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Theoretical estimation of adiabatic temperature rise from the heat flow data obtained from a reaction calorimeter

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ABSTRACT

A novel method for estimating the transient profile of adiabatic rise in temperature has been developed from the heat flow data for exothermic chemical reactions that are conducted in reaction calorimeter (RC). It has also been mathematically demonstrated by the present design that there exists a direct qualitative equivalence between the temporal evolution of the adiabatic temperature rise and the concentration of the limiting reactant for an exothermic chemical reaction, carried out in semi batch mode. The proposed procedure shows that the adiabatic temperature rise will always be less than that of the reaction executed at batch mode thereby affording a thermally safe corridor. Moreover, a unique reaction scheme has been designed to establish the independent heat effect of dissolution and reaction quantitatively. It is hoped that the testimony of the transient adiabatic temperature rise that can be prepared by the proposed method, may provide ample scope for further research.

1. Introduction

A semi-batch reactor is the soul of fine chemical industries. A vast majority of the chemical reactions associated with the manufacturing of speciality chemicals, are carried out in semi-batch reactors. Multi-purpose perks can be achieved by controlling the dosage of the limiting reactant in a semi-batch reactor. This includes the selectivity, preferential product distribution, heat production etc. Many of these reactions are sensitive to temperature and often exhibit thermal hazard characteristics. The production of fine chemicals is usually associated with large heat effect by either decomposing the product into the gaseous form or increasing the vapor pressure of the solvent/reactant in the system with disastrous consequences, like explosion. So, one needs to formulate a safe production policy to keeping thermal misfortune away. But the time and financial constraints restrict the pharmaceutical industries to undertake detailed thermo-chemical kinetic studies of these chemicals in order to develop a full-proof scale-up strategy that is inherently safe. Scale-up of fine chemicals synthesis, though appears simple, is in fact, a difficult engineering problem especially in the light of thermal runaway behavior. Reaction Calorimetric study often guides the engineers who are involved in "Scale-up" of the process, to formulate a prudent strategy.

A reaction calorimeter (RC) is essentially a semi-batch reactor (SBR) where usually the thermal effect of an exothermic reaction is assessed. The main objective of using RC is to regulate the heat evolution during the course of the reaction accurately. In a reaction calorimeter, thermal conversion is estimated since the thermal conversion is directly related to the chemical conversion. The adiabatic temperature rise (ΔT_{ad}), is probably one of the most important yardsticks to assess the safety of the chemical processes that show thermal hazard behavior. In fact, the adiabatic temperature rise is an admonishing indicator of the runway behavior of a reaction. In this article, a novel formulation to estimate the adiabatic temperature rise against time from the experimental thermal data obtained from RC has not only been proposed, but its direct correspondence to the reactant's depletion trajectory has also been established.

2. What role does a reaction calorimeter play?

Before proceeding on the conceptual development of the method for determining the adiabatic temperature rise, ΔT_{ad}, let us recount, it may appear clichèd though, the operating principle of a reaction calorimeter and the description of the primary variables that provide the necessary ammunitions to characterize the RC thermally, with telegraphic brevity. In a conventional reaction calorimeter, where only single homogeneous liquid phase reactions are carried out, one of the reactants (the *limiting reactant* in most cases) is slowly added to the calorimeter that houses the reaction mixture. As the reactants gets consumed, the temperature of the reaction mixture will rise with time, due to exothermicity. The dosing operation, as stated earlier, administers a congenial safety against thermal untowardness when compared to the

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thermal effect of the same reaction, executed in batch mode. This astute equipment has the discerning capability in keeping track of the temperature and while in doing so, if it senses the system would run thermally feral, it immediately triggers the emergency safety switch to prevent the accident to occur.

By operating the RC at isothermal mode, the temperature of the reaction mixture can be kept under control by removing the heat through the cooling system. So, one can expect that the basic data that are acquired by and can be retrieved from the RC are, $T_r(t)$, the reaction temperature, $T_j(t)$, the coolant temperature, the mass, $m(t)$ of the reaction mixture and the likes at any instant of time. Along with these fundamental variables, the RC also provides derived quantities like the temperature rate (dT/dt), the rate of mass addition (dm/dt), the specific heat of the medium, $C_p(t)$, etc. These variables form the basis of computing the required heat flow rates such as the heat flow rate, $q_f(t)$ through the wall, $q_r(t)$ due to the reaction etc. that would be used in the energy conservation equation in order to produce the true safety dossier where the information about the critical parameters like the $\Delta T_{\mathrm{ad}}(t)$, the thermal conversion $\mathcal{X}_{\mathrm{T}}(t)$, time variation of specific heat of the reaction mass, $C_p(t)$, etc. can be registered.

3. Motivation

It goes without saying that the reactant concentration has direct bindings with the adiabatic temperature rise in an exothermic reaction ($-\Delta H_r > 0$). For a self-heating reaction, the prevailing perception ascertains that the initial concentration of the reactant, $C_{\mathrm{A}}(0)$, has direct effect on the magnitude of the adiabatic temperature rise, ΔT_{ad}. For a homogeneous liquid phase reaction with simple rate order, with no change in density (ρ) no volume of mixing and no change in specific heat of the mixture due to reaction, the textbook expression for adiabatic temperature rise, ΔT_{ad}, against conversion, $X(t)$, for the steady state *plug-flow reactor* (PFR), *continuous stirred tank reactor* (CSTR) and the unsteady state *batch confine* (BR), are identical.

