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Application of Calorimetry Technique to Estimate Conversion of Polymerization Reactions in a Standard Lab-Scale Reactor

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Summary: Reaction calorimetry is a very useful tool for monitoring exothermic polymerization reactions as it uses the measurement of the liberated energy to calculate the reaction rates. Despite the estimation of conversion for homopolymerizations being well established for commercial calorimetry reactors or lab-scale reactors specially constructed to operate as calorimetry reactors, it is still a challenge to use calorimetry to estimate conversion in standard lab-scale reactors. In the present work, a standard lab-scale jacketed stainless steel tank reactor with an internal volume of 5 liters was instrumented to operate as a calorimetric reactor. Water was used as the heating/cooling fluid and its flow rate was kept constant. The isothermal calorimetry and isoperibolic calorimetry were used to determine the conversion of batch vinyl acetate emulsion polymerization. Both results were compared and showed that, even at a relatively high residence time of the cooling fluid in the jacket ($\sim$18 s) and significant heat loss, estimated conversions obtained by the measurements of reactor and jacket temperatures and by the mass and energy balances presented a good agreement with gravimetric data.

Keywords: emulsion polymerization; isoperibolic calorimetry; isothermal calorimetry

Introduction

The production of polymers with prespecified properties requires continuous monitoring and control of the process, in order to assure that the properties do not deviate from the desired ones. Therefore, the reactor must be equipped with accurate on-line sensors to measure these properties in real time. Free radical emulsion polymerizations are exothermic and therefore suitable to be monitored by calorimetry. The calorimetric technique doesn't give direct measurements neither of the polymerization rate, nor of the composition, but these can be obtained through the calorimetric data based on mass and energy balances of a stirred tank reactor. According to Gesthuisen et al. (2005),[1] several methods of reaction calorimetry could be applied for 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. In laboratories at industry and even in laboratories at universities significant information about the polymerization reactions carried out in lab scale reactors is lost because sampling is not always possible due to the difficulty of sampling during the reaction (high viscosity, heterogeneity of the reaction medium or pressurization of the reactor). The calorimetry technique, as a non invasive, fast, continuous and low cost technique, can allow the inference of valuable information regarding the evolution of the reaction that, in another way, could be lost.

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Despite the estimation of conversion for emulsion homopolymerization reactions being well established for commercial laboratory calorimetry reactors[2,3] or lab-scale reactors specially (high flow rate of the cooling fluid in the jacket) constructed to operate as calorimetry reactors,[4,5] it is still a challenge to use calorimetry to estimate conversion in standard lab-scale reactors as the reactor temperature control is not so effective and these reactions present relatively high residence time for the cooling fluid. The heat loss of standard lab scale reactors are, usually, very significant when compared to the heat of reaction. In this case, the jacket inlet temperature is often higher than the jacket outlet temperature and the reactor temperature, therefore, temperature profiles in the reactor and jacket do not follow the conventional profiles of isoperibolic (jacket temperature is constant and lower than the reactor temperature) and isothermal (reactor temperature is constant and higher than the jacket temperature) methods.

The objective of this work is to study the use of calorimetric techniques to monitor polymerization reactions in a standard 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 (jacket inlet and outlet temperature and reactor temperature data are acquired and stored at a PC). Water was used as the heating/cooling fluid and its flow rate was kept constant resulting in a relatively high residence time of 18s. The reactor temperature was controlled by a PI controller. The isothermal and isoperibolic calorimetry methods were used to determine the global conversion of batch vinyl acetate emulsion polymerization reactions.

Materials and Methods

The reactor setup including the reactor temperature control scheme is shown in Scheme 1. This unit possesses a remote control system of reactor temperature and agitation frequency including three boards for data acquisition AD/DA. The temperature data was acquired throw three thermocouples (PT100) positioned at different points of the reactor (jacket inlet and outlet and reaction medium) as shown in Scheme 1 (data acquisition points).

