

Iwona PUCZYŃSKA<sup>1</sup>, Jerzy SKRZYPSKI<sup>1</sup>, Mirosław IMBIEROWICZ<sup>1</sup>  
and Maria TROSZKIEWICZ<sup>1</sup>

## STUDY OF HEAT EFFECT MEASUREMENT METHOD DURING OXIDATION OF ORGANIC COMPOUNDS IN SUBCRITICAL WATER

### OPRACOWANIE METODYKI POMIARU EFEKTÓW CIEPLNYCH UTLENIANIA ZWIĄZKÓW ORGANICZNYCH W ŚRODOWISKU WODY PODKRYTYCZNEJ

**Abstract:** Combination of calorimetry and the oxidation process at elevated temperature and pressure to determine heat effects can be a good method to study mechanisms of chemical reactions.

**Keywords:** calorimetry, wet oxidation, reaction calorimetry, glucose oxidation

Calorimetry (Lat. *calor* = heat) is applied for measurement of heat evolving during chemical reactions or physical changes. Indirect calorimetry is used for calculation of heat that living organisms generate during producing of carbon dioxide and nitrogen waste or during oxygen consumption. The Dynamic Energy Budget theory support this theory and adds that heat generated by living organisms may be measured by direct calorimetry, in which the entire organism is placed inside the calorimeter for the measurement.

The specific heat formula is as follows:

$$q = mc\Delta T \quad (1)$$

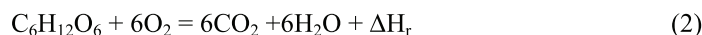
where:  $q$  - heat,  $m$  - mass,  $c$  - specific heat capacity,  $\Delta T$  - change in temperature.

Calorimetry is based on the fact that all chemical reactions and physical transformations generate or consume heat. The basis for calculation of accurate calorimetric data is the balancing of heat and mass flow.

### Oxidation of organic compounds at elevated temperature and pressure

A new technological innovation is the calorimetry at elevated temperature and pressure. Determination of heat effects during oxidation of glucose using oxygen, elevated temperature and pressure is the aim of the studies.

Glucose is often considered as useful chemical resource that could be used as a starting material in chemical or biochemical processes [1]:



The calorimetric measurements, researched in calorimetric reactor RC1, were used for these studies. A Mettler-Toledo reaction calorimeter with 2 dm<sup>3</sup> jacketed batch reactor equipped with a gas type stirrer was used as a pressure reactor (Fig. 1).

---

<sup>1</sup> Faculty of Process and Environmental Engineering, Technical University of Lodz, ul. Wólczańska 213, 90-924 Łódź, phone 42 631 37 09, email: skrzypsk@wipos.p.lodz.pl

The calorimetric principle applied in RC1 apparatus is based on a continuous measurement of the temperature difference between the reactor content ( $T_r$ ) and the heat transferred to fluid in the outer jacket ( $T_j$ ). At any given time, the heat transferred between the fluid in the jacket and the reactor content,  $q_{\text{flow}}$ , is given by:

$$q_{\text{flow}} = UA(T_r - T_j) \quad (3)$$

where  $U$  is the heat transfer coefficient and  $A$  is the heat exchange area. These parameters are determined by the calibration process.

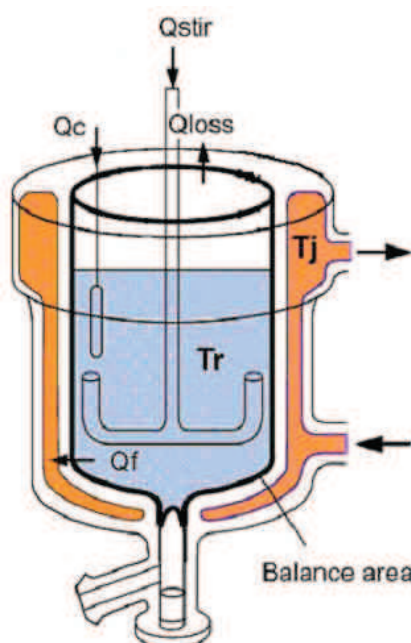


Fig. 1. Calorimetric reactor RC1 made by Mettler Toledo Company

The heat flow balance over the reactor is as follows:

