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Optimization of reaction calorimetry with supercritical fluids: A complete term-by-term analysis of the heat flow equation

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Abstract

A complete analysis of the heat flow equation in reaction calorimetry with supercritical fluids is presented. An especially developed reaction calorimeter is employed to study the challenges introduced by the supercritical state of the reaction mixture and the particularities that they generate in the calorimetric calculations. As a model reaction the free radical dispersion polymerization of methyl methacrylate is chosen. Each term of the heat flow equation is optimized with special attention to the accumulation term and the injection term. The overall heat transfer coefficient, being the most important variable of the heat flow equation, is estimated using four different approaches, both theoretical and experimental. Moreover, the injection phase of additional reactants is shown to generate undesirable temperature oscillations and an optimized injection strategy is found to eliminate the erroneous calorimetric calculations. As a result the enthalpy of reaction and the heat released by the reaction are very accurately estimated.
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Keywords: Calorimetry; Heat transfer; Monitoring; Optimization; Polymerization; Supercritical fluids

1. Introduction

Supercritical fluids (SCFs) have been continuously attracting scientific interest during the past decades because they represent an environmentally benign alternative for volatile organic compounds (VOCs) in the chemical industry [1]. The production and consumption of such organic compounds has been progressively phased out starting from the Montreal Protocol on Substances that Deplete the Ozone Layer, signed in 1987. The particularity that renders SCFs attractive is the possibility to tune their physical and chemical properties by slight changes of the temperature and/or the pressure in order to resemble those of a liquid or a gas [2]. Although research on SCFs initially started with water, the most widely used nowadays is carbon dioxide (CO_2). From a process development point of view CO_2 has a relatively easily attainable critical point ($T_c = 31.1\ ^\circ C$ and $P_c = 7.38$ MPa) and it is non-toxic and non-flammable. Furthermore, it is very cheap and it can be provided in high purity. Finally it is advantageous for biomedical and pharmaceutical applications due to its generally regarded as safe (GRAS) status.

Beginning from the first reactions reported with SCFs in the second half of the 19th century their industrial applications increased and the two most important applications came later with the commercialization of the BASF process for the production of ammonia in 1913 and the polymerization of ethylene under supercritical conditions in 1939 [3,4]. More recently, CO_2 has been widely employed as an extracting agent for the extraction of natural products, mainly for food ingredients and phytopharmaceuticals, and as a solvent for polymerization reactions [5,6]. Overall, supercritical reaction chemistry is advancing at a high pace and the need for kinetics information and safety analysis for process development and scale-up studies is increasing accordingly.

Heat flow reaction calorimetry is one of the analytical tools that can provide such information [7]. By definition it is a thermal analysis technique that monitors the evolution of a chemical reaction by measuring the heat that flows in or out of a reactor [8]. It provides an extensive engineering insight of the chemical process allowing for the development of model-based predictive control schemes for improved process control. Overall heat

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Nomenclature

A	heat transfer surface (m^2)
AIBN	2,2′-azoisobutyronitrile
c_p	reaction mixture constant pressure specific heat capacity ($J\,kg^{-1}\,K^{-1}$)
c_v	reaction mixture constant volume specific heat capacity ($J\,kg^{-1}\,K^{-1}$)
d_r	reactor's diameter (m)
d_s	stirrer's diameter (m)
h_{jacket}	jacket side film heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
h_r	reactor side film heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
k	reaction mixture thermal conductivity ($W\,m^{-1}\,K^{-1}$)
k_w	reactor wall thermal conductivity ($W\,m^{-1}\,K^{-1}$)
l	reactor wall thickness (m)
$m_i c_{v,i}$	are the mass (kg) and the constant volume specific heat capacity ($J\,kg^{-1}\,K^{-1}$) of each reactant (i) in the reactor
$m_{ins} c_{p,ins}$	are the mass (kg) and the constant pressure specific heat capacity ($J\,kg^{-1}\,K^{-1}$) of all the inserts in the reactor (e.g. ultrasound sensor, calibration heater, etc.)
MMA	methyl methacrylate
MTSR	maximum temperature of the synthesis reaction
N	stirrer's rotation speed (s^{-1})
P_c	critical pressure (MPa)
PDMS-mMA	poly(dimethylsiloxane)monomethacrylate
$\dot{Q}_{acc}$	rate with which heat accumulates in the reactor (W)
$\dot{Q}_{calib}$	rate with which heat is generated by the calibration heater in the reactor (W)
$\dot{Q}_{dos}$	rate with which heat is inserted in the reactor by the dosing of the reactants (W)
$\dot{Q}_{flow}$	rate with which heat flows from the reactor to the jacket (W)
$\dot{Q}_{loss}$	rate with which heat is lost either by the reactor, the jacket or the surrounding devices due to secondary reasons (e.g. radiation) (W)
$\dot{Q}_{mix}$	rate with which heat is generated due to mixing (W)
$\dot{Q}_r$	rate with which heat is generated by the reaction (W)
$\dot{Q}_{stir}$	rate with which heat is generated by the stirrer in the reactor (W)
$scCO_2$	supercritical carbon dioxide
SCF	supercritical fluid
T_c	critical temperature (°C)
T_j	jacket temperature (°C)
$\tilde{T}_j$	jacket temperature sinusoidal disturbance (°C)
δT_j	amplitude of jacket temperature sinusoidal disturbance (°C)
T_r	reactor temperature (°C)
$\tilde{T}_r$	reactor temperature sinusoidal response (°C)
δT_r	amplitude of reactor temperature sinusoidal response (°C)
U	overall heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
VOC	volatile organic compound

Greek letters

η	reaction mixture viscosity ($kg\,m^{-1}\,s^{-1}$)
ρ	reaction mixture density ($kg\,m^{-3}$)
φ	phase difference between the jacket sinusoidal disturbance and the reactor response
ω	frequency of jacket temperature sinusoidal disturbance (s^{-1})

transfer coefficients and reaction mixture specific heat capacities can be also measured. This information is crucial for the determination of safety variables, like the maximum temperature of the synthesis reaction (MTSR), in order to estimate the thermal risks of a process [9,10]. In the case of polymerizations, reaction calorimetry has been widely used and an extensive and elaborate review on the state of the art isothermal calorimeters and their applications comes from Moritz [11]. Preliminary results on the development of reaction calorimetry in SCFs have been previously reported [12]. In this study a more elaborate and complete approach in the construction of the heat flow equation is presented to achieve a more accurate monitoring of the studied reactions.

