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The Limit of DSC as a Preliminary Tool to Determine the Safety Parameters?

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Safety studies are essential during the process design, but how to determine the safety parameters of a chemical process? To determine the value of safety parameters, DSC is often mentioned as a reference tool because it is safer due to the small amount of sample used. The goal of this manuscript is to illustrate the deviation between safety parameters obtained by DSC and the ones obtained by calorimetric reactor. An accident scenario, due to a cooling failure has been carried out to obtain the maximum temperature of the synthesis reaction in an open reaction system.

1. Introduction

Safety study is an important part in the evaluation of chemical process. It is quite challenging to teach this science at undergraduate student because a good knowledge in chemical reaction engineering and thermal analysis are needed. Micro-calorimetric approach, particularly DSC, is often recommended to make the first assessment to get the safety parameters such as MTSR: maximum temperature of the synthesis reaction, TMR_{adr} and TMR_{add}: time to maximum rate under adiabatic condition for the desired reactions and degradation ones. However, results obtained by these micro-calorimetry methods should carefully extrapolate to industrial or lab-scale reactor (Lin and Tseng., 2012).

There are several reasons for these errors: absence of mixing in the crucibles, reaction in closed system and real adiabatic conditions. The goal of this article is to compare safety parameters obtained in case of cooling failure for an open lab-scale reactor and those obtained by DSC.

An example of biomass valorization is discussed: epoxidation of vegetable oil. Epoxidized vegetable oils can be used as biolubricant or for the synthesis of polymer. Furthermore, there are renewable, non-toxic and biodegradable. Safety and greener way of production is to synthesize *in situ* a peroxycarboxilic acid from the corresponding carboxylic acid and hydrogen peroxide (Figure 1). Several exothermic reactions occur in parallel as described by Santacesaria et al. (2011) and Salzano et al. (2012)

DSC experiments were performed in dynamic and isothermal mode, and lab-scale experiments were performed in semi-batch reactor under normal and cooling failure conditions.
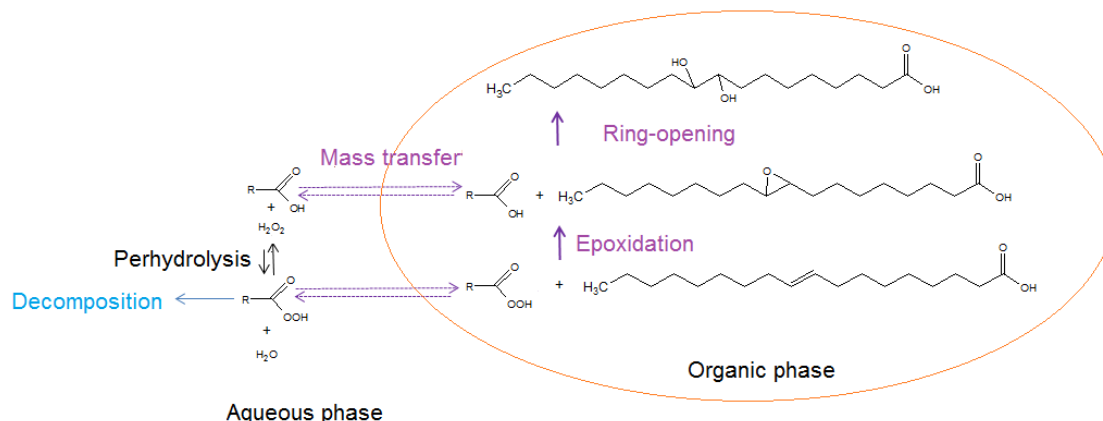
Figure 1: Simplified mechanism of oleic acid epoxidation by peroxycarboxylic acid.

2. Experimental section

2.1 Calorimetric semi-batch reactor

A detail description of the setup can be found in the article of Leveneur et al. (2012). In the first stage, oleic acid, hydrogen peroxide and water were added into the reactor. Then, when the reactor temperature was reached, pre-heated formic acid was added into the reactor. System was isoperibolic mode. To mimic a cooling failure scenario, circulation of the heat transfer fluid in the jacket was stopped. Table 1 shows the experimental matrix.

Table 1: Experimental matrix.

