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Effect of Cooling Fluid Flow Rate on the Estimation of Conversion by Calorimetry in a Lab-Scale Reactor

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Summary: Significant information about polymerization reactions carried out in lab-scale reactors is lost because sampling is not always possible due to the high viscosity, heterogeneity of the reaction medium or pressurization of the reactor. Thus, monitoring these reactions through calorimetry technique could be very valuable. Nevertheless, standard lab-scale reactors can present a relatively high residence time of the cooling fluid in the jacket and significant heat loss of the jacket to the surroundings. In the present work, the effect of the cooling fluid flow rate on the estimation of conversion through isothermal and isoperibolic calorimetry during a batch emulsion polymerization was investigated. Results show that the estimation of conversion through isothermal and isoperibolic calorimetry was not significantly affected by the cooling fluid flow rate using heat flow calorimetry. Nevertheless, when employing the energy balance of the jacket and the estimation of the global heat exchange coefficient between the jacket and the surroundings to estimate conversion (heat balance calorimetry) better results were obtained for lower cooling fluid flow rates.

Keywords: cooling fluid flow rate; emulsion polymerization; isoperibolic calorimetry; isothermal calorimetry

Introduction

Significant information about polymerization reactions carried out in lab-scale reactors are lost because sampling is not always possible due to difficulties during the reaction (high viscosity or pressurization of the reactor) or due to difficulties in obtaining reliable samples as the reaction medium could be quite heterogeneous. Thus, monitoring these reactions through calorimetry could be very valuable. The calorimetric technique estimates conversion based on mass and energy balances of the reactor being a very useful tool to monitor exothermic polymerization reactions, as it is non invasive, fast, continuous and low cost.[1] According to Gesthuisen et al.,[2] several methods of reaction calorimetry could be applied to laboratory reactors and can be distinguished into three cases: adiabatic calorimetry, isoperibolic calorimetry and isothermal calorimetry. Polymerization reactors in industry are operated in a range between isoperibolic calorimetry and isothermal calorimetry. The actual calorimetric method applied to the real case can be subdivided into heat flow calorimetry and heat balance calorimetry. In heat flow calorimetry, the jacket temperature is assumed to be dependent on the reactor temperature and considered to have no dynamics of its own. In heat balance calorimetry the balances of both, reactor and jacket, are evaluated, as the jacket dynamics are considered.[2]

During polymerization reactions and particularly in bulk polymerizations, the viscosity of the reaction medium can increase drastically and fouling at the reactor wall can occur. These typical features of many polymerization systems affect the heat transfer between the reaction medium and the

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jacket. Since in heat balance calorimetry the heat flow measured is independent of the changes in heat transfer properties between the jacket and the reaction medium during the reaction (the jacket dynamics are taken into account), this technique could present some advantages to study polymerization reactions.

Heat flow calorimetry, on the other hand, requires the determination of the heat exchange coefficient between the reaction medium and the jacket, which is a function of the properties of the reaction medium, in order to evaluate correctly the heat of reaction. Commercial lab-scale calorimeter reactors employ the heat flow calorimetry with a very high flow rate of the cooling fluid in the jacket, therefore the difference between the inlet and outlet jacket temperatures can be neglected.

In heat balance calorimetry, both inlet and outlet jacket temperatures need to be known, as a consequence the flow rate through the jacket must be accordingly low in order to result in a measurable difference between these jacket inlet and outlet temperatures $(T_{jin} - T_{jout})$. Nevertheless, this feature contradicts the fact that to obtain fast reactor temperature control the flow rate through the jacket should be high. Therefore, the advantage of heat flow calorimeters in comparison with heat balance calorimetry is better reactor dynamics, keeping in mind that the evaluation of additional parameters, as for instance the heat exchange coefficient between the reaction medium and the jacket, is required.[3]

Standard lab-scale reactors usually operates with an intermediate flow rate of the cooling fluid presenting a relatively high residence time in the jacket and significant heat loss of the jacket to the surroundings. Batch emulsion polymerizations usually present a peak of heat generation that may cause instability to the performance of the controller. Therefore, it should be expected oscillations on reaction temperature even at isothermal conditions that may affect the performance of the calorimetric technique.