2. Experimental part

2.1. Reaction calorimeter

The experimental set-up consists of a high pressure reactor coupled to an RC1*e* reaction calorimeter and has been especially designed and developed to work with supercritical fluids with the collaboration of Mettler-Toledo (Schweiz) AG (Fig. 1). The reactor's maximum operating pressure and temperature are 35 MPa and 300 °C, respectively. It is equipped with a Pt100 temperature sensor, a pressure sensor, a magnetic stirrer connected to a double stage turbine, an ultrasonic propagation velocity sensor, and a calibration heater. Additionally the reactor's cover has two sapphire windows allowing for optical observations with the use of an optical fibers endoscope. The reactor has three inlets/outlets used to charge and discharge it and is surrounded by a jacket to control its temperature. The reactor cover and flange temperatures are also controlled.

Temperature control is achieved by the RC1*e* calorimeter using silicon oil that circulates at high flow rate into the jacket. Two additional controllers are used to interface with a personal computer, which uses a special software (WinRC) to control the entire installation. The calorimeter can operate in the following three modes:

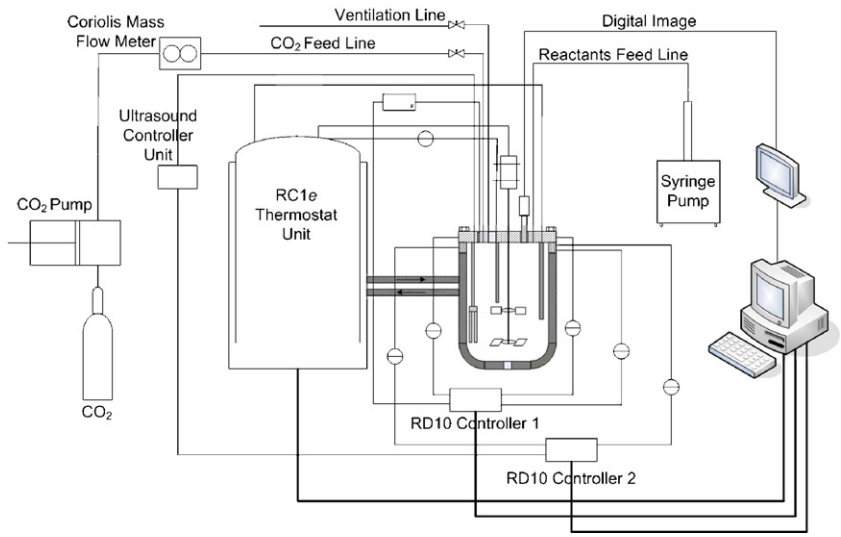

Fig. 1. Schematic representation of the experimental set-up consisting of the high pressure reactor and the RC1*e* calorimeter.

- *Isothermally*: The jacket temperature is varied so that the reactor temperature remains constant.
- *Isoperibolically*: The jacket temperature is set to a fixed value.
- *Adiabatically*: The jacket temperature follows exactly the reactor temperature.

Carbon dioxide is charged in the reactor using a high precision coriolis mass flow meter connected to a piston pump. The additional reactants are inserted in the reactor with a high pressure syringe pump.

2.2. Materials

Methyl methacrylate (MMA) (99+% purity, stabilized with ca. 0.004% hydroquinone) and 2,2′-azoisobutyronitrile (AIBN) were purchased by Fluka and were used as received. Poly(dimethylsiloxane)monomethacrylate (PDMS-mMA) was purchased by ABCR and had a weight average molecular weight of 5000 g mol^{-1}. Carbon dioxide (quality 30, purity 99.9+%) provided by Carbagaz was used without further purification.

2.3. Model reaction

The free radical dispersion polymerization of methyl methacrylate was chosen in this study as a model reaction for two reasons. Firstly, extensive experience and knowledge has been acquired in our group on the MMA polymerization during the past years, both in theoretical and experimental level [13,14]. Secondly, this reaction is one the most well studied polymerizations in SCFs [5,15]. Hence considerable information is available in the literature on its evolution and on the effect of all the reaction parameters, which is necessary for the interpretation of the experimental data and the optimization of the reaction calorimetry technique.

A prerequisite for correct and representative calorimetric calculations is that all the reaction conditions, especially temperature, are established before the reaction is actually launched. Consequently, one of the reactants has to be kept separately until the conditions are attained. In this case, the initiator (AIBN) was chosen. The protocol used in every experiment consists of nine steps in the following order. The reactor is charged with the reactants and sealed. It is purged with CO_2 for approximately 10 min to eliminate traces of oxygen and charged with the respective CO_2 mass. The desired reaction temperature is reached and the initiator, dissolved in a sufficient quantity of MMA, is injected into the reactor. The reaction is left to conclude, the reactor is cooled down and the CO_2 is slowly vented. Finally, the polymer is recuperated from inside the reactor for further analysis. The following set of conditions was chosen as a base case scenario and served as the point of reference during the heat flow equation optimization tests.

- Reaction temperature: 80 °C;
- Reaction pressure range: 20.0–25.0 MPa;
- Initial MMA mass in reactor: 205.12 g;
- Stabilizer used: poly(dimethylsiloxane)monomethacrylate (PDMS-mMA);
- Stabilizer mass: 25.28 g (10 wt.% PDMS-mMA/MMA);
- Injection solution composition: 2.528 g AIBN/47.68 g MMA (1 wt.% AIBN/MMA);
- Solution injection method: constant flow at 50 mL min^{-1};
- CO_2 mass: 680 g;
- Stirring speed: 400 rpm.

3. Results and discussion

According to the principle of calorimetry the heat released by a reaction constitutes an unmistakable trace of its evolution, hence the latter can be monitored. The heat flow equation around the reactor is based on the following heat balance:

$$[\text{accumulation}] = [\text{source}] + [\text{inflow}] - [\text{outflow}]$$

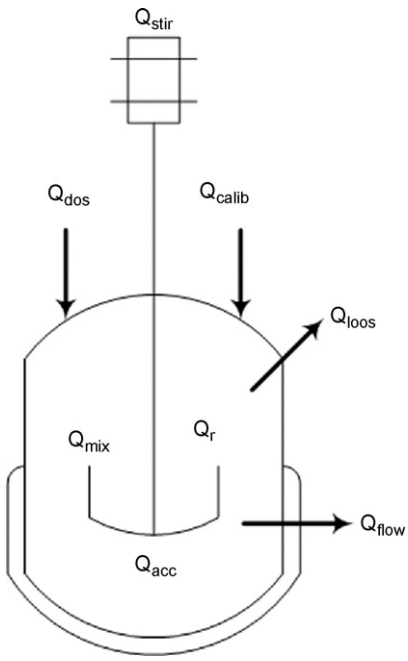

Fig. 2. Schematic representation of the heat flow equation.

