# A COMPARISON OF CALORIMETRIC MEASUREMENTS BY USING DIFFERENT REACTION CALORIMETERS

## R. Nomen, J. Sempere and E. Serra

Chemical Engineering Department, Institut Químic de Sarrià, Universitat Ramon Llull
Via Augusta 390, 08017 Barcelona, Spain

## Abstract

For a great number of European safety groups, reaction calorimetry is the key technique for analysis of the main reaction in the risk assessment of chemical processes. A comparison of calorimetric studies of model reactions, the N-oxidation of two substituted pyridines with hydrogen peroxide, made by several European groups, can open the door to standardization of the methodologies used. However, the intrinsic experimental complexity of the model reactions, which included dosing at high temperature, a multiphase system and evaporation, and the different evaluation criteria, produced a considerable dispersion between the results obtained by the various groups.

Keywords: comparison, hazards, instruments, reaction calorimetry

## Introduction

The industrial processes involving fine chemicals are usually carried out in stirred vessels, in batch or semi-batch operations. A typical process often consists in introducing the reactants into the reactor at room temperature, heating it up to the process temperature, and dosing the catalyst or the last reactant; after a prescribed time, the reaction is assumed to be completed and the final mixture is cooled back down to room temperature for its final work-up. It is also expected that all the heat generated by the reaction can be removed efficiently, and that all raw materials, products, by-products and wastes are stable in the range of operating temperatures.

In order to assess the risk of such operations, several runaway scenarios may be considered; the one proposed by Gygax [1] and extended by Stoessel [2] of Ciba Geigy is perhaps the most exhaustive.

In an ideal semi-batch process, the dosed reactant is consumed very rapidly, and its accumulation is negligible. In reality, most reactions are too slow, so there is an accumulation of unreacted materials. Determination of the self-heating potential of the reaction mixture is a general practice. The self-heating potential can be identified as the temperature increase of the reaction mass, $\Delta_{ad}T$, obtained by instantaneous and adiabatic reaction of all of the reactants in the reactor. If the final adiabatic temperature due to the synthesis reaction, MTSR, is high enough to induce new reactions at non-negligible rates, a new temperature increase is to be expected. Other

possible scenarios to define the consequences of a runaway have been described. The most optimistic case [2] would be $\Delta_{ad}T_{stop}$, which corresponds to the automatic halting of dosing after a cooling failure. The final case [3] could be $\Delta_{ad}T_{nonstop}$, in which dosing cannot be stopped after a cooling failure.

A thermal explosion can occur when the main reaction and potential decomposition processes take place at high rate, generating a huge amount of vapour and gases, which in turn produce high pressure in the vessel. In this case, in the design of mechanically safe equipment it is very important to consider the pressure profile during the runaway scenario [4].

Many industries have dedicated large efforts in recent years to the definition of internal guidelines in this area. Each methodology reflects its unique uses, activities and available instrumentation of each company, but all are very similar in protocols and concepts. This is the first impression of a project coordinated by us in Barcelona [4]. Our main objective is to compare the experimental results and conclusions of several groups studying the same process, according to their own criteria and methodology.

The second observation is that all the industries we worked with in the present project use reaction calorimetry to study the synthesis under industrial conditions. However, when the studied process involves calorimetric complexities (e.g. reflux), a huge dispersion of the data is observed. The aim of this paper is to describe the usual mistakes or misunderstandings in the planning, performance and evaluation of reaction calorimetry experiments and their influence on the results. Furthermore, a procedure that yields correct and real results from the calorimetry experiments can be suggested as a consequence of this work.

## Experimental

The model processes to be studied were the N-oxidations of two substituted pyridines, PY.1 and PY.2, with hydrogen peroxide, a complex metal oxide being applied as catalyst [5]. In order to standardize the experiments, our group furnished all participants with a detailed bench-scale procedure, including notes for a typical laboratory experiment.

The reactions were carried out at atmospheric pressure, at 100°C without solvent, with 3 h dosing time of an excess of peroxide into the pyridine, and a maturation time of an additional 3 h at 100°C.

