Reaction Inhibition as a Method for Preventing Thermal Runaway in Industrial Processes

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Summary: In this work inhibitors were used to prevent runaway reactions during methylmethacrylate suspension polymerization processes. The main problem that may more frequently occur in chemical reactors, carrying out free radical polymerization reactions, is the loss of temperature control. The addition of an inhibitor during polymerization processes can be considered as a good method to stop or at the least slow down the reaction. In this work two inhibitors were used: hydroquinone and 1,4-benzoquinone in a series of polymerization experiments. In order to identify situations that can lead to a runaway reaction, an early warning detection system based on the divergence criterion was used. When this system signalled an alarm, small amounts of inhibitor were added to the reaction mixture. The results showed that hydroquinone and 1,4-benzoquinone behave slightly differently and the reactor temperature can be kept within safe limits.

Keywords: inhibitors; mitigation system; reaction calorimetry; runaway; suspension polymerisation

Introduction

Loss of temperature control is one of the major reasons that can lead to thermal runaway in chemical reactors during exothermic reactions. Polymerization processes are characterized by a high exothermicity and a self-accelerating kinetics, that strongly influence the heat and mass transfer phenomena. If the rate of heat generation due to the chemical reaction exceeds the rate of heat removal by the cooling system, there is a positive feedback mechanism, since the temperature of the reaction mass will rise, increasing in turn the rate of reaction and heat generation. In this situation, if no the countermeasures are taken, a runaway reaction may occur and give rise to incidents.[1]

There are different ways of handling runaway reactions: venting, containment, venting with containment and reaction inhibition. The first three alternatives have been widely studied; whereas, reaction inhibition is rarely discussed because laboratory experimentation with runaway phenomena is considered to be too dangerous.[2] The advantages of reaction inhibition in comparison with the other methods is not only to mitigate runaway phenomena but also in some cases to prevent them. Reaction inhibition involves the injection of small quantities of a particular substance into the reactor at an early stage of runaway. The substance used can either completely stop the reaction (inhibitor) or lower the reaction rate (retarder).[3]

The inhibition system is ideally suited to processes involving free radicals in the initiation phase, such as suspension polymerization of methylmethacrylate (MMA). The use of aqueous suspensions permits carrying out the process in the presence of water as a means of heat dissipation, but leads to several difficulties, such as the

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homogeneity of the particle size, the stability of the suspension and the possible separation of the mixture into two phases with the formation of hot spots within the reactor. All these phenomena are strongly dependent on the operating conditions (reactor temperature and stirring). For this reason the control of suspension polymerization is of paramount importance and safety considerations are necessary to prevent runaway reactions.

Reaction Calorimetry

Reaction calorimetry is based on the solution of the differential energy balance equation, which is for a jacketed, stirred batch reactor[4]:

$$C_p \frac{dT_R}{dt} = UA(T_J - T_R) + Q_{chem} + Q_{loss} + P_{stirrer}$$

where T_R and T_J are the reactor and jacket temperatures, C_P the heat capacity of the reactor contents, UA the global heat transfer coefficient, Q_{chem} the chemical heat flow, Q_{loss} the heat flow from the reactor to the surroundings and $P_{stirrer}$ the power dissipated by the stirrer. In polymerization processes the heat generated by the chemical reaction is proportional to the quantity of monomer consumed. By an appropriate integration of Q_{chem} the conversion may be obtained.

Divergence Calculation

In a series of recent works[5,6] an innovative early warning detection system (EWDS) was used to identify runaway phenomena occurring during exothermic reactions. The EWDS allows to delimit runaway boundaries, by applying techniques from non-linear systems theory to characterise the sensitivity of chemical reactors. The runaway detection criterion is defined as when the divergence of the reactor becomes positive on a segment of the reaction path ($\text{div} > 0$). The divergence is a scalar quantity defined at each point as the sum of the partial derivatives of the mass and energy balances with respect to conversion and temperature. The algorithm used calculates the divergence from only temperature measurements through phase space reconstruction techniques. The results showed that the method is able to distinguish between runaway and non-runaway situations and it did not produce false alarms for the cases studied.[7] The output response of the EWDS algorithm can be given as variation of the phase space volume ΔV_{ps}.[8] According to Strozzi[5] the divergence and ΔV_{ps} have similar behaviour: when the divergence is positive, ΔV_{ps} is also positive. In order to parameterize the EWDS, preliminary heating and cooling tests on the reactor were carried out and a threshold value of ΔV_{ps} was set (ΔV_{ps}^{lim}). This limit allows EWDS to distinguish between a normal heating through the reactor wall and a chemical exothermic behaviour within the reactor, avoiding false alarms. If the $\Delta V_{ps} > \Delta V_{ps}^{lim} > 0$ is verified, a runaway alarm is triggered off.