The above expression can be transformed by substitution of each term with the corresponding heat terms as shown in Fig. 2.

$$\dot{Q}_{\mathrm{acc}} = \dot{Q}_{\mathrm{r}} + (\dot{Q}_{\mathrm{dos}} + \dot{Q}_{\mathrm{mix}} + \dot{Q}_{\mathrm{stir}} + \dot{Q}_{\mathrm{calib}}) - (\dot{Q}_{\mathrm{flow}} + \dot{Q}_{\mathrm{loss}}) \Rightarrow \dot{Q}_{\mathrm{r}} = \dot{Q}_{\mathrm{flow}} + \dot{Q}_{\mathrm{acc}} - \dot{Q}_{\mathrm{calib}} - \dot{Q}_{\mathrm{stir}} + \dot{Q}_{\mathrm{loss}} - \dot{Q}_{\mathrm{dos}} - \dot{Q}_{\mathrm{mix}} \quad (1)$$

Supercritical fluids demonstrate two major challenges as far as calorimetry is concerned. First of all, it is in their nature to demonstrate density fluctuations, which render the composition homogeneity in the reactor more difficult to achieve [16]. Therefore, it is important to assure that good mixing conditions are established in the reactor. For our experimental set-up, previous studies based on Wilson plot analysis by Lavanchy have showed that for pure $scCO_2$ a minimum of 200 rpm with the double stage turbine is necessary to achieve sufficient composition homogeneity [17]. The second particularity is that the reaction medium being in the supercritical state occupies the entire available volume in the reactor. This characteristic further implies that first the heat exchanging surface will be differently calculated than in classical calorimetry and second that the reactor cover and flange are in contact with the reaction medium, hence heat is also exchanged through these two elements and it has to be accounted for.

Therefore, a detailed analysis is necessary to identify the best solution for the calculation of each term of Eq. (1). In the following discussion if comparison between different strategies for the determination of a term is necessary, this is done based on the base case scenario of the model reaction and considering the best strategies for the rest of the terms. Results are compared based on the calculated enthalpy of reaction and reaction heat rate.

3.1. The heat flow term

The heat flow term ($\dot{Q}_{\mathrm{flow}}$) is the most important term since it accounts for the majority of the heat released by the reaction, and it is analytically calculated using Eq. (2).

$$\dot{Q}_{\mathrm{flow}} = UA(T_{\mathrm{r}} - T_{\mathrm{j}}) \quad (2)$$

The reactor temperature is measured by the temperature sensor installed, with an accuracy of 0.2 mK, and its value is considered representative for the entire volume. The jacket temperature is measured at the inlet of the jacket with an accuracy of 1 mK and its value is considered as homogeneous throughout the jacket. This approximation stands because the temperature regulating oil circulates at an extremely high flow rate and the temperature differences between the inlet and the outlet are two orders of magnitude lower than the detection resolution.

The heat exchanging surface, constitutes the first particularity as explained before, and is constant and equal to the entire inner reactor surface. For our experimental set-up this value was geometrically calculated and found to be 0.0477 m^2. In the case of liquid calorimetry the surface depends on the reacting mass and additional mathematical algorithms are used to take into account the vortex created by mixing.

Finally, the most important parameter in Eq. (2) is the overall heat transfer coefficient (U) between the reactor and the silicon oil. Typically this variable is measured before the reaction using a standard calibration procedure of the reaction calorimeter [18]. However, in the cases where U changes significantly during the reaction, like polymerization reactions, this variable needs to be measured also at the end of the reaction [19]. The overall heat transfer coefficient was measured before and after the model polymerization reaction and the respective values are:

$$U_{\mathrm{init}} = 326.6\,\mathrm{W\,m^{-2}\,K^{-1}} \quad U_{\mathrm{fin}} = 288.1\,\mathrm{W\,m^{-2}\,K^{-1}}$$

Furthermore, in calorimetry the intermediate values are of importance because they affect the heat flow calculations. In this analysis four different approaches are investigated for the U variation.

- Constant average value.
- Linear evolution between initial and final values.
- Evolution proportional to conversion.
- Application of the temperature oscillation technique.

3.1.1. Constant average value approach

The first approach essentially consists of calculating an average value between the initial and the final U values (307.4 $\mathrm{W\,m^{-2}\,K^{-1}}$). Although it is explained during the comparison of the four approaches that it does not introduce a significant error in the enthalpy of reaction calculation, it does not account for the dynamic evolution of this variable.

3.1.2. Linear evolution approach

In order to take into account the fact that during the polymerization reaction the composition of the reaction mixture changes, inducing a change in the overall heat transfer coefficient, the

more simplistic evolution, namely a linear change, is also investigated. Such an evolution is known to be used in cases like this one, where the intermediate values cannot be found. The improvement in this case comes from the acknowledgement of the overall heat transfer coefficient decrease and hence of the change in the mixture composition.

3.1.3. Proportional to conversion approach

The overall heat transfer coefficient can be more analytically expressed as the sum of three individual resistances, namely that of the reaction mixture boundary layer, of the metallic wall, and of the silicon oil boundary layer.

$$\frac{1}{U} = \frac{1}{h_r} + \frac{l}{k_w} + \frac{1}{h_{jacket}} \tag{3}$$

Moreover, Eq. (3) can be further expanded with the aid of dimensional analysis to express the reactor side film heat transfer coefficient as a function of the reactor and the mixture's properties.

$$\frac{1}{U} = \text{const.}\left(\frac{\eta}{\rho^2 c_v k^2}\right)^{1/3}\left(\frac{d_r^3}{N^2 d_s^2}\right)^{1/3} + \frac{l}{k_w} + \frac{1}{h_{jacket}} \tag{4}$$

The variables in the first parenthesis vary as the monomer is transformed in polymer and the apparent mixture properties (e.g. viscosity, η) change. The rest of the variables in Eq. (4) though, remain constant throughout the reaction, because the experiments with the model reaction are carried out under isothermal conditions. Therefore, it is reasonable to assume that the overall heat transfer coefficient evolution is directly linked to the reaction evolution, hence the conversion.

The calculation of U proportional to the conversion is essentially an iterative process. Initially the average value of U is used to find the reaction heat rate curve and then the conversion. Then, using the conversion curve and the initial and final U values, provided by the calibration processes, the new U estimation is derived proportional to the conversion. The calculations continue in this iterative way until a set tolerance is achieved for the enthalpy of reaction value.

3.1.4. Temperature oscillation technique approach

The forth and last approach in the calculation of the overall heat transfer coefficient is by using a non-stationary method. It is essentially based on the production of temperature oscillations of the jacket temperature and the monitoring of the system's response. This technique has been originally developed by Reichert and co-workers and applies also in the case of producing an oscillating heat signal using the calibration heater [20,21]. To date the technique has been used in several emulsion polymerization systems and biochemical applications [22,23].