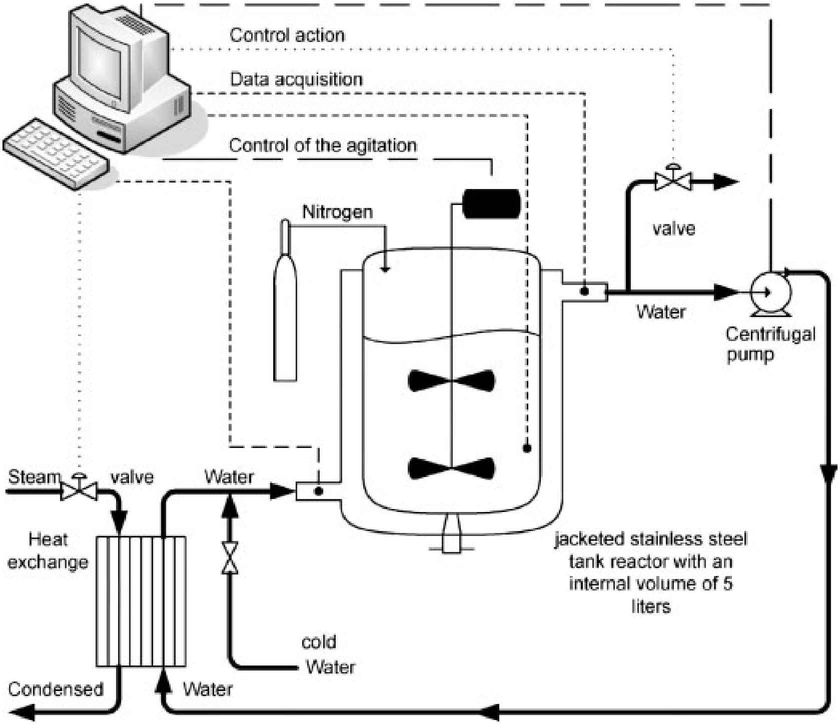
The heating/cooling fluid flow rate was kept constant throw the centrifugal pump, keeping a pressure of approximately 2 *Kgf/cm*^{2} at the jacket. The reactor temperature control was attained by a PI controller that controls two pneumatic valves that are responsible for the dosage of the steam (supplied by a boiler) through the heat exchanger and of cold water through the jacket.

In all reactions, the reactor was initially charged with distilled water, buffer agent (sodium bicarbonate) and surfactant (sodium lauryl sulfate - SLS) and the reactor was heated to the reaction temperature. 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 (potassium persulfate) 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. The reactants were used as received. Table 1 presents the recipes employed in all reactions.

Determination of the Global Conversion of the Reaction Through Calorimetry

Using Isothermal Calorimetry

In this procedure, the reaction temperature set-point was setup and a proportional controller (PI) manipulated the jacket inlet temperature in order to control the reaction temperature. To obtain the polymerization rate, it was necessary to solve the mass and energy balances of the reactor and the jacket.



Scheme 1.
Reactor setup.

For a batch reaction, the energy balance of the reactor is given by eq. (1):

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

The terms Q_r and Q_j are the rate of heat generated by the polymerization reaction and the rate of heat exchanged through the 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 lower 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.

As the isothermal condition was not reached, the term of the left side of eq. (1) was different from zero. In this term T_r is the temperature of the reactor, m_r is the total mass of reaction medium and

Table 1.
Recipe of reactions.

Reactants	R1	R2	R3	R4
Vinyl Acetate	800.60	1260.00	1260.00	1260.00
Water	3250.00	2940.00	2940.00	2940.00
Na_2CO_3	8.00	8.00	8.00	8.00
$K_2S_2O_8$	12.00	9.00	9.00	4.50
SLS	10.00	10.00	10.00	10.00

$Cp_r(J/gK)$ is the specific heat of the reaction medium calculated by the following equations[6] considering the main compounds present in the reactor:

$$Cp_A = \left(\frac{1}{86}\right) \times (3.621 + 6.676\ 10^{-2}T - 2.103\ 10^{-5}T^2 - 3.965\ 10^{-9}T^3)(4.187) \quad (2)$$

$$Cp_W = \left(\frac{0.239\ 10^{-3}}{18}\right) \times (5.263\ 10^4 + 2.412\ 10^2 T - 8.509\ 10^{-1}T^2 + 10^{-3}T^3) \times (4.187) \quad (3)$$

$$Cp_r = Cp_A z_M + Cp_W z_W \quad (4)$$

where, Cp_A (J/gK) and Cp_W (J/gK) are, respectively, the specific heats of vinyl acetate and of water, z_M and z_W are the mass fractions of monomer and water in the reactor.

The energy balance of the jacket is given by:

$$m_j Cp_j \frac{dT_j}{dt} = -Q_j + \dot{m}Cp_{cooling}(T_{jin} - T_{jout}) - Q_{lossj} \quad (5)$$

In the energy balance of the jacket, Cp_j is the specific heat of the cooling fluid $Cp_{cooling}(J/gK)$, calculated by eq. (3). The mass of cooling fluid present inside the jacket m_j, is equal to 4150 g and the mass flow rate of cooling fluid in the jacket, $\dot{m}$, was considered constant and equal to $\dot{m} = 222.222\ g/s$.

