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Characterize your reaction at a glance. RTCal a new real time calorimetry technique

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RTCal™ is a novel technology that provides heat flow profiles in real time.

RTCal™ is complementary to the traditional heat flow method and adds additional data which translates into better information. The ease-of-use makes RTCal™ a true walk-up tool that substantially enhances the capabilities and applications of the Reaction Calorimeter RC1e.

Measurements with RTCal™ are independent of the properties or the behavior of the reaction mass. Thus, investigation of previously difficult-to-study chemistries, such as polymerizations or reactions that may require immediate interaction, will become easier. The aspect of user-friendliness is further enhanced by iControl; the new reactor control and evaluation software which combines functionality with flexibility and a simple and straightforward graphical user interface.

1. Introduction

RTCal™ is the new Real Time Calorimetry for the RC1e™ (Mettler-Toledo). The patented measurement technology RTCal™ is based on heat flux sensors located in the jacket of a double-walled reactor vessel. Vertically and horizontally positioned sensor bands detect the heat flow Qrtc across the wall of the reactor online and in real time.

The heat flow information is sub-sequently processed, stored and directly displayed as Watts. Depending on the depth of information that you wish to obtain the system can additionally compute the overall heat of reaction Qr_est including heats of dosing and accumulation and the integrated value IntQr_est in real time.

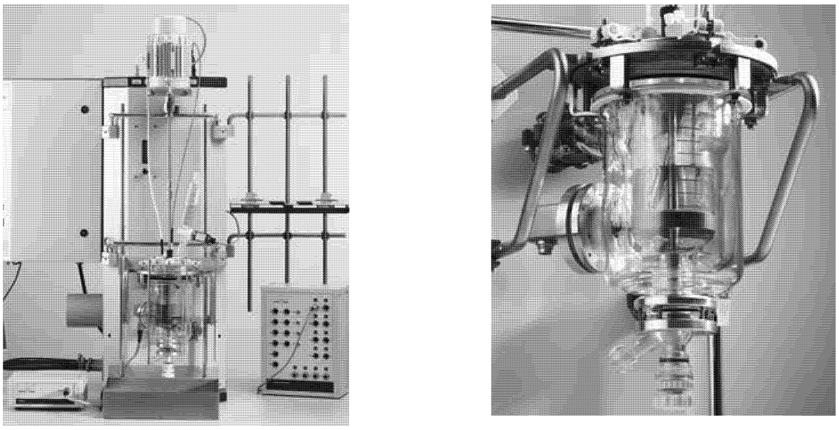

***Figure 1**: RTCal reactor with integrated sensors. The sensors consist of a horizontal band all around the reactor and a long sensor band in the back.*

Experiments with RTCal™ are independent of the properties or the behavior of the reaction mass. Hence, no calibration procedures need to be run before, during or after the reaction which reduces the experiment time substantially compared with traditional methods.

The RTCal™ methodology can be run as a sole method on the RC1e™ (Mettler-Toledo) or complementary to the more traditional heat flow calorimetry (Visentin, F 2005). The enhanced set of information allows the user to derive more detailed conclusions and gives full confidence in experimental results.

***Figure 2**: RTCal reactor in the new iControl RC1e software: Heat flow Qrtc, reaction heat Qr_est, and its integration IntQr_est are shown in real time during the experiment. Reactions can be optimized directly based on the information, e.g. by immediate changes of a dosing rate.*

RTCal™ is controlled and the results are evaluated by a new software, iControl (see Figure 1). The new graphic user interface improves the analysis in easy evaluation environment and shows all relevant data as trends or digital data at any time. The "Direct Mode" allows the user to immediate change all the parameter (stirring speed, temperature heat/cool rate, dosing, etc…) recording individual tasks and generate the procedure automatically (see Figure 3)