The relation reads

$$\Delta T_{\mathrm{ad}}(t) = \frac{(-\Delta H_r)C_{\mathrm{A}}(0)}{\rho C_p}X(t) \tag{1}$$

For complete conversion ($X(t_{\mathrm{f}}) = 1$), where t_{f}, termed as the *expiry time*, represents the time at which the conversion is complete.

$$\Delta T_{\mathrm{ad}}(t_f) = \frac{(-\Delta H_r)}{\rho C_p}C_{\mathrm{A}}(0) = \lambda C_{\mathrm{A}}(0)$$

where λ, describing the ratio between the molar heat of reaction and the specific (volumetric) thermal capacity, symbolizes the *specific thermal hazard potential*. The above equation also reinforces the extant intuitive knowledge that the ΔT_{ad} is proportional to the initial concentration, $C_{\mathrm{A}}(0)$, legitimately.

The conspicuous absence of the *semi-batch reactor* in the above archive of reactors has prompted us to foray into developing a model for the temporal evolution of the adiabatic temperature rise and correspondingly establish a qualitative equivalence between $\Delta T_{\mathrm{ad}}(t)$ and $C_{\mathrm{A}}(t)$. In the ensuing sections we intend to derive a theoretical relation between the $\Delta T_{\mathrm{ad}}(t)$ and $q(t)$ obtained from the RC and then establish a relation between the concentration of the reactant A, $C_{\mathrm{A}}(t)$ and the $\Delta T_{\mathrm{ad}}(t)$.

4. Literature survey

Sizeable numbers of literature information [1–10] are available on the use of RC for safer design of industrially practiced semi-batch reactors. There exists (mostly from the manufacturers of RC like METTLER TOLEDO etc. and the pharmaceutical companies), excellent technical repository [1–7], where one not only can find all the necessary tools for making a reactor thermally safe, but also can be versed with possible strategic guidelines to prevent the disastrous consequences that could arise due to thermal untowardness.

Though there exists plethora of literature on calorimetric studies of various chemical reactions, the theoretical investigations [11–22] on the same aspects are rather limited. Steinbach and colleagues [12,13], Westerterp and colleagues [14–16] and Rota and colleagues [19–22] have noteworthy contributions in drawing the safety precinct for thermally hazardous reaction carried out in semi-batch mode. However, we, to the best of our knowledge, have not come across any literature information that has addressed this particular query. In fact, this lack of knowledge has augmented our motivation to pursue this endeavor.

5. Model development for the $\Delta T_{\mathrm{ad}}(t)$

Let us consider the following reaction

$$\mathrm{A} + \mathrm{B} \xrightarrow{-\Delta H_r > 0} \mathrm{C}$$

in a semi-batch reactor operating at adiabatic mode, where the limiting reactant A is slowly dosed to the reaction mixture containing another reactant B in huge excess so that the reaction can be considered as a pseudo first order reaction. This could possibly be the simplest situation where a reaction calorimeter apes exactly a semi-batch reactor in terms of direct correspondence between the adiabatic temperature rise, $\Delta T_{\mathrm{ad}}(t)$, and the concentration of the limiting reactant A, $C_{\mathrm{A}}(t)$. With the progress of the material addition, the reactor experiences the consumption as well as the accumulation of the limiting reactant at the same time. This is contrary to the expected observations for the chemical reactions carried out in conventional reactors, where the reactant material always undergoes depletion.

For an exothermic reaction with finite kinetic rate, the consumption of the reactant renders its effect by increasing the temperature of the reacting mass till the end of t_{d}, defined as the *dosage time*, when the dosing terminates. However, the concentration of the reactant that would have accumulated at the expiry of the dosing period, will leave its thermal imprints until the completion of the reaction at t_{f}, the time of culmination of the reaction. So, a semi-batch reactor, as its name suggests, operates as a continuous reactor till the end of dosing and a batch reactor at the termination of dosing. We must pause to reiterate here that our primary motivation is to develop a model to predict the transient evolution of $\Delta T_{\mathrm{ad}}(t)$ in a semi-batch reactor from the experimental heat flow rate, $q(t)$.

5.1. Model formulation

Consider the model reaction described above. The only knowledge that we have is that the reaction is exothermic. Barring this, we are illiterate about any other information, such as the heat of reaction, rate of reaction etc. But we have at our disposal, the complete temporal profile of the heat evolution rate, $q(t)$ acquired through RC. In order to develop the model, let us proceed with the following assumptions.

1. The system is well mixed.
2. Adiabatic condition is adhered during the entire course of the reaction.
3. The heat effect is due to reaction only.
4. The densities and specific heats of the dosing reactant and the reaction mixture are same at any time.
5. The limiting reactant is dosed at T_{o}.
6. The reaction onset temperature is T_{o} and is deemed as the reference temperature.