Jacket temperature [°C]	50-70
$[H_2O_2]_{o,aq}$ [mol/L]	8.0-8.9
$[H_2O]_{o,aq}$ [mol/L]	35-40
[Oleic acid]$_{o,org}$ [mol/L]	3.15
F_{FA} [mol/min]	0.02-0.5
Addition time [min]	2-40
Time of cooling failure [min]	2.15-4.00

2.2 DSC experiments

Chemicals and concentration used for DSC were the same as the ones for calorimetric reactor. Because semi-batch operation is not possible, thus, all the chemicals were added at once into a gold-plated high pressure crucible (M20 crucible from Swiss Institute for the Promotion of Safety & Security). Table 2 shows the experimental matrix.

Table2: Experimental matrix.

Total mass [mg]	5-6
[Heating rate [°C/min]	2-4
Temperature range [°C]	50-140

2.3 Analysis

Concentrations of peroxyformic and formic acid were analyzed by titration towards a solution of sodium hydroxide and hydrogen peroxide was analyzed by a solution of ammonium cerium sulphate. Concentration of oxirane was determined by a method of Jay.

3. Results and discussion

Figure 2 is a well-known representation of cooling failure scenario in semi-batch mode.
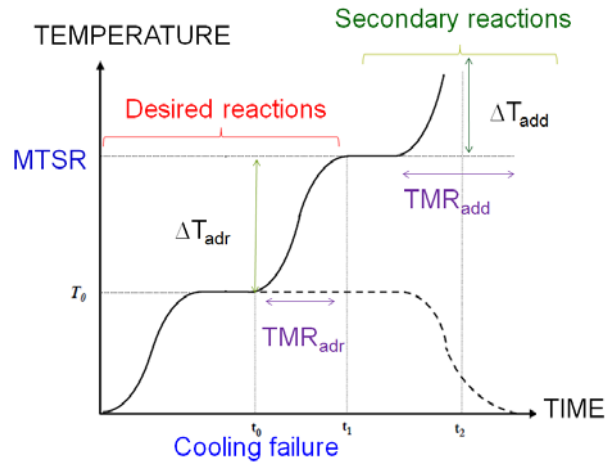

Figure 2: Cooling failure scenario and definition of safety parameters.

The different equation of safety assessment can be found in the book of Stoessel (2008).

The maximum temperature for synthesis reaction can be defined as:

$$MTSR = T_P + \Delta T_{adr} = T_P + \frac{Q_r}{m_r.\hat{C}_{PR}} \tag{1}$$

where T_P is the process temperature, ΔT_{adr} is the adiabatic temperature rise for the reaction system, Q_r is the amount of enrgy released by the reaction, m_r is mass of chemicals and C_{PR} is the heat capacity of the reaction mixture.

The time to maximum rate under adibatic condition for the synthesis part TMR_{adr} can be obtained by:

$$TMR_{adr}\left(T_P\right) = \frac{\hat{C}_{PR}.R.T_P^2}{q_P.E_{a,synthesis}} \tag{2}$$

where q_p is the power released by the rection at the process temperature and $E_{a,synthesis}$ is the global activation energy. The system part is divided into different reaction (perhydrolysis, epoxxidation and ring opening), thus this value is a global one.

The time to maximum rate under adibatic condition for the degradation part TMR_{add} can obtained by:

$$TMR_{add}\left(MTSR\right) = \frac{\hat{C}_{PR}.R.\left(MTSR\right)^2}{q_{MTSR}.E_{a,Degradation}} \tag{3}$$

where q_{MTSR} is the power released by the reaction system at MTSR, and $E_{a,degradation}$ is the global activation energy for the degradation part.