Inflow = Accumulation + Outflow of the heat

$$(Q_r + Q_c + Q_{\text{stir}}) = (Q_a + Q_i) + (Q_f + Q_{\text{dos}} + Q_{\text{loss}} + Q_{\text{reflux}} + \dots) \quad (4)$$

$Q_r$  - heat generation rate of chemical or physical process,  $Q_c$  - calibration power,  $Q_{\text{stir}}$  - energy input due to stirrer (heat production in the reaction mass),  $Q_a$  - heat storage (accumulation) by the reaction mass,  $Q_i$  - heat storage (accumulation) through the inserts,  $Q_f$  - heat flow through the reactor wall,  $Q_{\text{dos}}$  - heat input due to dosing. Power that is needed to bring the inflow from  $T_{\text{dos}}$  to  $T_r$ ,  $Q_{\text{loss}}$  - heat flows through the reactor head assembly (radiation, conduction),  $Q_{\text{reflux}}$  - quantity of heat dissipated in the reflux condenser.

$Q_r$  is the sum of all the individual heat effects in the reaction medium that result from simultaneous chemical reactions and phase changes such as evaporation, crystallization,

dissolution and mixing. In the evaluation of an experiment, this unknown heat generation rate must be determined using the measurable heat effects.

To do this, the heat balance equation is rearranged, the term  $Q_{\text{stir}}$  neglected and several terms combined:

$$Q_r = Q_{\text{flow}} + Q_{\text{accum}} + Q_{\text{dos}} + Q_{\text{loss}} + Q_{\text{reflux}} \quad (5)$$

where:  $Q_{\text{flow}} = Q_f - Q_c$  (heat flow through the reactor wall - calibration power),  $Q_{\text{accum}} = Q_a + Q_i$  (heat accumulation by the reaction mass and inserts),  $Q_{\text{dos}}$  - heat input due to dosing. Power that is needed to bring the inflow from  $T_{\text{dos}}$  to  $T_r$ ,  $Q_{\text{loss}}$  - heat flows through the reactor head assembly (radiation, conduction),  $Q_{\text{reflux}}$  - quantity of heat dissipated in the reflux condenser.

The evaluation cannot calculate each individual contribution to  $Q_r$  separately if several chemical reactions/physical transformations occur at the same time. The calculation, eg of heats of mixing or heats of vaporization therefore requires particular experimental measures to separate the individual effects from one another. In general, it is advisable to make all the disturbing heat effects (eg due to stirring, evaporation or dispensing) as small as possible or keep them as constant as possible. Heat effects that remain constant during the reaction under investigation appear in the baseline of  $Q_r$  and make no contribution to the integration of the reaction enthalpy. Usually, this applies to the contribution of  $Q_{\text{stir}}$ , which is the reason why it is not specially specified in the basic equation.

Our calculations rest on calorimetric rules. The reaction enthalpy is determined by integrating the peak of the heat generation rate  $Q_r$ . In the evolution we define the start and end point of possible reaction and its baseline (we use a pure water as baseline). Between the start and end pairs for the reaction limits, the integral is calculated as the area between  $Q_r$  curve and the baseline  $Q_b$  (Fig. 2).

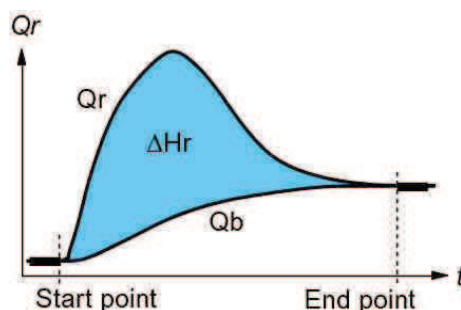


Fig. 2. Heat flow curves of possible reaction and its baseline

Overall heat generated during the process  $\Delta H_r$  was estimated from the following equation:

$$\Delta H_r = \int_S^E (Q_r - Q_b) \cdot dt$$

where:  $\Delta H_r$  - reaction enthalpy [J/mol],  $Q_r$  - heat generation rate, calculated from the sum of the selected heat flow terms [W],  $Q_b$  - baseline for  $Q_r$  [W].