The objective of this work is to study the effect of the cooling fluid flow rate on the estimation of conversion by calorimetry during emulsion polymerization reactions in a lab-scale reactor. To attain this objective, a standard lab-scale jacketed stainless steel tank reactor with an internal volume of 5 liters was instrumented to operate as a calorimetric reactor (reactor temperature, jacket inlet and outlet temperature and surrounding temperature data are acquired and stored at a PC). Water was used as the heating/cooling fluid and its flow rate was controlled and kept constant during each reaction through the opening/closure of the entry valve. The reactor temperature was controlled by a PI controller. The isothermal calorimetry employing heat flow and heat balance calorimetry and isoperibolic calorimetry employing heat flow calorimetry were used to determine the evolution of conversion during batch vinyl acetate emulsion polymerization reactions.

Materials and Methods

The reactor setup including the reactor temperature control scheme is shown in Figure 1. This unit possesses a remote control system of reactor temperature and agitation including three boards for data acquisition. Temperature data were acquired by four thermocouples (PT100) positioned at different points of the reactor (jacket inlet and outlet, reaction medium and surroundings) as shown in Figure 1.

The heating/cooling fluid flow rate was kept constant by a valve that allows the variation of the flow rate in the jacket between each reaction. The flow rate was measured during the reactions by a turbine type hydrometer installed at the jacket outlet. The reactor temperature control was attained by a PI controller that controls two pneumatic valves that are responsible for the dosage of the steam (supplied by a boiler) through the heat exchanger and of the water through the jacket.

In all reactions, the reactor was initially charged with distilled water, buffer agent

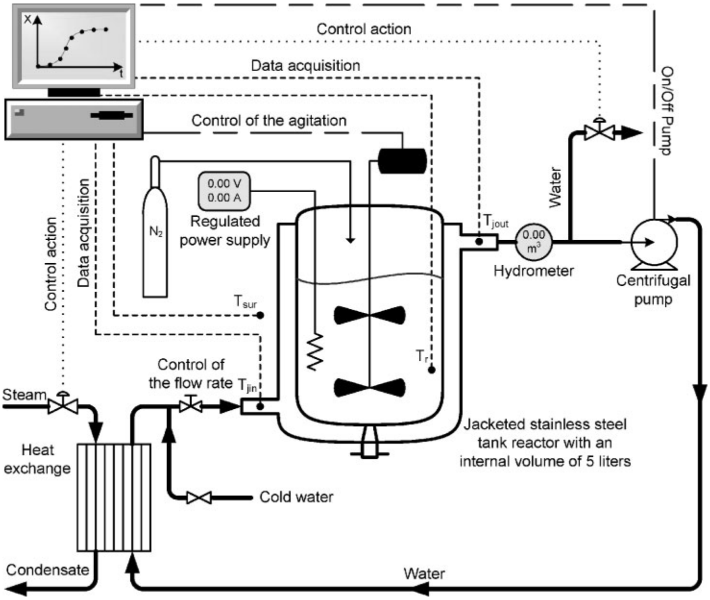

Figure 1.
Reactor setup.

(sodium bicarbonate) and surfactant (sodium lauryl sulfate - SLS) and the reactor was heated to the reaction temperature set at 50 °*C*. After that, monomer (vinyl acetate) was added to the reactor. When the reaction temperature was reached again, after the addition of the monomer, the initiator was charged (aqueous solution of potassium persulfate preheated at a temperature of 40 °*C* just before feeding to the reactor) starting the reaction. Nitrogen was used throughout the reaction to guarantee an inert atmosphere. Samples were collected during the reaction to determine the conversion through gravimetry. The stirring frequency was set to 400 *rpm* and solids content of the reaction was of 30 *wt*%. The reactants were used as received. Table 1 presents the formulations employed in the reactions.

Determination of Conversion Based on Calorimetric Measurements.

Using Isothermal Calorimetry and Applying Heat Balance Calorimetry

In this technique, the temperature of the reaction medium T_r was kept constant by an integral proportional controller (PI) manipulating the jacket inlet temperature. And the energy balances of both, reactor and jacket were evaluated, taking jacket dynamics into account.For a batch reaction, the energy balance of the reactor is given by the following equation:

$$m_r Cp_r \frac{dT_r}{dt} = Q_r + Q_j + Q_s - Q_{lossr} \qquad (1)$$

The terms Q_r and Q_j are the rate of heat generation by the polymerization reaction and the rate of heat exchange through the

Table 1.
Formulation of vinyl acetate emulsion polymerization reactions.