In theory, a sinusoidal disturbance is added to the jacket temperature, defined by the controlling mechanism of the reactor, of the form:

$$\tilde{T}_j(t) = \delta T_j e^{i\omega t} \tag{5}$$

and it induces a response of the reactor temperature of the form:

$$\tilde{T}_r(t) = \delta T_r e^{i(\omega t + \varphi)} \tag{6}$$

Based on the assumption that over the time of one period the contributions of all the terms in the heat flow equation, except the heat flow term and the accumulation term, are equal to zero, the following equations for the calculation of the overall heat transfer coefficient can be derived.

$$\text{(from the real part)} \quad UA = \frac{c_v \omega \delta T_r \sin\varphi}{\delta T_r \cos\varphi - \delta T_j} \tag{7}$$

$$\text{(from the imaginary part)} \quad UA = \frac{-c_v \omega}{\tan\varphi} \tag{8}$$

$$\text{(combination of the two)} \quad UA = \frac{c_v \omega}{\tan[\arccos(\delta T_r/\delta T_j)]} \tag{9}$$

A comparative study on the results of the above three equations by De Luca et al. has shown that Eq. (9) is the more robust being the less sensible in errors on the amplitudes of the experimental data and is therefore the chosen one [24].

In practice, the WinRC software that controls the reactor operation has a special pre-designed phase called "SmartCal". This feature makes use of the previously mentioned technique of temperature oscillation calorimetry and permits the calculation of the overall heat transfer coefficient at the same time with the heat of reaction.

3.1.5. Comparison results

The four approaches are compared in terms of the predicted overall heat transfer coefficient evolution and the calculated enthalpy of reaction and the results are presented in Fig. 3 and Table 1. The differences in the calculated enthalpy of reaction are very small and the justification, although the overall heat transfer coefficient evolution has changed dramatically, is twofold. First, the difference between the average U value and the varying ones is small with respect to their absolute values. Second, for the calculation of the enthalpy of reaction the integral of the heat flow term is used and the differences of the surfaces below the curves in Fig. 3 are small.

As far as the temperature oscillation calorimetry approach is concerned, it must be explained that the disturbed initial values

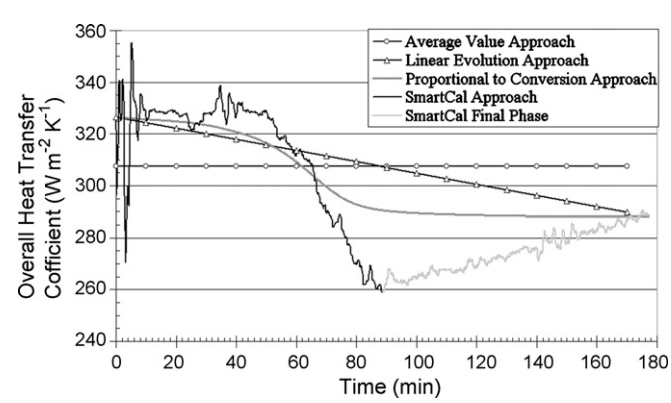

Fig. 3. Comparison of the overall heat transfer coefficient variation between the four proposed approaches.

Table 1
Enthalpy of reaction values calculated using the four proposed approaches for the overall heat transfer coefficient

	Enthalpy of reaction (kJ mol^{-1})
Average value	55.72 ± 1.17
Linear evolution	57.37 ± 1.21
Proportional to conversion	57.04 ± 1.20
Temperature oscillation calorimetry	58.56 ± 1.23
Literature value	57.20 ± 0.60

(0–10 min) are justified because during that period of time the jacket and the reactor temperatures are strongly disturbed by the injection of the additional reactants. This effect results in a non-harmonic oscillation of both temperatures that in turn gives the disturbed values, which are not reliable.

Furthermore, during the final phase of the reaction (conversion above 95%), the SmartCal results show an increase of the overall heat transfer coefficient. Such an increase cannot be fully explained and is bound to be the result of several physical phenomena including the formation of some particle agglomerates or even particle coalescence, repartitioning of $scCO_2$ between the continuous and the polymer phase due to the changing composition and others. Experimental results from O'Neill et al. show that the absence of MMA at the final reaction stages, produces a loss of stabilization due to the decreased solvency of the stabilizer tail in the continuous phase resulting in particle agglomeration and some degree of coalescence [25]. Additionally, Wissinger and Paulaitis have shown that at elevated pressures in the presence of $scCO_2$ the glass transition temperature of PMMA drops significantly and its liquid state assists agglomeration and coalescence [26,27].

Based on the above observations and conclusions and although none approach improved the obtained results spectacularly, the method of choice, is the proportional to conversion approach due to the following advantages:

- It has a relative theoretical background.
- The resulting U curve shape is verified by the temperature oscillation approach as being the correct sigmoid type.
- It does not have the drawbacks of the temperature oscillation approach.
- This approach is certain to deliver much better calorimetric results when monitoring reactions in non-isothermal mode or more exothermic reactions where the larger ($T_r - T_j$) will make the jacket heat flow term more important for the final outcome.
- It results the most accurate value for the enthalpy of reaction.

3.2. Reactor cover and flange contributions

The second particularity in reaction calorimetry with SCFs comes from the reactor cover and flange. Since the reaction medium is in contact with the entire reactor inner surface, heat is exchanged also through these two elements. Therefore, their contribution has to be taken into account in the heat flow term. This addition does not only improve the calculated reaction heat rate and enthalpy of reaction but also the dynamic response of the calorimeter, as have been shown in previous studies [28].

$$\dot{Q}_{\text{flow}} = UA(T_r - T_j) + U_{\text{flange}}A_{\text{flange}}(T_r - T_{\text{flange}}) + U_{\text{cover}}A_{\text{cover}}(T_r - T_{\text{cover}}) \quad (10)$$