As an area between recorded thermal curves  $Q_r$  and baseline  $Q_b$ .

## Calibration

The first important aim was the calibration because of the possible process' disturbances. The calorimetric reactor had to be calibrated due to the extreme conditions of the reaction such as the diphase system (gas-liquid) and increased temperature and pressure. To avoid measurement mistakes and to determine the heat effects correctly it was necessary to calibrate the system.

- A. Firstly, the value of  $U$  (*the heat transfer coefficient*) and  $A$  (*the heat exchange area*) was calculated.  $UA$  is the function of stirrer rotation velocity.
- B. To avoid disturbances resulting from additional processes (adsorption and desorption heat, the heat losses from rotation's energy) it was necessary to create the baseline. That is why the same experiments for water (in the same conditions and by using the same parameters as in the main experiments) were carried out.

## Results

Figure 3 shows the correlation between  $U$ ,  $A$  and  $T$  (temperature), using different velocity of the stirrer rotation ( $R$ ). The parameter  $UA$  depends on temperature and the velocity of stirrer rotation ( $R$ ). If the velocity of stirrer rotation increases,  $UA$  increases too.

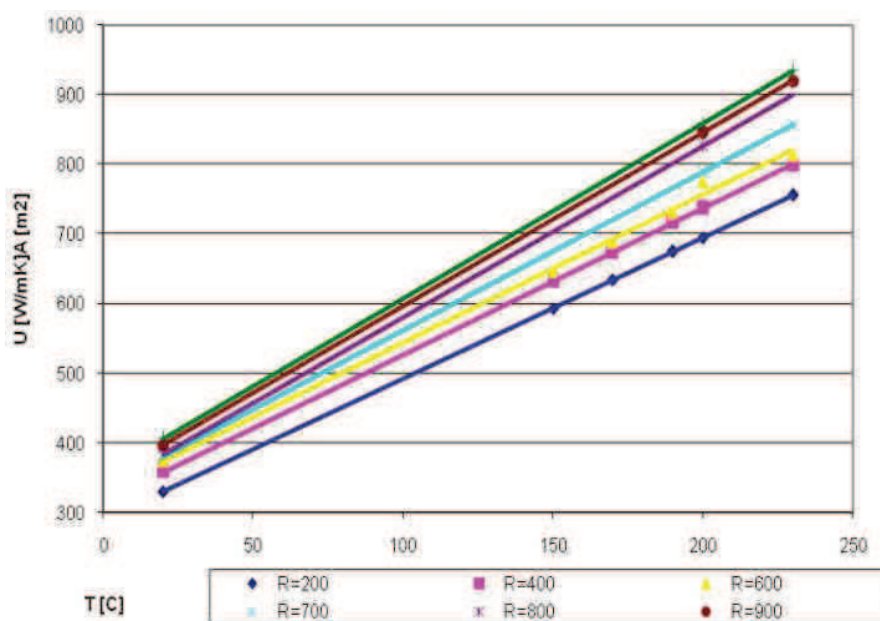


Fig. 3. The correlation between  $UA$  and  $T$ , using different velocity of the stirrer

Figure 4 shows the comparison of correlations between  $UA$  and  $R$  in minimum and maximum temperatures of experiments: 20 and 200°C.