Reactants	Vinyl acetate	Water	$NaHCO_3$	$K_2S_2O_8$	SLS
Mass (*g*)	1260.0	2940.0	8.00	9.00	10.00

jacket, respectively. The heat added to the reactor by stirring Q_s, is considered negligible when compared to the other terms. The term Q_{lossr} corresponds to the heat loss of the reactor to the surroundings. In this reactor no condenser was used, and the reactor was opened only for sampling. The contact area of the reactor to the surroundings is about 9 times smaller than the contact area with the jacket. In addition, the global heat transfer coefficient of the reaction medium (liquid) with the jacket is much higher than that of the head space of the reactor (gas) with the surroundings. Therefore, Q_{lossr} was considered negligible.

The terms T_r, m_r and $Cp_r(J/gK)$ in Eq. (1) are, respectively, the reaction temperature, the total mass and the specific heat of the reaction medium. The latter being calculated by the following equations [4,5] in order to take the main components of the reaction medium into account:

$$Cp_{H_2O} = \left(\frac{0.239\ 10^{-3}}{18}\right)(5.263\ 10^4 + 2.412\ 10^2 T_r - 8.509\ 10^{-1} T_r^2 + 10^{-3} T_r^3)(4.187) \qquad (2)$$

$$Cp_{VAc} = \left(\frac{1}{86}\right)(3.621 + 6.676\ 10^{-2} T_r - 2.103\ 10^{-5} T_r^2 - 3.965\ 10^{-9} T_r^3)(4.187) \qquad (3)$$

$$Cp_{PVAc} = 1.466 \qquad (4)$$

$$Cp_r = z_{H_2O} Cp_{H_2O} + z_{VAc}(Cp_{VAc}(1 - X_{calor}) + Cp_{PVAc} X_{calor}) \qquad (5)$$

where, Cp_{H_2O}, Cp_{VAc} and Cp_{PVAc} are, respectively, the specific heats $(\text{in}\, J/gK)$of water, vinyl acetate and poly(vinyl acetate), z_{H_2O} and z_{VAc} are the mass fractions of water and monomer in the reactor and X_{calor} is the calorimetric conversion estimated in the previous instant.

The energy balance of the jacket is given by:

$$m_j Cp_j \frac{dT_j}{dt} = -Q_j + \dot{m} Cp_{cooling}(T_{jin} - T_{jout}) - Q_{lossj} \qquad (6)$$

In the energy balance of the jacket, Cp_j is the specific heat of the cooling fluid, water, calculated by the following equation [4,5]:

$$Cp_j = \left(\frac{0.239\ 10^{-3}}{18}\right)(5.263\ 10^4 + 2.412\ 10^2 T_j - 8.509\ 10^{-1} T_j^2 + 10^{-3} T_j^3)(4.187) \qquad (7)$$

The internal volume of the jacket is 4.15 *liters* being the mass of cooling fluid inside the jacket m_j, approximately equal to 4150 *g* and the mass flow rate of cooling fluid in the jacket, $\dot{m}$, was defined for each reaction according to the value desired for the difference between jacket inlet and outlet temperatures with the purpose of evaluating the calorimetric technique used.

The average temperature of the jacket T_j was calculated by the following equation: [6]

$$T_j = (T_{jout} - T_{jin}) / \ln(T_{jout}/T_{jin}) \qquad (8)$$

where, T_j is the temperature of the jacket and T_{jin} and T_{jout} are, respectively, jacket inlet and outlet temperatures. The derivative of the jacket temperature was calculated by the following equation:

$$dT_j/dt = (T_{jt} - T_{j(t-\Delta t)})/\Delta t \qquad (9)$$

where, T_{jt} is the temperature of the jacket at time *t*.

The global heat loss of the jacket to the surroundings Q_{lossj} is described by Eq. (10). The parameter U_jA_j (global heat exchange coefficient between the jacket and the surroundings) was estimated before the beginning of the reaction with the reactor charged and heated to the reaction temperature. Once steady-state conditions were reached, the temperatures of the reaction medium, jacket inlet and outlet and surroundings were measured. Therewith, the value of U_jA_j was estimated considering the energy balances ($Q_r = 0W$) and through Eq. 11:[7]