The determination of the overall heat transfer coefficients for the cover and the flange was carried out using a method proposed by Lavanchy and is based on the difference of the baseline when different set temperatures are given for the flange and the cover respectively, with respect to the reactor temperature [17]. However, this is only possible before the polymerization reaction because the sensitivity of the polymer particles' dispersion at the end of the reaction does not permit the application of the method. Hence, to determine the end value it was approximated that the ratio of the initial over the final value for the jacket U value stands also for the flange and cover U values. This approximation can be justified by looking at Eq. (3). Since the reaction is carried out in an isothermal mode, it is logical to assume that the second and the third terms in the right-hand side, which depend on the reactor itself and the temperature regulating oil, do not change. The only part that changes is the reaction mixture film heat transfer coefficient. The latter, though, is bound to change in the same way for all three parts of the reactor that surround the reaction mixture. The measured initial values and the estimated final values were found to be:

$$U_{\text{cover,init}} = 279.0\,\text{W m}^{-2}\,\text{K}^{-1}$$
$$U_{\text{cover,fin}} = 252.4\,\text{W m}^{-2}\,\text{K}^{-1}$$

$$U_{\text{flange,init}} = 466.5\,\text{W m}^{-2}\,\text{K}^{-1}$$
$$U_{\text{flange,fin}} = 422.0\,\text{W m}^{-2}\,\text{K}^{-1}$$

Like in the case of the jacket overall heat transfer coefficient not only the initial and final values are important for the calorimetric calculations but their evolution also. Therefore, a strategy has to be decided on how these terms are going to be accounted for. Contrary to the jacket case, the average values for the flange and cover U values are the method of choice. The reason for

Table 2
Comparison between the average value approach and the proportional to conversion approach for the flange and cover overall heat transfer coefficients

	Percentage of heat finally attributed to the reaction in the base case scenario	Heat of reaction improvement when the proportional to conversion approach is applied	ΔH_r improvement when the proportional to conversion approach is applied
$\dot{Q}_{\text{cover}}$	0.07	0.002‰	Infinitesimally small
$\dot{Q}_{\text{flange}}$	0.19	0.005‰	Infinitesimally small

Table 3
Theoretical and experimentally measured specific heat capacity values for the reaction mixture of the model reaction ($J\,kg^{-1}\,K^{-1}$)

	Before the reaction	After the reaction
Theoretical c_v ($J\,kg^{-1}\,K^{-1}$)	1372.9	1558.9
Experimental c_v ($J\,kg^{-1}\,K^{-1}$)	1392.9	1554.7
Theoretical c_p ($J\,kg^{-1}\,K^{-1}$)	2481.0	2535.5

this decision lies upon the fact that much more computing effort provides very little in terms of calorimetric results, as can be seen in Table 2.

3.3. The accumulation heat term

The third particularity of SCFs is also linked to the fact that the entire reactor volume is occupied and relates to the specific heat capacity of the reaction medium. The latter is necessary for the calculation of the rate with which heat accumulates in the reactor, as presented in Eq. (11).

$$\dot{Q}_{acc} = \sum_i (m_i c_{v,i} + m_{ins} c_{p,ins}) \frac{dT_r}{dt} \tag{11}$$

In classical calorimetry the constant pressure heat capacity (c_p) for the reaction mixture would be used, whereas in this case the constant volume specific heat capacity (c_v) has to be used. The reason is that since the mixture occupies the entire reactor volume any change results in a pressure variation, rather than in a volume one and the latter remains constant. Given that the specific heat capacities of SCF mixtures are very difficult to calculate using an equation of state, and that there are very scarce experimental data to date on such mixtures, two strategies remain to be compared. The estimation of the c_v of an ideal mixture using mass fractions and values from the National Institute of Standards (NIST) and the experimental measurement of the c_v using a standard calibration procedure of the reaction calorimeter. Table 3 shows this comparison adding also the respective theoretical c_p values to illustrate the possible error.

Using the above values and the assumption of a linear evolution between them, the enthalpy of reaction was calculated for the polymerization model reaction under the base case conditions and the results are presented in Table 4. The experimentally measured values are considered to be more trustful and therefore chosen as the best strategy. It is also important to note that the model reaction was carried out in isothermal mode which ensured that the reactor temperature variations were the smallest possible. As a result the effect of the accumulation term in the overall calculations was also very small. In other cases where reactions are carried out in adiabatic mode or where reactions are much more violent even at isothermal mode (e.g. the precipitation polymerization of acrylic acid in $scCO_2$) the effect of a correct consideration of the accumulation term is bound to be more substantial and a different evolution path between initial and final values might be more appropriate.

Table 4
Calculated enthalpy of reaction values for the three compared specific heat capacity strategies

	Enthalpy of reaction ($kJ\,mol^{-1}$)
Theoretical c_v	57.08 ± 1.21
Experimental c_v	57.04 ± 1.20
Theoretical c_p	54.34 ± 2.20
Literature value	57.20 ± 0.60

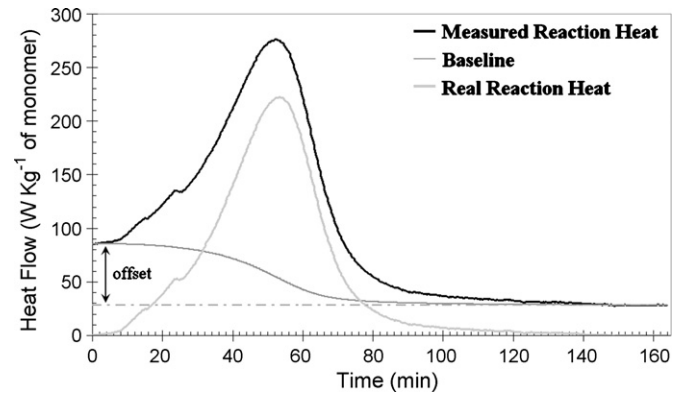

Fig. 4. Illustration of the measured reaction heat, the real reaction heat and their respective baseline.

In the accumulation term, the several sensors inserted in the reactor also participate. Their contribution though is constant in every experiment and was experimentally determined to be $87.46\,J\,K^{-1}$.

3.4. The calibration heat term

The calibration heat term essentially consists of the heat released by the heater in the reactor. Its name refers to its main utility, which is to perform calibrations in order to measure the overall heat transfer coefficient (U) between the reaction mixture and the temperature regulating oil and the reaction mixture's specific heat capacity. As far as the calorimetric monitoring of the model reaction is concerned this term does not participate in the calculations since the heater is not used during the reaction, therefore it is not further investigated.

3.5. The stirring heat term

The stirring heat term refers to the heat released by the stirrer during its operation. This heat release is constant, meaning that even before the reaction is initiated some heat is being exchanged and Eq. (1) gives $\dot{Q}_r > 0$. Therefore, according to standard calorimetric practice a baseline term is introduced to account for these contributions that are not associated with the reaction itself (Fig. 4). As a result the real reaction heat rate is calculated from the following equation.

$$\dot{Q}_{Reaction} = \dot{Q}_r - \dot{Q}_b \tag{12}$$

The baseline can have many different forms but the recommended one for chemical reactions where the heat flow introduced in the baseline depends upon the changing composition of the reaction mixture, is the proportional to conversion type. In polymerization reactions this is particularly true,

because the physical properties of the monomer and the polymer differ a lot, causing a significant difference at the heat generated by the stirrer.