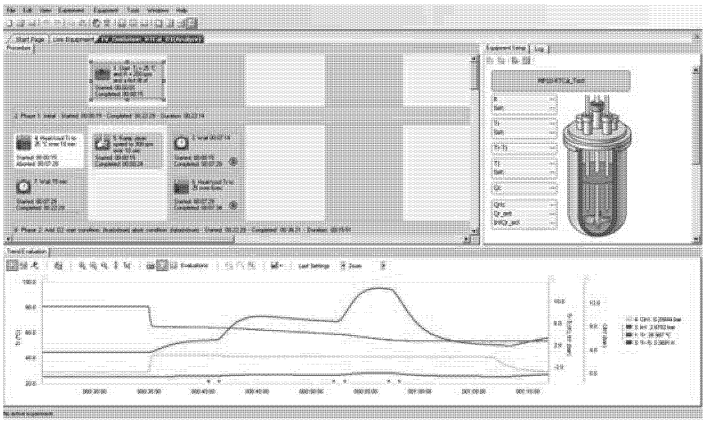

***Figure** 3: Screen-shoot of the expeiment window showing the "Procedure", the "Equipment set-up" and the "Trend evaluation" during a running experiment.*

2. Experimental section and results

The experiments were performed using a RC1e Reaction Calorimeter that combines two different calorimetric principles, heat flow and the new RTCal^{TM}.

The sample volume of the reactor is 70 to 500 ml, and it is able to withstand pressure from 20 mmbar to 1 bar. The maximum temperature of the reactor is approximately 160 °C, and the minimum temperature depends only on the cryostat used down to -50°C. Isothermal conditions are maintained using the RC1e internal thermostat (Riesen et. al. 1985, Mettler-Toledo).

The data acquisition is done using iControl software (see below).

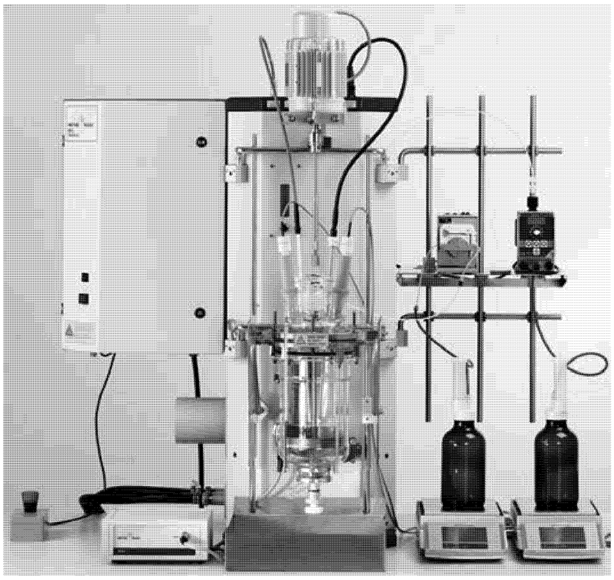

Figure 4*: Equipment set-up for the reactions: RC1e Reaction Calorimeter with a new 500 ml RTCal reactor run by the iControl RC1e software.*

2.1 Esterification reaction

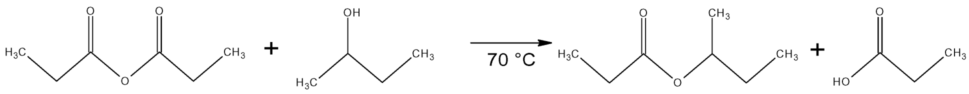

Figure 5*: Simplified reaction scheme for esterification reaction*

Table 1**:** *Recipe used for the esterification experiment.*

Solvent:	Butanol
Substrate:	Propionic anhydride
Stirrer speed:	500 rpm[a]
Temperature in the reactor:	70°C

The standard measurements were made according to the following procedure. Firstly, the reactor was filled with butanol absolute and the stirrer was set at 500 rpm and the desired reaction temperature was set up to 70°C. In a second step the propionic anhydride was filled during 20 minutes.