$$Q_{lossj} = U_jA_j(T_j - T_{sur}) \tag{10}$$

$$U_jA_j \int_0^t (T_j - T_{sur})dt = \int_0^t Q_{lossj}dt \tag{11}$$

All the terms in the energy balances are known directly except the heat generated by the reaction which involves the derivative of the reactor temperature. In order to avoid problems related to noise propagation, an observer for Q_r was employed as proposed by Othman.[8] Considering therefore the following augmented system, with Q_r as a new state with an unknown dynamic ε_{Q_r}:

$$\begin{bmatrix} \dot{T}_r(t) \\ \dot{Q}_r(t) \end{bmatrix} = \underbrace{\begin{bmatrix} 0 & \frac{1}{m_rCp_r} \\ 0 & 0 \end{bmatrix}}_{A} \begin{bmatrix} T_r \\ Q_r \end{bmatrix} + \begin{bmatrix} \frac{Q_j(t) - Q_{lossr}(t)}{m_rCp_r} \\ \varepsilon_{Q_r} \end{bmatrix} \text{ and} \tag{12}$$
$$y = C \times \begin{bmatrix} T_r \\ Q_r \end{bmatrix} = [1 \quad 0] \times \begin{bmatrix} T_r \\ Q_r \end{bmatrix}$$

The system given by Eq. 12 is linear and the Kalman criterion of observability could be applied. In this case:

$$\begin{bmatrix} C \\ CA \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & \frac{1}{m_rCp_r} \end{bmatrix}$$

therefore, the system is observable if and only if $m_rCp_r \neq 0$, which is always the case. The observability of Q_r requires also the knowledge of the sum of $(Q_j - Q_{lossr})$ that is obtained continuously throughout the reaction. A high gain observer of Q_r is given by the following system, setting the observer tuning parameter $\theta = 0.02$:[1,8]

$$\begin{cases} \dot{\hat{T}}_r(t) = \frac{Q_j(t)}{m_rCp_r} + \frac{\hat{Q}_r(t)}{m_rCp_r} - 2\theta[\hat{T}_r(t) - y(t)] \\ \dot{\hat{Q}}_r(t) = -\theta^2 m_rCp_r[\hat{T}_r(t) - y(t)] \end{cases} \tag{13}$$

The calorimetric global conversion X_{calor} was obtained by:

$$Q_{\max} = m_{VAc}(-\Delta H) \tag{14}$$

$$X_{calor} = \left(\int_0^t Q_r dt\right) \Big/ Q_{\max} \tag{15}$$

where, $Q_{\max}$ is the total heat that would be generated at 100% conversion, m_{VAc} is the mass of monomer in the reactor and $(-\Delta H) = 1040.305 J/g$ is the heat of polymerization of vinyl acetate.[5]

Using Isothermal Calorimetry and Applying Heat Flow Calorimetry

In this technique, the heat balance of the jacket was not considered just the average cooling fluid temperature. The temperature of the reactor was kept constant using the same controller (PI) and T_j was calculated by Eq. (8). Nevertheless, to calculate Q_r with Eq. (13) it is necessary to determine the term Q_j by the following equation:

$$Q_j = U_rA_r(T_j - T_r) \tag{16}$$

On-line estimation of U_r (heat exchange coefficient between the reaction medium and the jacket) is a difficult task since it depends on the medium viscosity and on the deposits on the reactor wall, both of which are difficult to be measured during the reaction. In stirred vessels, A_r (wetted surface area available for heat transfer between the reaction medium and the jacket) is also difficult to be measured precisely. For systems with constant U_rA_r this term can be determined by calibration before the reaction and then introduced in the energy balance to estimate Q_r. If U_rA_r varies only slightly during the reaction, a linear interpolation of U_rA_r between its calibrated values at the start and at the end of the reaction might be acceptable. Quite often, in batch emulsion polymerization reactions U_rA_r is considered a function of the conversion.[8]

In this work, U_rA_r (global heat exchange coefficient between the reaction medium and the jacket) was estimated by the following procedure: the reactor was charged (without initiator solution) and heated to the reaction temperature. Once steady-state conditions were reached, a constant power was supplied by an electric resistance heater ($P = 200$ W), and the temperatures were monitored until they reached the new steady-state. Therewith, the initial value of U_rA_r ($U_{ri}A_{ri}$) was estimated using the following equation:

$$U_{ri}A_{ri}\int_0^t (T_r - T_j)dt = \int_0^t Q_c dt \qquad (17)$$

where Q_c corresponds to the electric power dissipated throw the electric resistance. This procedure was repeated after the end of the reaction in order to re-estimate U_rA_r ($U_{rf}A_{rf}$).