Although the absolute value of the stirring heat is not necessary for the calorimetric monitoring of the model reaction, according to the above discussion, nevertheless it is possible to measure it. Several previous studies have reviewed the existing methods for measuring the power consumption in stirred vessels and have concluded that heat flow calorimetry is among the most suitable [29,30]. This measurement is based on the adiabatic operating mode of the reaction calorimeter. In the case of the model reaction the heat released by the double stage turbine in the reactor was measured and it was found to be:

$\dot{Q}_{\mathrm{stir,init}} = 6.40\,\mathrm{W\,kg^{-1}}$ of reacting mass

$\dot{Q}_{\mathrm{stir,fin}} = 3.67\,\mathrm{W\,kg^{-1}}$ of reacting mass

The experimental values validate the calculated decrease in $\dot{Q}_{\mathrm{r}}$.

3.6. The heat loss term

The heat loss term was introduced in Eq. (1) because it finds application in classical liquid calorimetry. It accounts for secondary heat losses to the environment through radiation and conduction from the reactor head assembly. However, in this case where the reactor's cover and flange have become also temperature controlled, and their contributions are taken into account in the heat flow term, this term has become obsolete. Therefore, the heat loss term is not taken into account in any calorimetric calculation of this analysis.

3.7. The mixing heat term and the dosing heat term

Unlike the previous heat terms, mixing and dosing are treated together, as one term, henceforth called the "injection heat term, $\dot{Q}_{\mathrm{inject}}$". The reason lies behind the need to establish the reaction conditions before the reaction is actually initiated for correct calorimetric calculations, as explained in the experimental part. Therefore, the only time that heat is released or absorbed because of mixing is during the dosing of the additional reactants.

A methodology has been developed to measure the heat introduced in the system during injection and is based upon the adiabatic operating mode. Essentially the reactor is charged with the initial quantities of monomer and stabilizer, following protocol, and the temperature is set 5 °C below the actual reaction temperature. The reaction calorimeter is set in adiabatic mode and the reactor temperature is left to ramp until 5 °C above the reaction temperature. Then the reactor is cooled down to the initial temperature and the adiabatic mode is reset. The only difference is that this time, when the temperature of the reactor reaches that of the reaction the additional reactants are injected in the reactor and the system is left again to reach 5 °C above the reaction temperature. Finally, the difference between the accumulation terms of the two runs is only the extra heat rate due to the injection in the second one (Fig. 5). Mathematically the

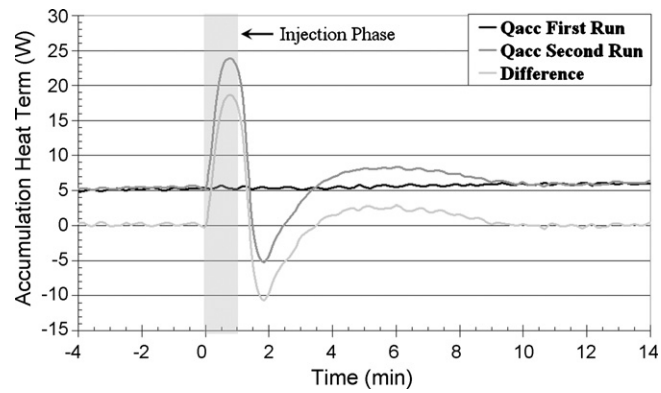

Fig. 5. Calculation of the injection heat term as the difference between the two runs of the mixing and dosing evaluation method.

above method is expressed as follows:

$$\text{first run}: \quad \dot{Q}_{\mathrm{acc}} = \sum_i (m_i c_{\mathrm{v},i} + m_{\mathrm{ins}} c_{\mathrm{p,ins}}) \frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t} = \dot{Q}_{\mathrm{stir}} \quad (13)$$

$$\text{second run}: \quad \dot{Q}_{\mathrm{acc}} = \sum_i (m_i c_{\mathrm{v},i} + m_{\mathrm{ins}} c_{\mathrm{p,ins}}) \frac{\mathrm{d}T_{\mathrm{r}}}{\mathrm{d}t} = \dot{Q}_{\mathrm{stir}} + \dot{Q}_{\mathrm{dos}} + \dot{Q}_{\mathrm{mix}} \quad (14)$$

$$\text{difference between the two runs}: \quad \Delta\dot{Q}_{\mathrm{acc}} = \dot{Q}_{\mathrm{dos}} + \dot{Q}_{\mathrm{mix}} = \dot{Q}_{\mathrm{inject}} \quad (15)$$

The forth particularity of reaction calorimetry with SCFs is identified in the injection phase. The addition of extra mass after having reached and stabilized the reaction conditions generates a destabilization in the temperature of the reactor. In the case of classical liquid calorimetry, this change is mainly due to a possible temperature difference between the reactor content and the injected reactants. The existence of the vapor phase above the liquid absorbs any possible pressure change, due to the increasing mass in an isochoric system, by condensation. However, in the case of supercritical fluids this addition phase becomes more complex due to the entire reactor volume occupation. The

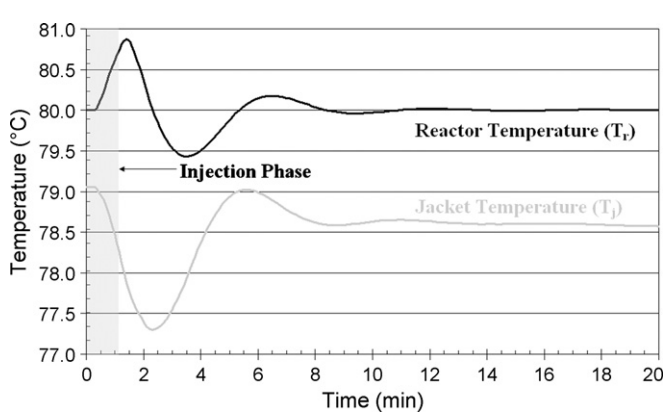

Fig. 6. Reactor and jacket temperature oscillations during the injection phase of the model reaction.