The average temperature of the jacket T_j was calculated by the following[7]

$$T_j = (T_{jout} - T_{jin})/\ln(T_{jout}/T_{jin}) \quad (6)$$

where T_j is temperature of the jacket and T_{jin} and T_{jout} are, respectively, jacket inlet and outlet temperatures.

The global loss to the surroundings of the jacket Q_{lossj} was obtained throw eq. (7). The parameter UA_j was estimated at the beginning of the reaction considering $Q_r = 0\ W$.

$$Q_{lossj} = UA_j(T_j - T_{sur}) \quad (7)$$

In this technique, Q_j was calculated by the energy balance of the jacket (eq. 5).

The polymerization rate, Rp, was calculated by the following equation:

$$Rp = Q_r/(-\Delta H) \quad (8)$$

where, $(-\Delta H) = 1040.305\ J/g$ is the molar heat of polymerization of vinyl acetate.[8]

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

$$X_{calor} = \int_0^t \frac{dM}{dt} \bigg/ M_0 = \int_0^t R_p/M_0 \quad (9)$$

where M_0 is the total monomer mass fed to the reactor.

When isothermal conditions are obtained and the reactor temperature is kept constant, the heat transfer coefficient is not necessary if the difference between jacket inlet and outlet temperature is sufficiently large[1] and the heat loss of the jacket to the surrounding is negligible. Nevertheless, this is not an usual condition of standard lab scale reactors.

Some considerations were assumed in the solution of eq. (1) to (9): the density of the cooling fluid was constant ($\rho_{water} = 1\ g/mL$); 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; the effect of the agitation heat was despicable.

Using Isoperibolic Calorimetry

In this technique, the temperature of the jacket is kept constant, and the temperature of the reactor is not controlled. As T_j is constant, the energy balance of the jacket is not required and T_j was calculated by eq. (6). Nevertheless, to calculate Q_r throw eq. (1) it is necessary to determine the term Q_j

by the following equation:

$$Q_j = UA(T_j - T_r) \tag{10}$$

UA was estimated by the following procedure: the reactor was charged and the opening of the valves was adjusted to obtain a constant temperature in the jacket (open-loop). At the steady-state, the inlet and outlet temperatures of the jacket and of the reactor were measured. In sequence, a constant power was applied through a probe (electric resistance), and again the temperatures were monitored until they reached the steady-state. Soon afterwards, the inlet and outlet temperatures of the jacket and of the reactor were measured. Therefore, the initial value of UA was estimated using the following equation:

$$UA = Q_c/(T_r - T_j) \tag{11}$$

where Q_c corresponds to the electric power dissipated throw the probe.

Such procedure was repeated after the end of the reaction in order to re-estimate UA. On-line estimation of U (global heat exchange coefficient) 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 (m^2) is also difficult to be measured precisely. For systems with constant UA, this term can be determined by calibration before the reaction, then introduced in the energy balance to estimate Q_r. If U varies only slightly during the reaction, a linear interpolation of UA between its calibrated values at the start and at the end of the reaction might be acceptable. Quite often, in batch emulsion polymerization reactions UA is considered a function of the conversion.[9] The polymerization rate of the monomer, Rp and the calorimetric global conversion X_{calor} were calculated through eq. (8) and (9), respectively.

Results and Discussion

Isothermal Calorimetry

Figures 1 and 2 show that the profile of Q_{lossj} calculated by the isothermal calorimetry technique is very similar to that obtained by gravimetry. Reaction R2 was carried out with the same formulation of reaction R1, but at a lower reaction temperature, what justifies the reduction in the value of Q_{lossj} because the difference between the jacket temperature and the surrounding temperature is lower than in reaction R2.

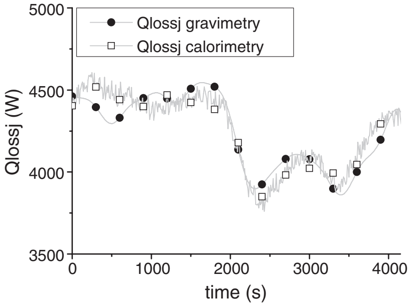


Figure 1.
Heat loss of the jacket, Q_{lossj} of R1.