The groups used different reaction calorimeters: power compensation, isoperibolic, and heat flow types. The isothermal power compensation calorimeter consisted of a 1 L open glass reactor with a mechanical stirrer and a combined jacket [6]. The isoperibolic calorimeter was a 1 L jacketed stainless steel closed reactor [7]. The heat flow reaction calorimeter was the RC1 instrument from Mettler-Toledo [8]. In the present work, this last instrument was used in many different configurations. Some groups used a 2 L open glass reactor with a mechanical stirrer, a metal-teflon heated cover, and a reflux condenser directly attached to the cover (type I). Other groups used a 2 L open glass reactor with a mechanical stirrer, a metal-teflon heated cover, and a reflux-distillation device operating in reflux

mode (type II). Other groups used a 1 L glass reactor with a mechanical stirrer with stainless steel anchor, and a reflux-distillation device operating in reflux mode (type III). The remaining groups used a 1 L open glass conical reactor, with a mechanical stirrer, a metal-teflon heated cover, and a reflux condenser directly attached to the cover (type IV).

## Results and discussion

The shapes of heat of reaction curves for both studied substituted pyridines were similar in all the experiments. The first values of the total heat of reaction obtained by the various groups, however, were very different. For the product PY.1, they can be grouped in three ranges: $-1000$, $-1500$ and $-2000$ kJ (kg PY.1)$^{-1}$. For PY.2, they were in the range of $-1730$ to $-2850$ kJ (kg PY.2)$^{-1}$. If this is considered a standard synthesis with a typical heat of reaction of $-100$ kJ kg$^{-1}$, one can not imagine the possible consequences of such a dispersion of the results.

The shape of the evaluated heat of reaction obtained in one of the heat flow calorimeters for PY.1 is shown in Fig. 1, in which the dosing and the shape of the reaction power for an ideal and infinitely fast reaction are also represented. The evaluated data obtained by each group are given in Table 1.

After a more detailed analysis, a value of $-1500$ kJ kg$^{-1}$ can be accepted as the most probable. A value of $-500$ kJ kg$^{-1}$ is attributed to the decomposition of all the excess hydrogen peroxide in the experiment carried out by group F in a stainless steel reactor and it must be subtracted from the initial value reported by this group. Another value of $-500$ kJ kg$^{-1}$ is assigned to the heat of reaction spent in the evaporation, measured as the heat exchanged in the condenser; this was not measured by group A and not considered in the first evaluation by group B. Finally, a deviation of $-500$ kJ kg$^{-1}$ in the evaluation by group C can be explained by how the individuals followed the protocols and evaluation methods.
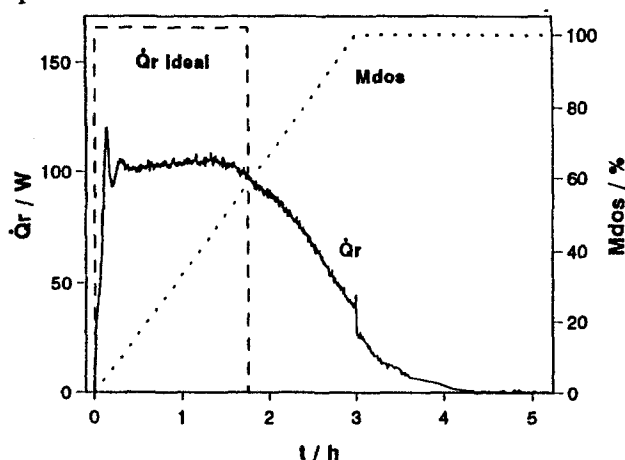


Fig. 1 Shapes of the reaction power, $\dot{Q}$r, dosing, Mdos, and reaction power for an infinitely fast reaction, $\dot{Q}$r ideal, for the process with PY.1

