accurate to determine all the thermochemical and kinetic parameters required to simulate the dynamics of a potentially runaway system. Particularly, the most important advantages in the use of Peltier cells calorimeters for either safety or quick optimization purposes are: a) a low cost in terms of hardware employed in the study; b) a quick start up of the system due to the presence of the Peltier cells for thermal (heat and cool) conditioning; c) the wide choice of reactors nominal volumes (calorimetric experiments can be done down to a 100 mL scale).

In conclusion, the results achieved within this work demonstrate that a pure calorimetric approach to study reaction kinetics for safety purposes is highly promising and suggests possible future applications to other complex reacting systems.

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