Figures 3 and 4 and Figures 5 and 6 show the evolution of temperatures and reaction rate during reactions R1 and R2, respectively. It can be observed in Figure 3 that with the addition of the initiator the control of the reactor temperature began to actuate, reducing the jacket inlet temperature and producing the inverse effect when the heat generated by the reaction decreased. However, due to the weak performance of the PI controller the isothermal condition was not reached,

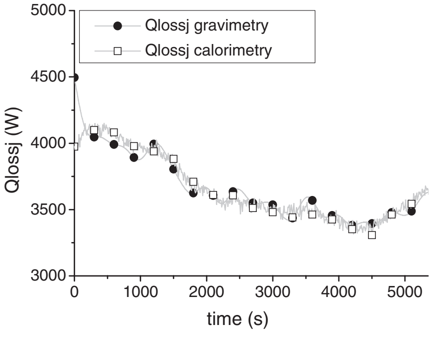


Figure 2.
Heat loss of the jacket, Q_{lossj} of R2.

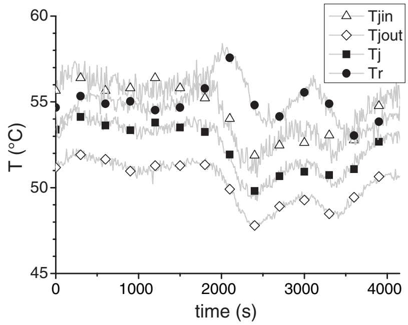


Figure 3.
Temperature profiles of R1.

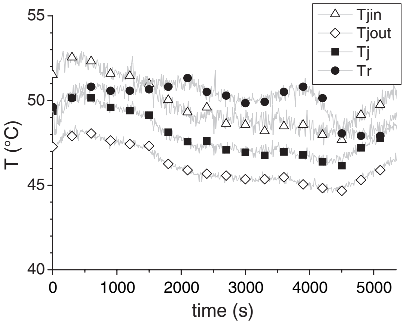


Figure 5.
Temperature profiles of R2

and for this reason the variation of the reactor temperature was taken into account in the calculation of Q_r.

The value of ΔT_j stayed practically constant along the reaction with T_{jin} always higher than T_{jout} along the reaction due to the relatively high residence time (~18 s) of the cooling fluid in the jacket and the considerable heat losses, which indicates that Q_{lossj} is very expressive compared to the other terms of the energy balance. Figure 4 shows some oscillations in the profile of the generated heat. These are related to the variations in the temperature of the reactor, caused by the heat of the reaction and by the action of the PI controller. Besides it can be observed that the maximum peak of the generated heat corresponds to the beginning of the gel effect.

The decrease of the reaction temperature in 5 °C in reaction R2 reduced the polymerization rate, increasing the reaction time and reducing the amplitude of the oscillations in the reaction temperature as can be observed in Figure 5. According to Figure 6 the decrease of the temperature reduced the maximum value of Q_r in relation to that obtained in reaction R1. Comparing the conversion obtained by the calorimetric technique with that obtained by the gravimetric technique it is possible to observe a good agreement in both reactions.

Isoperibolic Calorimetry

Reaction R3 was carried out with the same formulation of reaction R2 carried out in isothermal calorimetry (solids content of 30% and T = 50 °C). Reaction R4 had the same formulation as R3 except for the amount of initiator that was reduced to the half.

The global heat exchange parameter UA was obtained before and after the reaction. UA decreased during the polymerization and it was considered to change with the conversion since the viscosity of the latex

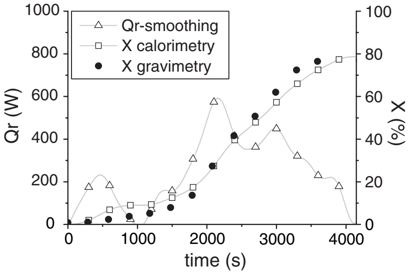


Figure 4.
Heat of reaction (Q_r) and conversion (X) of R1.

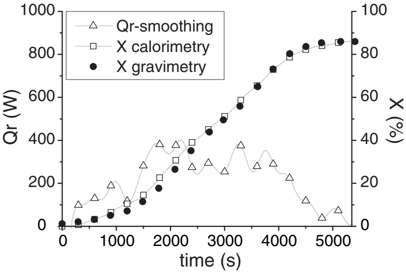


Figure 6.
Heat of reaction (Q_r) and conversion (X) of R2.