**Table 1**

| Groups | A | B | C | D | F |
|---|---|---|---|---|---|
| $\Delta_r H/\text{kJ kg}^{-1}$ | −995 | −1100 | −1980 | −1486 | −1987 |
| $\Delta_r H_{(corr)}/\text{kJ kg}^{-1}$ | | −1510 | −1450 | | −1487 |
| $\dot{Q}_{r,max}/\text{W kg}^{-1}$ | 192 | 157 | 229 | 183 | 319 |
| $\Delta_{ad} T/K$ | 121 | 121 | 178 | 155 <br> $102^{stop}$ <br> $266^{non\ stop}$ | 155 |

| | Power compensation | Heat flow calorimetry | | | Isoperibolic calorimetry |
|---|---|---|---|---|---|
| | | Type II | Type II | Type I | |

It should be noted that at the end of the process, 6 h after the initiation of dosing, about 20% of the total amount of added hydrogen peroxide was still present in the reaction mass. This value was confirmed by all groups except F, which failed to detect oxidant power at the end of the process due to the metal vessel of the calorimeter. The value shown in Table 1 for group F was corrected, by subtracting from the measured reaction heat, the heat corresponding to the decomposition of 20% of the hydrogen peroxide.

The reaction mixture starts refluxing during the dosing of hydrogen peroxide. This implies a very poor reflux during a long time period. If the condenser were not directly attached to the reactor cover, e.g. by using a complete reflux-distillation device, heat would be lost and the heat required for heating of the reflux-distillation device would be missing in the condenser. In our process, this is estimated to be −500 kJ kg$^{-1}$.
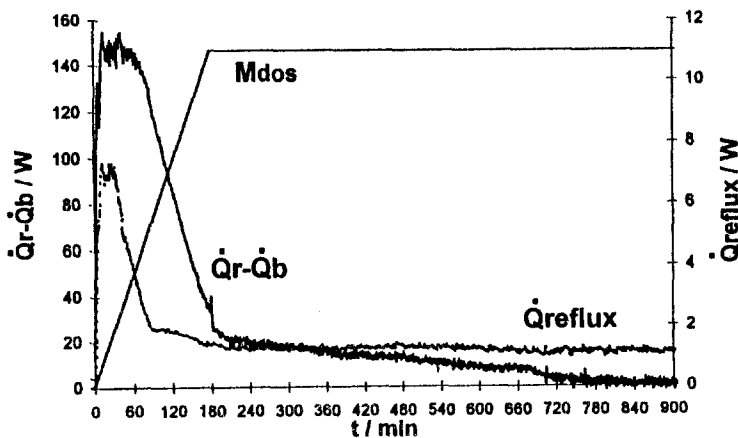


Fig. 2 Shapes of the reaction power, $\dot{Q}_r$-$\dot{Q}_b$, dosing, Mdos, and power eliminated in the condenser, $\dot{Q}$reflux, for the process with PY.2

**Table 2**

| Group | G | H | I | D | J |
|---|---|---|---|---|---|
| $\Delta_r H$/kJ kg$^{-1}$ | –2850 | –1440 | –1790 | –2493 | –1810 |
| $\Delta_r H_{(90°C)}$/kJ kg$^{-1}$ | | –1735 | | | |
| Experiment time/h | 10 | 9 (90°C) | 9 | 15 | 10 |
| $c_p$/J kg$^{-1}$ K$^{-1}$ | 3239 | – | 5433 | 3965 | 3113 |
| $\Delta_{ad} T$/K | 327 | 229 | 119 | 215<br>71$^{stop}$<br>343$^{non\ stop}$ | 207 |
| | | | Heat flow calorimetry | | |
| | Type IV | Type II | Type III | Type I | Type IV |

Figure 2 depicts the dosing and the reaction power curves for PY.2, obtained with the heat flow reaction calorimeter, with the type I glass reactor.

Table 2 lists the values obtained by the groups that studied the process with PY.2. Many groups performed experiments for a longer time than prescribed the original method. The reaction times are also included in the Table.