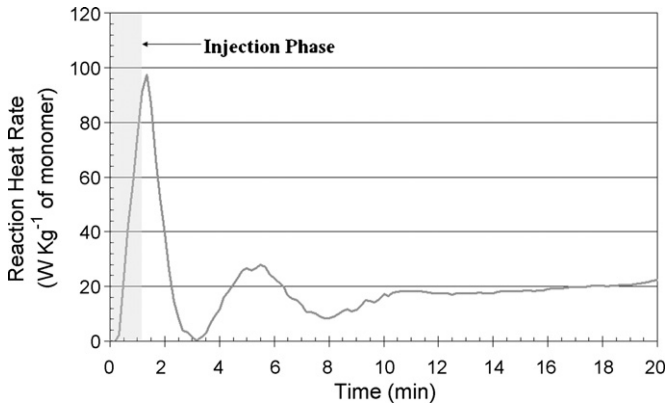

Fig. 7. Calculated reaction heat rate during the first 20 min of the model reaction.

absence on the vapor phase results in pressure variations during the injection, which in turn destabilize the temperature of the system. It is observed that the reactor temperature increases rapidly and that as a consequence the reaction calorimeter tries to maintain isothermal conditions and reduces the jacket temperature respectively, which in turn causes both temperatures to oscillate around their steady state values. As a result the calorimetric calculations during this period of time are not representative of the reaction. Figs. 6 and 7 show the reactor and the jacket temperature oscillations and the erroneous calorimetric calculations during the first 20 min of the model reaction under the base case conditions. Although the temperature oscillations are only of some tenths of a degree the resulting error in the calculated reaction heat rate is much more substantial. Under no circumstance can the model reaction release almost 100 W kg^{-1} of monomer within the first 2 min. The resulting heat signal is the product of non representative calculations due to the temperature oscillations.

The source of the above problematic situation is the fact that in an isochoric system, like a batch reactor, every change in mass results in a change of the system's pressure and that, when working with SCF mixtures, translates into a change of temperature. Consequently it is found that, during the injection of the additional reactants, the reactor temperature changes due to the pressure change. Fig. 8 shows how the reactor pressure change rate follows the reactor temperature change rate and leads to the conclusion that the smaller the

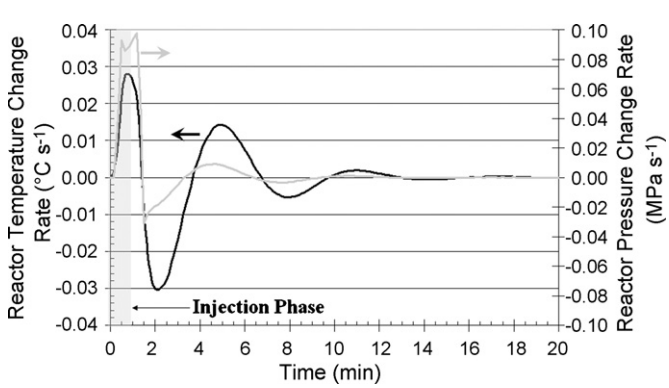

Fig. 8. Reactor temperature and pressure change rates during the first 20 min of the model reaction.

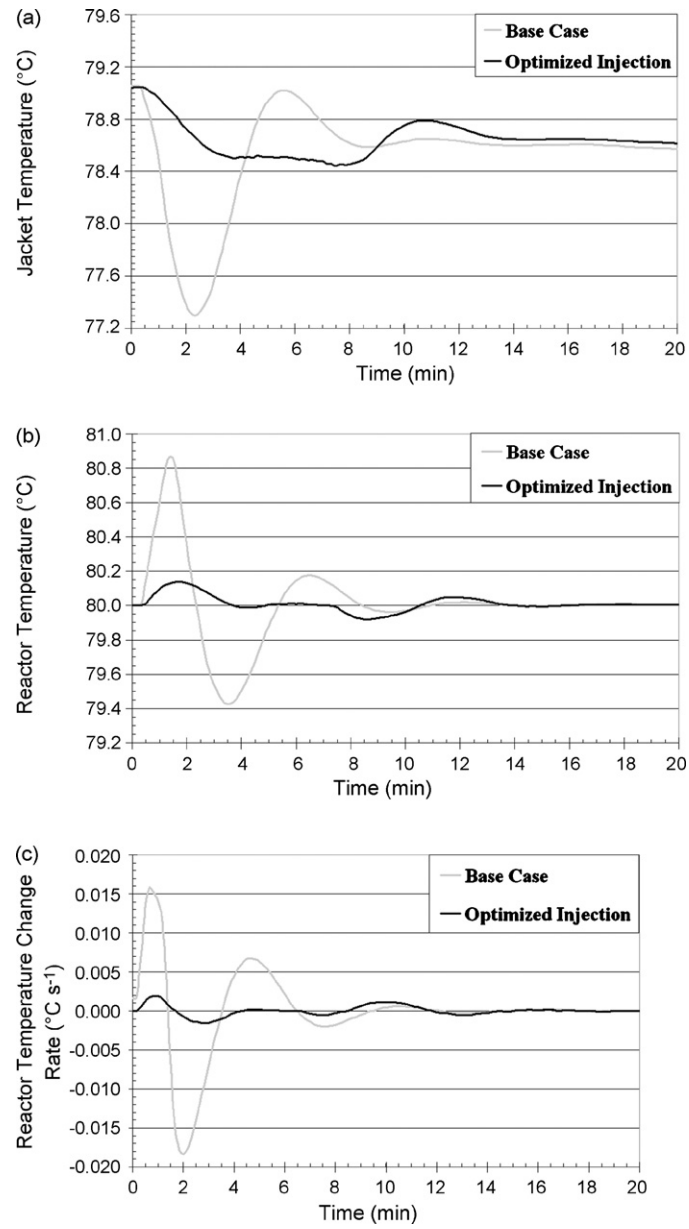

Fig. 9. Comparison of the experimental results between the base case and the optimized injection test for (a) the jacket temperature, (b) the reactor temperature and (c) the reactor temperature change rate.

change rate of the pressure and the smoother this change is achieved, the smaller the reactor temperature change rate is, which in turn means less reactor temperature oscillations.

Based on the above conclusion, an optimized injection phase has been designed for the model reaction. Instead of injecting the additional reactants with a flow rate of 50 mL min^{-1}, they were injected at 5 mL min^{-1}. Furthermore, the volume of the initiator solution was optimized through a series of solubility tests and 40% less monomer is used to solubilize the initiator. The resulting total volume is 32.76 mL instead of 52.68 mL. The improvements in terms of temperature oscillations and reactor temperature change rate are presented in Fig. 9.

Table 5
Direct comparison of the conditions before and after the term-by-term analysis

	Before	After
Specific heat capacity type	c_p	c_v
Reactor elements contributing to the heat flow term	Jacket	Jacket + cover + flange
Calculation of injection heat term	No	Yes
Injection flow rate	50 mL min^{-1}	5 mL min^{-1}
Injected solution volume	52.68 mL	32.76 mL

3.8. Results on the term-by-term optimization analysis

The results of the optimization on each term of Eq. (1) to take into account the particularities of working with SCFs can be clearly illustrated by a direct comparison between the calorimetric results before the analysis and after. Table 5 highlights the points where optimized solutions were introduced.