Experimental Part

Preliminary experiments of suspension polymerization were carried out under isoperibolic batch conditions (T_J constant) to determine the best operating conditions: reaction set temperature, stirring rate and quantities of reagents. The experiments were continued under isothermal conditions (T_R constant) in order to acquire important information about thermodynamic, kinetic and process parameters. All the experimental runs were carried out in a jacketed, stirred stainless steel reactor (200 mL). The apparatus is very simple and uses commercially available components. In the last experiments the divergence criterion, introduced by Strozzi,[5] was used on-line to identify situations that can lead to a runaway reaction. When the EWDS signalled an alarm, small quantities of inhibitor/retarder were added to the reaction mixture.

Monomer and initiator were supplied by Fluka: the monomer is MMA (stabilized with ~0.0025% of hydroquinone); the radical initiator is α,α'-azoisobutyronitrile (AIBN). The suspension was prepared by mixing in the calorimeter MMA and water to which previously was added of a suspension stabilizer (0.742 g of agar, supplied by Sigma Aldrich). A total suspension volume of 150 ml was used. The reaction was started by the introduction of 0.157 g of AIBN dissolved in 4 ml of MMA.

A predetermined quantity of inhibitor was weighted and dissolved at room temperature in 6 ml of water. Two inhibition substances were investigated: hydroquinone (Hq) and 1,4-benzoquinone (Bq), supplied by Sigma Aldrich. An initiator/inhibitor molar ratio of 0.38–7.5 was used. In order to understand if the action of Hq and Bq is directed to the main radicals that come from initiator or to the growing polymer chains, two kinds of experimental tests were carried out: in some experiments the inhibitor was added at the start of reaction, immediately after the introduction of the initiator; in other ones the inhibitor addition was made when the divergence criterion detected an anomalous temperature behavior.

Results

The aim of the preliminary experiments was to determine the best operating conditions to carry out the actual experiments of reaction inhibition. These conditions must be such as to simulate malfunctions or failures in the real process. The increase of the monomer/water ratio could be compared with an accidental accumulation of monomer in the reactor, which represents one of the principal causes of runaway events in polymerization processes.[2] In fact, an accumulation of monomer in industrial semi-batch reactors (due to a malfunction of the feed pumps of reagents

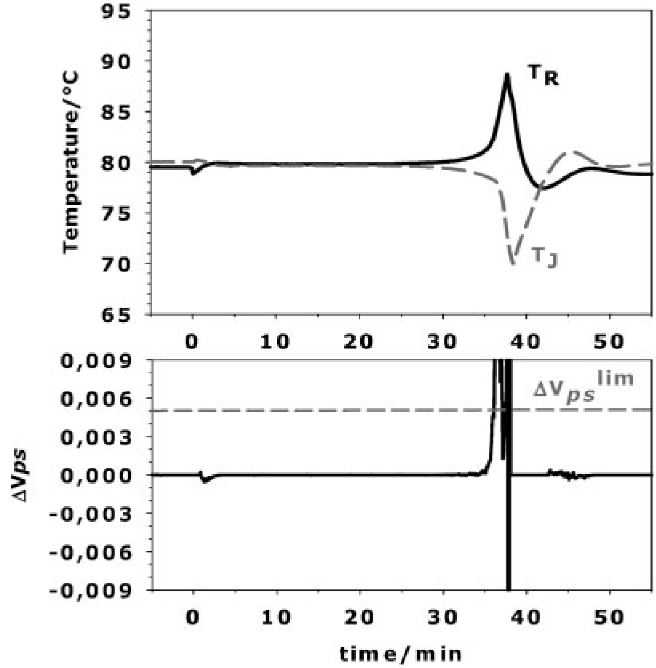


Figure 1.
Profiles of reactor (T_R) and jacket temperature (T_J) (upper part) and phase space volume change ΔV_{ps} (lower part) vs. time for an isothermal experiment without inhibitor; reaction conditions: $T = 80$ °C, stirring rate = 400 rpm; monomer/water molar ratio of 0.5.