Once the values of $U_{ri}A_{ri}$ and of $U_{rf}A_{rf}$ (value of a previous reaction) were known the value of the U_rA_r was estimated by the following equation: [9]

$$U_rA_r = U_{ri}A_{ri} + (U_{rf}A_{rf} - U_{ri}A_{ri})\Phi_p^{\varphi} \qquad (18)$$

where, φ is a parameter that can be adjusted [10] however in this work φ was considered $\varphi = 1$, and Φ_p is the latex solids content.

Some considerations were assumed in the solution of eq. (1) to (18): the density of the cooling fluid was constant ($\rho_{water} = 1g/mL$); compounds introduced in small amounts (example: initiator, surfactant) were not included in the calculation of the specific heat of the reaction mixture; the specific heats of the components of the reactor and of the jacket (example: wall, agitator, sensor) were neglected; the reactor was perfectly mixed.

Using Isoperibolic Calorimetry and Applying Heat Flow Calorimetry

In this technique, the temperature of the jacket is kept constant, and the temperature of the reactor is not controlled. Thus the energy balance of the jacket is not required and the isoperibolic conditions were reached, with the controller (PI) based on T_{jout}. The rate of heat generated by the polymerization reaction Q_r, the rate of heat exchanged through the jacket Q_j, and the calorimetric global conversion X_{calor} were calculated by Eq. (13),(16) and (15), respectively.

Results and Discussion

Table 2 shows the calorimetric technique applied to each reaction, as well as the respective jacket flow rate of the heating/cooling fluid, which was kept constant during the reactions. In order to estimate Q_r from the heat balance, all the terms involved in the energy balance must be known. In fact, the unknown variables in the energy balance are U_jA_j and U_rA_r. The variation in the value estimated of U_jA_j among the reactions occurs due to the difference between jacket inlet and outlet temperatures $\Delta T_j = (T_{jin} - T_{jout})$, which in turn is related with the jacket flow rate and the difference between the jacket temperature and the surrounding temperature. As these variables were measured, it was possible to find the value of U_jA_j, that was constant during the reactions.

The conductive heat flow through the jacket varies linearly with the temperature difference $(T_j - T)$, what leads to variations of the value estimated for U_rA_r among the different reactions. The parameter U_rA_r depends on the solids content (or on the latex viscosity) and on the wetted surface area available for heat transfer, then U_rA_r varies during the reactions. In Table 2 it can be seen that U_rA_r decreases with time as expected (the initial value ($U_{ri}A_{ri}$) is larger than the final value ($U_{rf}A_{rf}$)), since the viscosity of the reaction medium increases and some reactor fouling occurs during the reaction. For reactions

Table 2.
Calorimetric data of the vinyl acetate emulsion polymerizations.

	R1	R2	R3	R4
Calorimetry technique	Isothermal	Isothermal	Isoperibolic	Isoperibolic
Jacket flow rate (L/min)	23.66	6.84	24.45	7.08
$U_{ri}A_{ri}(W/K)$	129.5	81.3	186.7	94.6
$U_{rf}A_{rf}(W/K)$	92.0	66.4	85.5	74.1

carried out using the same technique and with similar formulations it is possible to use the same value of $U_{rf}A_{rf}$ allowing thus the estimation of the evolution of U_rA_r before the reaction. The values of $UjAj$ obtained for experiments R1 and R2 were, respectively, 56.7 and 10.2 W/K. The difference in the values of $UjAj$ observed between these experiments, conducted at different flow rates in the jacket, are related to two factors: 1) Differences in the flow regimes in the jacket, for the lower flow rate (R2) the flow in the jacket is laminar, whereas for the higher flow rate (R1) the flow is at the transition region between laminar and turbulent flow. 2) The estimation of $UjAj$ is quite sensitive to jacket inlet and outlet temperature measurements (especially in the case of the higher flow rate in the jacket (R1)), which in turn could present errors of up to ±0.1 °C due to the PT100 sensors employed in this work. This second factor represents an undesirable characteristic of the heat balance approach for a standard lab-scale reactor.

Figures 2 and 3 show the performance of the controller through the behavior of the control valves during reactions R2 and R3 carried out in isothermal and isoperibolic calorimetry, respectively. It can be observed in Figure 2 that the isothermal condition was not reached, and that the isothermal calorimetry depends more of the performance of the controller than the isoperibolic calorimetry (Figure 3). According to the results shown in Figure 3, the same controller (PI), however based on T_{jout}, leads to isoperibolic conditions as the temperature of the circulating fluid in the jacket is constant.