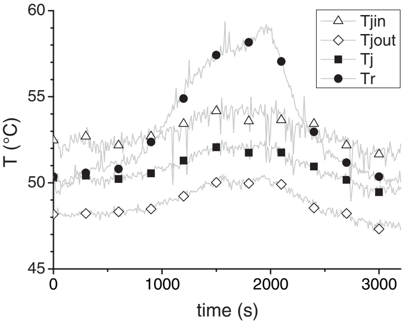


Figure 7.
Temperature profiles in R3.

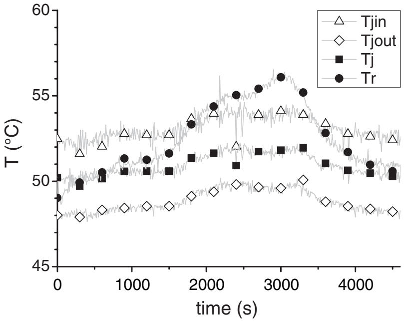


Figure 8.
Temperature profiles in R4.

increased with the solids content. The heat losses to the surroundings of the reactor, Q_{lossr} were considered negligible.

In isoperibolic calorimetry the inlet jacket temperature is kept constant. If the jacket flow rate is high enough, the jacket temperature stays almost constant during the reaction. However, as can be observed in Figure 7, the temperature of the jacket did not stay constant along the reaction as the cooling fluid flow rate was not high enough. Besides that, it is possible to observe that the jacket inlet temperature increased with the increase of the reaction temperature due to the heat of polymerization. Therefore, the value of the measured jacket inlet temperature, T_{jin}, was affected by the heat conducted by the reactor wall and did not corresponded to the real temperature of the cooling fluid entering the jacket that was kept constant. The heat conduction was very high as the reactor was made of steel. The positions of the thermocouples that measured the inlet and outlet jacket temperature were very similar and connected to the reactor. Analyzing Figures 7 and 8 one can observe that ΔT_j stayed practically constant along the reactions, indicating that the heat conduction through the reactor wall must have interfered with both thermocouples in the same way. Therefore, to calculate the conversion the temperature of the jacket was considered constant along the reaction and equal to the temperature measured at the steady state before the beginning of the reaction.

Reaction R3 was faster than reaction R2 because the reaction temperature was higher as the reactor temperature was not controlled. Analyzing Figure 9 it is observed a very good agreement between the conversion obtained by gravimetry and calorimetry.

Figures 8 and 10 refer to reaction R4, where the amount of initiator was reduced

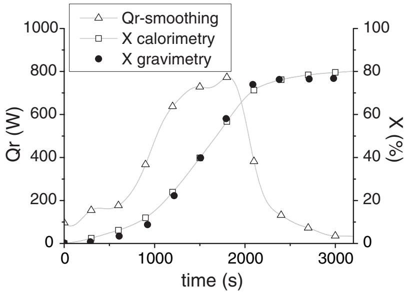


Figure 9.
Heat of reaction (Q_r) and conversion (X) in R3 – with T_j constant.

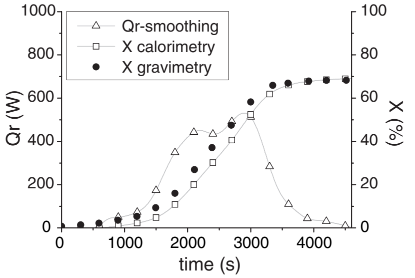


Figure 10.
Heat of reaction (Q_r) and conversion (X) in R4 – with T_j constant.

to the half in comparison with reaction R3, these figures show that the time of reaction increased as the polymerization rate was lower. The analysis of Figure 10 shows a very good agreement between the conversion obtained by gravimetry and calorimetry.

Conclusions

The present work demonstrated that both calorimetric techniques (isothermal and isoperibolic) can be applied to monitor emulsion polymerization reactions in a standard lab-scale reactor with relatively high residence time of the cooling fluid.

This kind of reactor presents some difficulties to apply isothermal calorimetry as isothermal conditions may not be attained (the reaction temperature oscillates along the reaction) and the heat losses to the surroundings are very significant.

The isoperibolic technique presented better results when compared to isothermal technique. Nevertheless, this technique implies in a variation of the reaction temperature that many times may not be acceptable as it may affect product properties and reactor safety. Results also indicate that the position of the thermocouples should be regarded with much attention as the measured value of the temperature could be affected by heat conducted by the reactor wall.

The choice between both techniques depends of the formulation of the reaction, the allowed reaction temperature range and of the characteristics of the reactor.

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