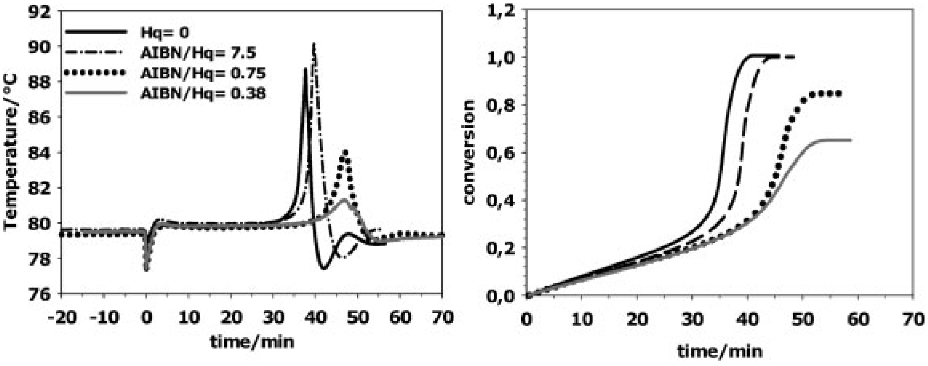
for example) can properly be simulated by using a laboratory batch reactor in which the total quantity of monomer is charged from the beginning.

The analysis was approached by maintaining the following variables constant and by varying them one at a time: stirring rate (400–800 rpm); reaction set temperature (50–80 °C) and monomer/water (0.28–1.14). The results showed polymerization rate and reactor temperature increment to increase with the reaction set temperature and diminish with the stirring rate. A high monomer/water ratio also caused more violent heat generation. However a reversal of behaviour occurred for values of this ratio greater than 0.5, as the quantity of initiator had become insufficient with respect to the monomer concentration.

Therefore the most appropriate conditions that can lead to a runaway reaction for testing the inhibition system efficiency were: high reaction set temperature (80 °C), low stirring rate (400 rpm) and a monomer/water ratio of 0.5.

The upper part of Figure 1 shows the profiles of reactor and jacket temperature vs. time, for an isothermal batch experiment carried out under these conditions without inhibitor. After ~38 min from the start of reaction the reactor temperature quickly increased because of the self-accelerating kinetics and reached a maximum value of 88.7 °C. The lower part of Figure 1 shows the profile of the phase space volume change (ΔV_{ps}) vs. time for the same experiment. The dashed horizontal line indicates the threshold value of ΔV_{ps} (ΔV_{ps}^{lim}), that was determined by preliminary reactor heating and cooling tests. If the $\Delta V_{ps} > \Delta V_{ps}^{lim} > 0$ is verified, a runaway alarm is triggered off. In fact the EWDS produced an alarm at 36 min and 6 sec after the start of reaction, ~2 min before the maximum temperature was reached in the reactor. This time is sufficient to introduce an inhibitor into the reactor to halt or slow the reaction.

Figure 2 shows the effect of different quantities of Hq introduced at the start of reaction immediately after the initiator. By comparing the experimental profiles it can be observed that the reactor temperature increased even if in presence of inhibitor. A lower AIBN/Hq ratio determined a better control of the process, as the reactor temperature increment was limited. Conversion profiles show that the polymerization reaction slowed down with Hq and the final conversion value was lower depending on the inhibitor concentration. The EWDS produced a lot of alarms for all the experimental runs except for the experiment with a AIBN/Hq ratio of 0.38.



(a) (b)

Figure 2.

(a) Reaction temperature and (b) conversion profiles vs time for isothermal batch experiments with introduction of different AIBN/Hq molar ratio at the start of reaction; reaction conditions: T = 80 °C, stirring rate = 400 rpm; monomer/water molar ratio of 0.5.