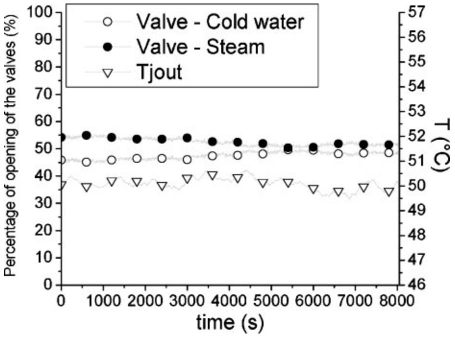

Figure 3.
Behavior of heating and cooling fluid control valves and jacket outlet temperature (T_{jout}) during isoperibolic reaction R3.

Figures 4 and 7 show the evolution of temperature during reactions R1 and R2, respectively. It can be observed that due to the weak performance of the PI controller the isothermal condition was not reached, and for this reactions the variation of the reactor temperature was taken into account in the calculation of Q_r. Figure 5 shows the profile of the heat generated by reaction R1 carried out in isothermal conditions with a high flow rate in the jacket and a good agreement could be observed between gravimetric data and the estimation of conversion by heat flux calorimetry.

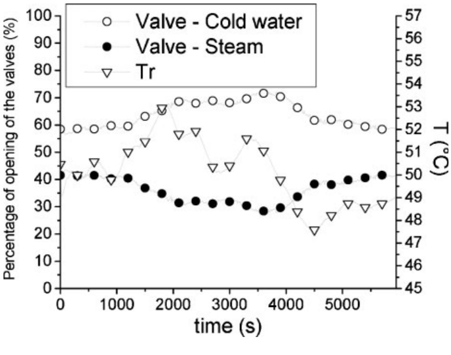

Figure 2.
Behavior of heating and cooling fluid control valves and reactor temperature (T_r) during isothermal reaction R2.

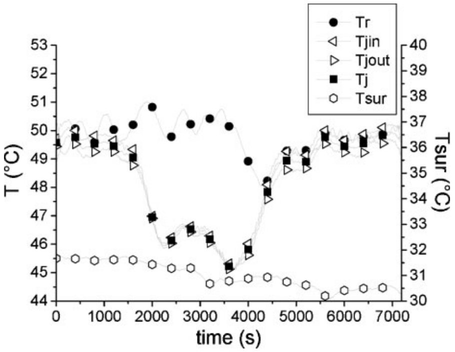

Figure 4.
Temperature profiles of R1.

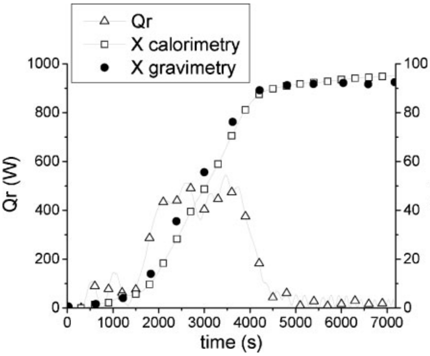

Figure 5.
Heat of reaction (Q_r) and conversion (X) of R1 applying heat flow calorimetry.

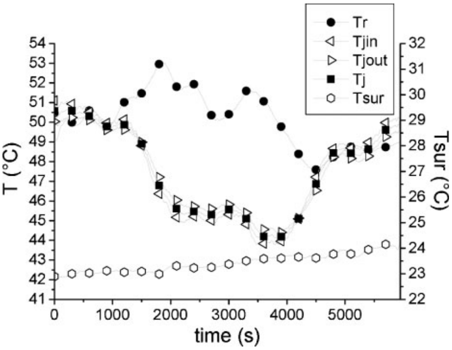

Figure 7.
Temperature profiles of R2.

Figure 6, on the other hand, that compares the estimations of the heat of reaction and conversion applying heat balance calorimetry to reaction R1 with gravimetric data, shows a rather poor agreement due to the high flow rate in the jacket. It is important to note that due to the high value of U_jA_j, the term Q_{lossj} is very sensible to small variations of $(T_j - T_{sur})$which may lead to a gross error on the estimation of conversion.