3.1 Calorimetric semi-batch reactor
Two kind of experiments were performed, one with accident and the other one without. Figure 3 shows the evolution of reaction temperature versus time.
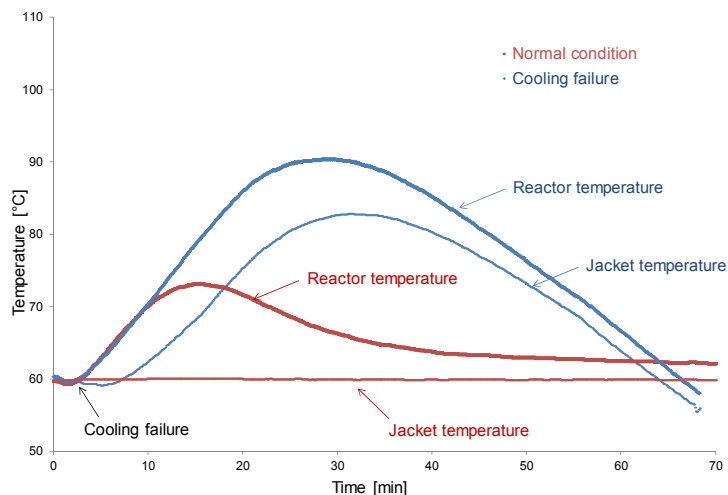
Figure 3: Comparison of experiment carried out with and without accident with a temperature process of 60 °C and at a formic acid feeding rate of 25 g/min.

From experiments carried out under normal condition, it is possible to calculate the total energy released by the reaction Q_r and, thus, getting the adiabatic temperature rise and TMR_{adr}. By integration, it was found that the total amount of energy released (in our experimental conditions) was around 1000 J/g in normal conditions.

At 60 °C, heat exchange capacity was calculated to be 2.57 $K.g^{-1}.K^{-1}$ and by using Eq(1) a MTSR equal to 450 °C was found. The experimental value was measured to be 91 °C and the value of TMR_{adr} is at 30 min after cooling failure. The difference of MTSR value is due to the fact that a part of the solution is evaporated and the system is pseudo-adiabatic.

3.2 DSC measurement
By using the dynamic mode, it is possible to see if there some secondary reactions can occur.
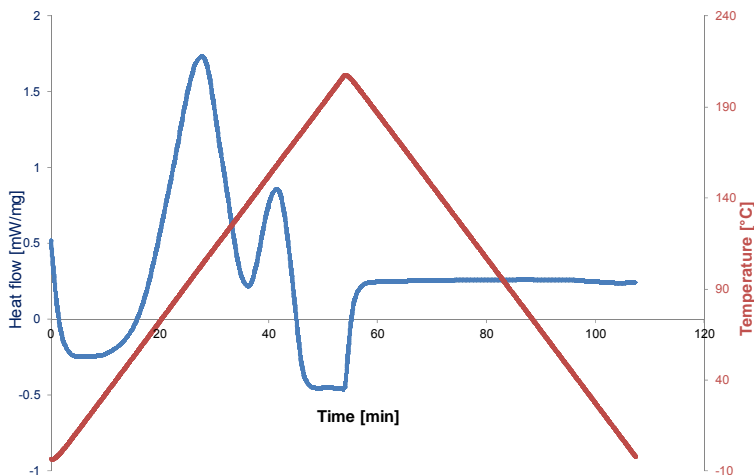

Figure 4: DSC measurement for epoxidation of oleic acid by peroxyformic acid.

Figure 4 shows a typical experiment of DSC for the epoxidation of peroxyformic acid in dynamic mode. The presence of two peaks is due to two different mechanisms, the first one is for the synthesis part (perhydrolysis, peroxyformic acid decomposition, epoxidation and ring-opening) and the other for the degradation part, i.e., secondary reactions. By using the Kissinger method, one can get the activation energy, as Eq. (4) described:

$$\ln\left(\frac{a}{T_{max}^2}\right) = \ln(\text{constant}) - \frac{E_a}{R.T_{max}} \tag{4}$$

where a is the heating rate.