As in the case of PY.1, those groups that did not measure the heat exchanged in the condenser (H), or used a complete reflux-distillation device (I and J), underestimated the real heat release during the process.

The second aspect for both pyridines was that, 6 h after the initiation of dosing, the experimental procedure indicates that the reaction might be completed. For that reason and since the heat flow exhibits a quasi-flat curve, all the groups except G, I and D evaluated the data only up to this time. However, at this time, the initial baseline has not been recovered. If the process is continued, the real end of the reactions is detected (Fig. 2).

The continuous measurement of evolved oxygen shows that after a reaction time of 6 h, gas is still emerging from the reactor. Chemical analysis reveals that 20% of the total amount of added hydrogen peroxide is still present in the reaction mass. Further, just as power release becomes zero, the oxygen release falls to zero too.

Chemical analysis of the reaction mixture, involving pyridine, pyridine N-oxide, and hydrogen peroxide, demonstrates that the main reaction is completed before the end of dosing. Therefore, it is possible to say that there is an unnecessary extra amount of hydrogen peroxide in the described process, and also that the reaction time prescribed is too long.

For the combined reactions of N-oxidation and decomposition of all the excess hydrogen peroxide, the total heat released is –1987 kJ (kg PY.1)$^{-1}$ or –2493 kJ (kg PY.2)$^{-1}$. If we assume that the most accepted value for the decomposition of hydrogen peroxide is –98 kJ mol$^{-1}$ and that there is an excess of 0.71 mol per mol of PY in the reaction mixture, the reaction enthalpy evaluated for both N-

oxidations is $-167\pm4$ kJ mol$^{-1}$. The estimation of the standard enthalpy of reaction in the gas state gives $-185$ kJ mol$^{-1}$ from the literature data, and $-176$ kJ mol$^{-1}$ from single bond contributions. The deviations are more than acceptable if the strong non-ideality of the system is taken into account.

In order to perform reaction calorimetry experiments when reflux or strong evaporation are expected, some guidelines can be suggested as a consequence of the present work:

The condenser should be directly attached to the reactor cover.

Geometries in which the condensed liquid could be in contact with the free reactor wall (e.g. conical reactors) should be avoided in order to prevent vapour amplification [9].

The use of a heatable reactor cover, thermostated at a temperature 2°C higher than the process temperature, is very convenient.

The instrument should be calibrated only when the temperature of the cover is stable.

The system should be calibrated before and after the process, and, if possible, at the process temperature and 5°C below it. If strong physical changes are observed, additional calibrations will facilitate the evaluation of the process.

If the system is under reflux, the method of calibration proposed in reference [10] is highly recommended.

For an isothermal experiment, the level of the baseline should be the same before and after the reaction. Some small changes can be produced by the variation in the vapour pressure of the system, which modify the heat losses of the instrument.

It is very important to use the real temperature of the dosed material in the evaluation. The heating effect of a thermostated cover should be taken into account when its temperature is very different from ambient.

Some groups that participated in this experiment did not consider some of the above-mentioned recommendations, which led to the observed dispersion in the data. In most cases, this did not have a great effect on the final safety evaluation, but the philosophy in the definition of risk scenarios is strongly dependent on the final numbers.

## Conclusions

The total heat of reaction, measured by isothermal heat flow reaction calorimetry for the catalyzed formation of N-oxides of substituted pyridines by using hydrogen peroxide under the described operation conditions, is $-167\pm4$ kJ mol$^{-1}$. The total heat of this process is 241 kJ mol$^{-1}$ for PY.1 and 232 kJ mol$^{-1}$ for PY.2, this difference being due to the different mass ratio of hydrogen peroxide used in each case.

The comparison of the results obtained by the groups that participated in our project, demonstrates that reaction calorimetry is a key tool for loss prevention in chemical synthesis processes, but accurate acquisition and evaluation of data is re-

quired. Some guidelines to the performance of reaction calorimetry experiments, especially under reflux conditions, are proposed, with a view to the acquisition of accurate results.

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