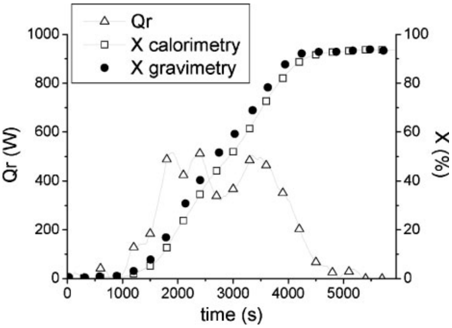

Figure 8.
Heat of reaction (Q_r) and conversion (X) of R2 applying heat flow calorimetry.

Observing Figure 8 it is possible to note a good agreement between gravimetric data and calorimetric estimation when applying heat flow calorimetry even at relatively high residence time of the cooling fluid in the jacket. Analyzing the results shown in Figure 9 regarding reaction R2 one can observe that decreasing the flow rate in the jacket (Table 2) it is possible to obtain a better estimation of conversion in heat balance calorimetry when compared to R1 due to the decrease of the value of U_jA_j.

Figures 10 and 12 show the temperature evolutions during reactions R3 and R4, which were carried out in isoperibolic

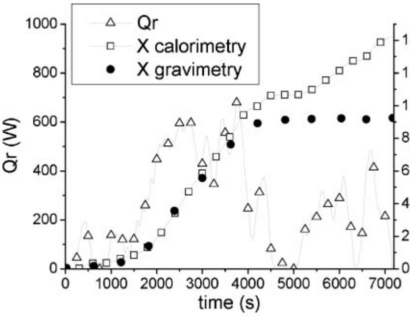

Figure 6.
Heat of reaction (Q_r) and conversion (X) of R1 applying heat balance calorimetry.

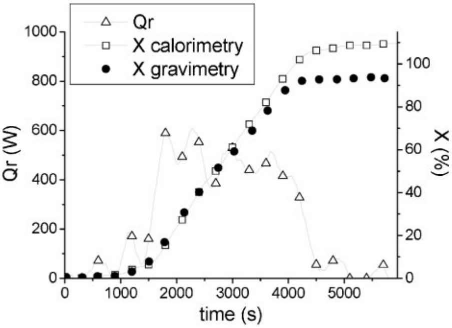

Figure 9.
Heat of reaction (Q_r) and conversion (X) of R2 applying heat balance calorimetry.

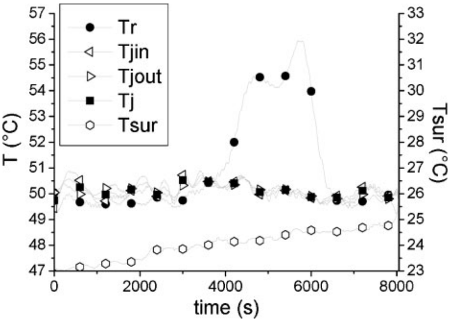

Figure 10.
Temperature profiles of R3.

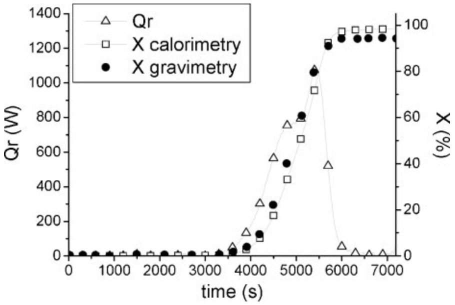

Figure 13.
Heat of reaction (Q_r) and conversion (X) of R4 applying heat flow calorimetry.

calorimetry. In this technique, the jacket flow rate must be high enough in order to assure that the jacket temperature stays almost constant during the reaction. During reaction R3, with a higher jacket flow rate, T_{jin} was always higher than T_{jout}, even in the region of higher heat generation between 4000 and 6500 seconds of reaction. This behavior was not observed in the reactions with lower flow rates in the jacket (R2 and R4), as it is shown in Figures 7 (isothermal calorimetry) and 12 (isoperibolic calorimetry). In Figures 11 and 13, it is possible to observe a good agreement between calorimetric and gravimetric conversions of both reactions (R3 and R4).

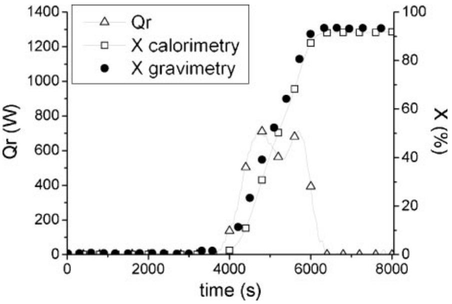

Figure 11.
Heat of reaction (Q_r) and conversion (X) of R3 applying heat flow calorimetry.