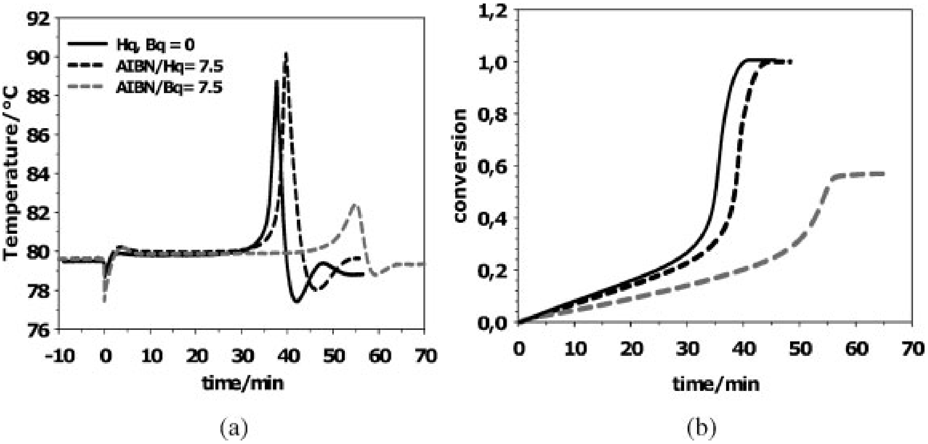


Figure 3.
(a) Reaction temperature and (b) conversion profiles vs time for isothermal batch experiments with introduction of Hq and Bq at the start of reaction; reaction conditions: T = 80 °C, stirring rate = 400 rpm; monomer/water molar ratio of 0.5.

Figure 3 shows a comparison between the two inhibition substances. Benzoquinone behaved differently: a low concentration of Bq (AIBN/Bq ratio of 7.5) was sufficient to halt the runaway phenomenon. The reactor temperature increment was successfully limited to ~2 °C and the EWDS did not signal any alarms. At the same concentration of Hq the rapid increment of the reactor temperature occurred with a little delay but then the temperature increment was even higher with respect to the reaction without inhibitor.

In other experiments the introduction of Hq and Bq was made when the EWDS detected an anomalous temperature behavior. As Figure 4 shows, the addition of inhibitor at the first alarm (indicated by the dashed vertical line on the graph) was efficient to control the process only for Bq. Its introduction immediately halted the runaway phenomenon and the conversion

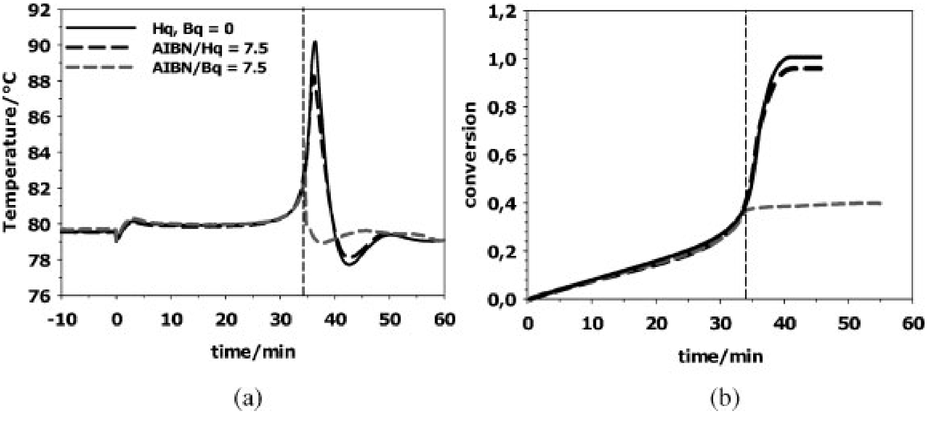


Figure 4.
(a) Reaction temperature and (b) conversion profiles vs time for isothermal experiments with Hq and Bq introduced at the first alarm produced by EWDS; reaction conditions: T = 80 °C, stirring rate = 400 rpm; monomer/water molar ratio of 0.5.

stopped at a final value of ~40%. The addition of Hq at the same concentration was not sufficient to control the process and the reactor temperature increment was only partially limited.

Conclusions

In this work reaction inhibition is used to mitigate runaway phenomena that might occur during the free radical suspension polymerization of MMA. Two substances were investigated: hydroquinone and 1,4-benzoquinone. The results showed that both substances behave as retarders slowing down the polymerization rate and halting the runaway phenomenon. Benzoquinone is more effective than Hq because it requires a lower quantity to produce the same effect of mitigation. In order to not lose the reaction batch in case of runaway event, a smaller concentration of Bq could be used in a way of not completely stopping the reaction and obtaining a higher final conversion value. It would be necessary to verify whether introduction of the inhibitor does not modify the desired product quality.

Reaction inhibition, coupled with a detection system such as EWDS, can be considered a good method to control the process and keep the reaction temperature within safe limits.

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