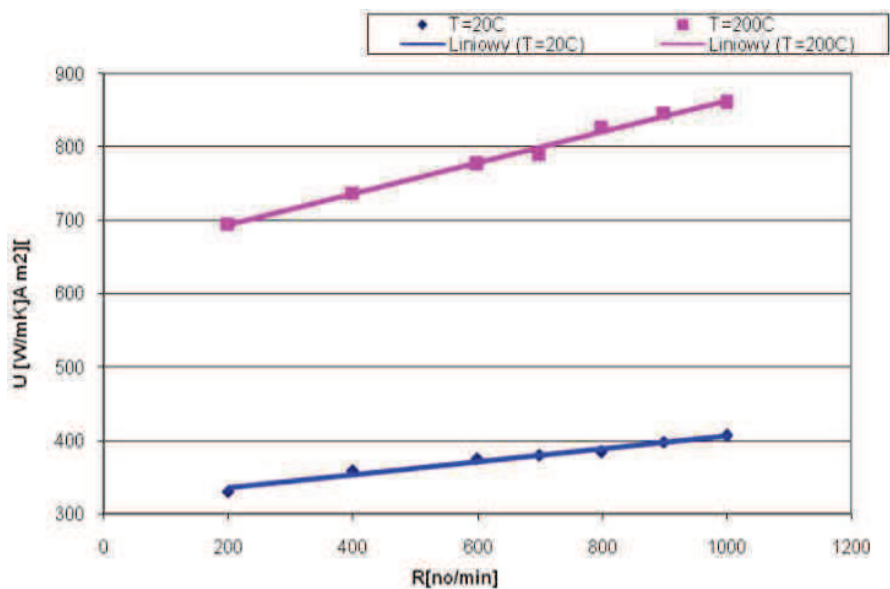


Fig. 4. The comparison of UA for different velocities of the stirrer in T = 20°C and T = 200°C

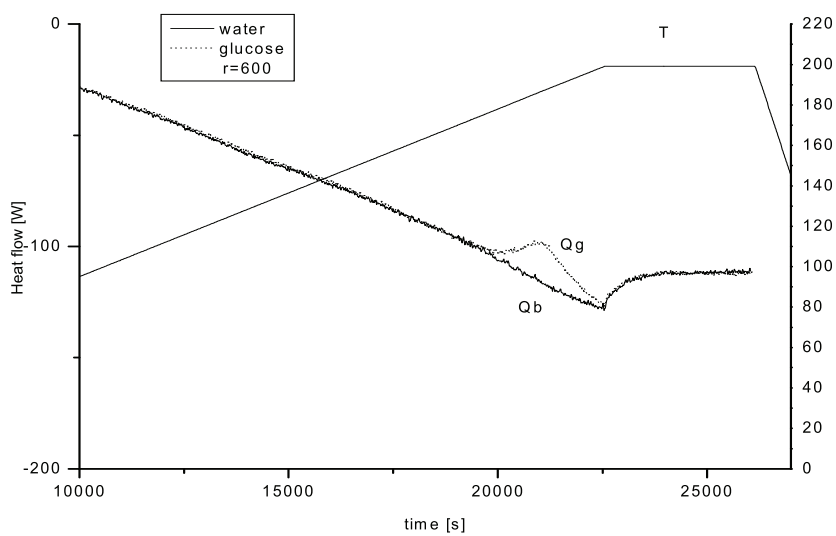


Fig. 5. Changes of water and glucose solution heat flow in RC-1 reactor ( $C_0 = 1600$  ppm of glucose)

Figure 5 shows curves of water (baseline- $Q_b$ ) and glucose solution ( $Q_g$ ) heat flow in time and temperature. We do not observe any reaction during the first 18000 s of the

reaction. When the temperature reaches 200°C, we can see the area between  $q_g$  curve and the baseline curve ( $Q_b$ ). It is the result of heat effects. The area between these curves is heat of glucose decomposition in wet oxidation reaction. We can calculate a decrease of *total organic carbon* (TOC) in glucose solution too. The area converted into decreasing TOC unit gives us minor heat of reaction.

### Conclusions

This method applied for determination of heat effects in binary system (gas - liquid) at elevated temperature and pressure can be suitable for the research on chemical reactions' mechanism.

### References

- [1] Goto M., Obuchi R., Hirose T., Sakaki T. and Shibata M.: *Hydrothermal conversion of municipal organic waste into resources*. *Bioresource Technol.*, 2004, **93**(3), 279-284.

## OPRACOWANIE METODYKI POMIARU EFEKTÓW CIEPLNYCH UTLENIANIA ZWIĄZKÓW ORGANICZNYCH W ŚRODOWISKU WODY PODKRYTYCZNEJ

Wydział Inżynierii Procesowej i Ochrony Środowiska, Politechnika Łódzka

**Abstrakt:** Zaproponowana metodyka wyznaczenia efektów cieplnych reakcji utleniania związków chemicznych może stać się dobrym narzędziem do badania mechanizmów ich przebiegu.

**Słowa kluczowe:** kalorymetria, mokre utlenianie, kalorymetria reakcyjna, utlenianie glukozy