By varying the value of a, it was possible to determine the activation energy for the synthesis part, which correspond to the reaction illustrating by Figure 1; and to determine the activation energy for the secondary reaction. Figure 5 shows this concept.
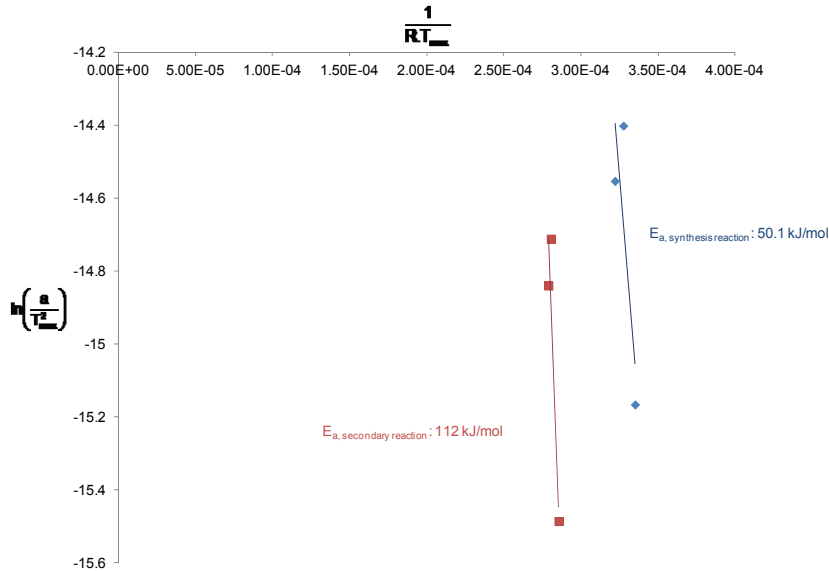

Figure 5: Kissinger relation.

The use of the isothermal mode (Figure 6) can determine the temperature range of the synthesis part and a relation between the power released and the temperature as:

$$q_{rx}[T] = q_{rx}[T_{ref}]\exp\left(\frac{-E_a}{R}.\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \tag{5}$$

value of activation energy for the synthesis part can be calculated by using isothermal conditions as illustrated by Figure 6.
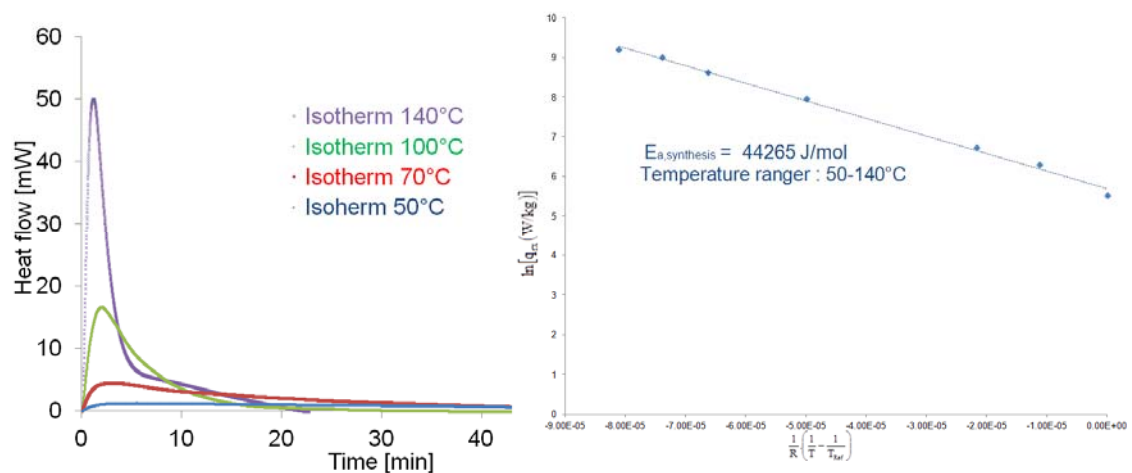

Figure 6: DSC isothermal mode.

In the case of experiment carried out under adiabatic condition, temperature is under synthesis regime even after 140°C.

Table 3: Safety parameters calculated from DSC measurement.

T_P [°C]	50	60	70
C_P [J/g/K]	2.25	2.25	2.25
q_{RX} [W/g]	0.25	0.41	0.65
MTSR [°C]	400	410	420
$TMR_{adr}(T_P)$ [min]	2.91	1.92	1.30

One can notice that TMR_{adr} measured by DSC method is 15 times lower than the one obtained by using semi-batch reactor.

4. Conclusions

Safety parameters, such as MTSR and $TMR_{adr,}$ for oleic acid epoxidation at 60 °C were measured to be 91 °C and 30 min, respectively, in case of lab-scale reactor. In case of DSC, in same temperature condition, same safety parameters were measured to be 400 °C and 2.91 min, respectively. This observation illustrates the wrong way to use DSC results for open lab-scale reactor. Indeed, evaporation should be taken into account for such lab-scale reactor and have a strong effect on safety parameters. One should consider DSC value only for closed reactor system. In such case, DSC is a powerful method to detect secondary reactions and safety parameters.

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