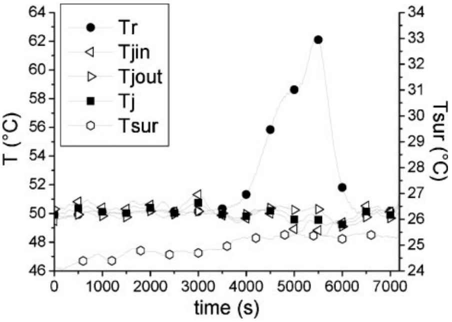

Figure 12.
Temperature profiles of R4.

Conclusions

The effect of the cooling fluid flow rate on the estimation of conversion through two different calorimetric procedures (heat balance calorimetry and heat flux calorimetry) was investigated in isothermal and isoperibolic conditions. The isothermal conditions were not attained as the reaction temperature oscillated during the reaction (up to +/− 3 °C). As the objective of this work is to apply calorimetric technique to a standard lab-scale reactor, this temperature variation could be regarded as a possible disturbance of calorimetric measurements on such reactors.

Heat balance calorimetry presents the advantage of not requiring the knowledge of the global heat exchange coefficient between the reaction medium and the jacket that is the main difficulty of using non-adiabatic calorimetry. Nevertheless, it could only be employed on isothermal conditions as on isoperibolic conditions

T_{jin} varies in order to keep T_{jout} constant. In addition, this approach resulted very sensitive to small variations of the jacket temperatures which could lead to gross errors on the estimation of conversion at the end of the reactions when the heat released by the reaction is low. Decreasing the flow rate in the jacket slightly better estimations of conversion were obtained due to the decrease of the value of U_jA_j. This indicates that the heat balance approach for the estimation of the conversion in a standard lab-scale reactor should be regarded with care.

Heat flux calorimetry presented a different behavior when compared to heat balance calorimetry as a very good agreement between gravimetric data and estimated conversion was observed even at low cooling fluid flow rates (6–7 L/min) for isoperibolic and isothermal conditions. One would expect that at low cooling fluid flow rate the estimation of conversion by heat flux calorimetry could be affected. Nevertheless, in these experiments the calorimetric measurements were not affected, possibly, due to the experimental procedure employed (batch emulsion homopolymerization reaction with 30% of solids content) that leaded to a peak of generated heat oscillating between 500-1100 W. At these conditions, heat flow calorimetry has shown to be robust enough to be applied in standard lab-scale reactors.

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[1] S. BenAmor, D. Colombié, T. McKenna, *Ind. Eng. Chem. Res.* **2002**, *41*, 4233.

[2] R. Gesthuisen, S. Krämer, G. Niggemann, J. R. Leiza, J. M. Asua, *Comp. & Chem. Eng.* **2005**, *29*, 349.

[3] S. Fortini, Reaction calorimetry in supercritical fluids a study of the dispersion polymerization of methyl methacrylate in supercritical carbon dioxide, Ph.D., École Polytechnique Fédérale De Lausanne, Lausanne, Switzerland, **2006**.

[4] R. C. Reid, J. M. Prausnitz, B. E. Poling, "*The Properties of Gases and Liquids*", McGraw-Hill, New York **1987**.

[5] J. Brandrup, E. H. Immergut, "*Polymer Handbook*", 3rd ed., J. Wiley & Sons, New York **1989**.

[6] R. N. Landau, *Thermochim. Acta* **1996**, *289*, 101.

[7] M. Esposito, C. Sayer, R. A. F. Machado, P. H. H. Araújo, *Macromol. Symp.* **2006**, *245-246*, 390.

[8] N. Othman, Advanced strategies for composition control in semi-continuous emulsion polymerization, Ph.D., Université Claude Bernard Lyon I, Villeurbanne, France, 2000.

[9] I. Sáenz de Buruaga, P. D. Armitage, J. R. Leiza, J. M. Asua, *Ind. Eng. Chem. Res.* **1997**, *36*, 4243.

[10] I. Sáenz de Buruaga, Control en línea de reactores de polimerización en emulsión basado em medidas calorimétricas, Tesis Doctoral, Universidad del País Vasco, San Sebastián, España, **1998**.