The results are presented in Figs. 10 and 11. As far as the reaction heat rate evolution is concerned the main improvement is focused on the early stages of the reaction. This part of the calculation has been considerably improved by the new injection rate as well as by the smaller solution volume injected. The curve before the analysis has two major errors.

First it shoots up to almost 200 W kg^{-1} of monomer at the very first minute of the reaction, which is not realistic. The reaction, although highly exothermic, cannot release so much heat in the first minutes. This calorimetric mistake is attributed to the erroneous application of the constant pressure specific heat capacity in the accumulation term and to the fact that the dosing power is not removed. After the analysis the signal is completely filtered from the above disturbances and reveals the real reaction evolution.

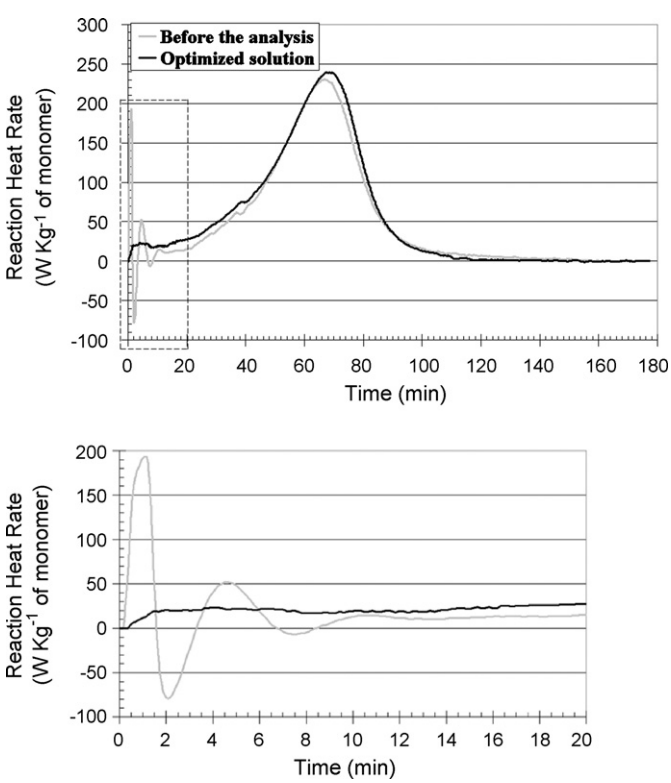

Fig. 10. Comparison of calculated reaction heat rate before and after the analysis.

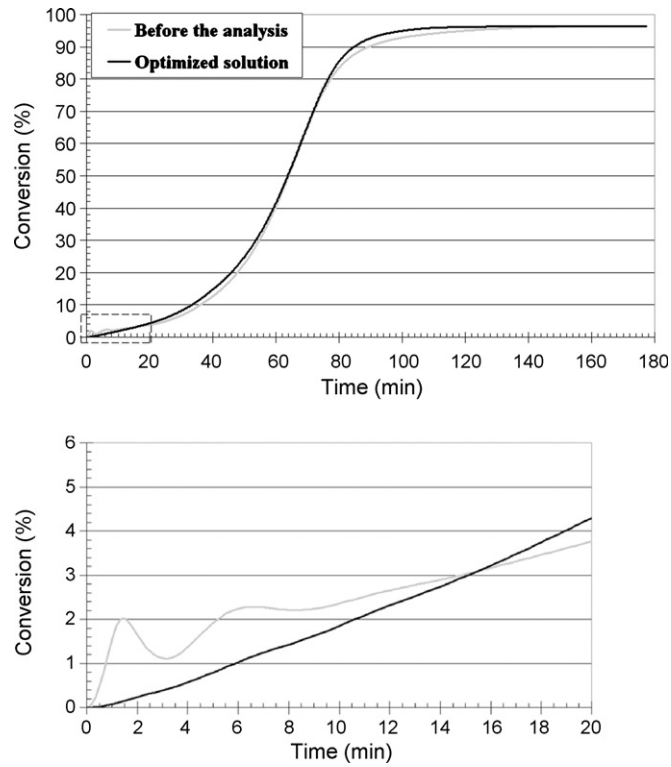

Fig. 11. Comparison of calculated conversion before and after the analysis.

The second major error of the curve before the analysis is that after the initial peak the calculated reaction heat rate becomes negative. This is physically impossible since the reaction is exothermic and it cannot absorb heat. This numerical mistake is again due to the accumulation term that is overestimated by using the constant pressure specific heat capacity and also due to the temperature oscillations from the rapid injection of the reactants. After the analysis the measured heat rate remains strictly positive.

In terms of conversion, the before-the-analysis erroneous heat rate oscillations' integration results in a rapid increase of the conversion followed by a conversion decrease. The latter is impossible since there is no depolymerization reaction.

Finally, Table 6 gives the values for the enthalpy of reaction. Given that the literature value for the free radical dispersion polymerization of methyl methacrylate is 57.20 ± 0.6 kJ mol^{-1}, the after the analysis calculated value is much more precise [31,32].

Table 6
Calculated enthalpy of reaction values before and after the analysis and the respective literature value

	Enthalpy of reaction, ΔH_r (kJ mol^{-1})
Before the analysis	54.09 ± 2.22
After the analysis	57.04 ± 1.20
Literature value	57.20 ± 0.60

The improvement is not as important as for the heat rate and the conversion but it demonstrates the precision that reaction calorimetry in supercritical conditions can achieve.

4. Conclusions

In this study a specially developed reaction calorimeter has been employed to investigate the importance and the correct consideration of every heat term in the heat flow reaction calorimetry under supercritical conditions. As a model reaction the free radical dispersion polymerization of MMA in $scCO_2$ was chosen. Every term of the heat flow equation was studied separately, taking into consideration the particularities introduced by the fact that SCF mixtures occupy all the available reactor volume and the best solutions were chosen based on the results of the reaction heat rate and the enthalpy of reaction.

The most important points of the analysis include the use of the constant volume specific heat capacity of the reaction mixture for the accumulation term, the introduction of the injection power in the mixing and dosing heat terms during the addition of reactants, the inclusion of the reactor's cover and flange contributions in the heat flow term and the optimization of the injection phase for the elimination of the problematic temperature oscillations.

Overall the optimized heat flow equation can calculate the model reaction heat rate and its enthalpy with high accuracy and the improved accumulation term guarantees the correct calorimetric monitoring also under more thermally disturbed conditions, such as more exothermic reactions.

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