To determine the energy introduced by dosing, q_{Dos}, the heat capacity of the feed (~2 $kJ \cdot kg^{-1} \cdot K^{-1}$) (NIST) was used. The reaction was followed for approximately three hours, until no further reaction was observed.

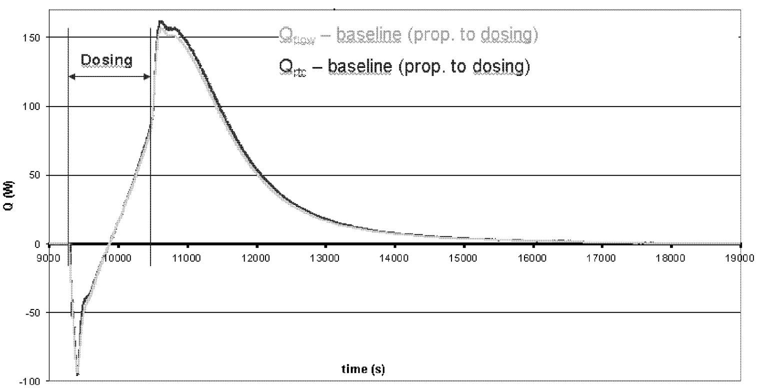

***Figure 6**: Comparison between the measured heat signal obtained with the standard method (heat flow) and the new RTCal^{TM} method (Real Time Calorimetry). Reaction conditions: substrate: propionic anhydride; solvent: butanol; temperature: 70°C; stirrer speed: 500 rpm.*

Figure 6 shows the comparison between the heat flow measure with the standard method and the heat flow measured with the new RTCal^{TM} principle. As can be seen the two trends are in good agreement.
The target of this esterification is the strong heat of dosing do to the addition of the propionic acid.
The reaction according to the conditions of Table 1 gives the following enthalpies. The integration of Qr could be done using the heat term given by the standard method Q_{flow} or using the new Q_{rtc} signal. The numerical results are shown in Table 2.

***Table 2:** Reaction enthalpies for the esterification experiment.*

Experiment integration based on	**Qr**	**Qflow**	**Qrtc**	**Deviation (%)**
Esterification integration results	-67.4 kJ/mol	-54.9 kJ/mol	-56.9 kJ/mol	+ 3.5

This high consistency demonstrates the high accuracy of the measurements that come from the two different methods.

2.2 Grignard Reaction

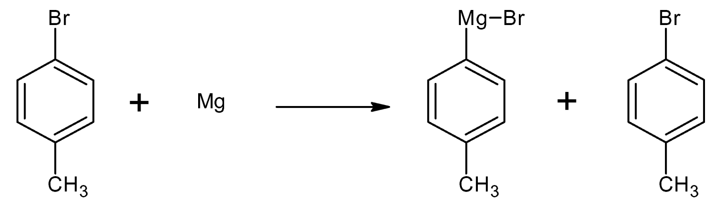

***Figure** 7: Simplified reaction scheme for the Grignard experiment.*

***Table 3**: Recipe used for the Grignard reaction*

Solvent:	THF + toluene
Reagent 1:	Magnesium
Reagent 2:	Parabromotoluene + toluene
Stirrer speed:	500 rpm[a]
Temperature in the reactor:	70°C

The standard measurements were made according to the following procedure. Firstly, the reactor was filled with THF, toluene and magnesium and the stirrer was set at 500 rpm and the desired reaction temperature was set up to 40°C. In a second step the parabromotoluene and toluene was filled during 20 minutes.

To determine the energy introduced by dosing, q_{Dos}, the heat capacity of the feed (~2 $kJ \cdot kg^{-1} \cdot K^{-1}$) (NIST) was used. The reaction was followed for approximately three hours, until no further reaction was observed.

The reaction was started with THF, Toluene, and Magnesium (118g in total) at 40°C. The temperature was kept constant by dosing Parabromtoluene and Toluene (196 g in total) into the reactor. The resulting reaction is shown below: