HEAT EFFECTS DUE TO DILUTION DURING AROMATIC NITRATIONS BY MIXED ACID IN BATCH CONDITIONS

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Although the heat produced by aromatic nitration is relatively large in comparison to the heat produced by dilution, knowledge of the rate of heat generation due to dilution of the mixed acid is important for predicting the dynamic behaviour of discontinuous nitration processes. In this paper a mathematical model, its implementation and experimental validation of the heat effects due to dilution are described and discussed.

Keywords: aromatic nitrations, batch processes, heat effects of dilution, mathematical modelling

Introduction

Aromatic nitrations with mixed acid (H_2O–HNO_3–H_2SO_4) as the nitrating agent are one of the oldest and most common industrial reactions. However, there still exist a considerable number of problems in predicting their dynamic behaviour in discontinuous reactors, due to the simultaneous occurrence of chemical reaction and mass transfer phenomena, that leads to a complex problem while characterising and scaling-up these processes. In addition, nitrations involve high exothermicity and side reactions.

For these reasons, it is not surprising that a considerable amount of incidents, concerning runaway reactions, occur in such processes [1]. Consequently, a better

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understanding of this kind of processes is of great importance for the safe and economic design, as well as optimal operation of nitration plants.

This work is part of an investigation programme undertaken with the purpose of studying the dynamic behaviour and the influence of different initial and operating conditions in discontinuous nitration processes [2]. In the frame of this investigation, an extensive experimental programme has been carried out using adiabatic and heat flow calorimetry, and pilot reactor experiments, supported by chemical analysis. In parallel, a numerical simulator for predicting the dynamic behaviour of reactions carried out in the RC1 reaction calorimeter [3] has been developed and experimentally validated [4] to use it to aid experimental design and quantitative data analysis.

This paper describes one section of this research, that concerning the mathematical model, and the implementation and experimental validation of the rate of heat generation due to dilution.

In the nitration of an aromatic compound by means of a mixture of concentrated nitric and sulphuric acids, the total heat liberated is equal to the heat of nitration plus the heat of dilution due to change in composition of the mixed acid. Although heats of nitration are relatively large, the knowledge of the rate of heat generation due to dilution is important in discontinuous nitration processes to calculate accurately the rate of heat generation due to reaction. In addition, calculation of heat of dilution is complicated since the mixed acid composition varies as the reaction goes on, generating water and consuming nitric acid, also fresh mixed acid is introduced in semibatch conditions.

Mathematical modelling of rate of heat generation due to dilution

The enthalpy change that accompanies the mixing or dilution of two or more substances is called the heat of dilution, and it may be calculated in the integral form as the change between the final and the initial state (before and after mixing) of the sum of the relative partial molar enthalpies times the number of mole of each component [5]. Thus,

$$\Delta H_d = \sum_{k=1}^{n} \Delta(n_k \cdot L_k) \tag{1}$$

where n_k and L_k are the number of moles and the relative partial molar enthalpy of the kth component (pure compounds are used as standard states of reference), respectively.

In order to obtain the rate of heat generation due to dilution, it is necessary to consider a differential change with respect to time of the heat of dilution, hence,

$$q_{\rm d} = \frac{{\rm d}H_{\rm d}}{{\rm d}t} = \sum_{k=1}^{n} \left(n_{\rm k}\frac{{\rm d}L_{\rm k}}{{\rm d}t} + L_{\rm k}\frac{{\rm d}n_{\rm k}}{{\rm d}t} \right) \qquad (2)$$

In the particular case of a discontinuous nitration process there are two possible contributions: firstly, the addition of a constant composition of mixed acid to the reacting mass and secondly, the dilution by water which is produced as nitric acid is consumed by the chemical reaction (Fig. 1). Introducing these terms into Eq. 2, it is possible to obtain
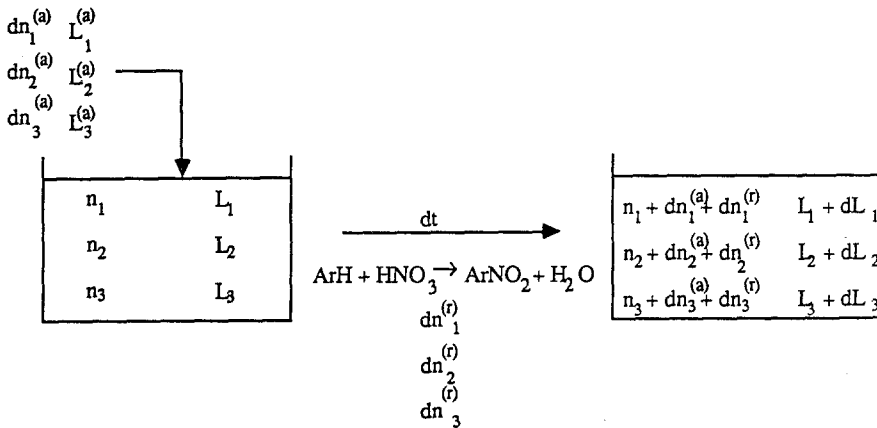
Fig. 1 Differential energy balance. The subscripts 1, 2 and 3 refer to water, nitric and sulphuric acids, respectively, whereas the superscripts (a) and (r) refer to addition and reaction

$$q_{\rm d} = \sum_{k=1}^{3} \left[n_{\rm k}\frac{{\rm d}L_{\rm k}}{{\rm d}t} + L_{\rm k}\left(\frac{{\rm d}n_{\rm k}^{(a)}}{{\rm d}t} + \frac{{\rm d}n_{\rm k}^{(r)}}{{\rm d}t} \right) - L_{\rm k}^{(a)}\frac{{\rm d}n_{\rm k}^{(a)}}{{\rm d}t} \right] \qquad (3)$$

where ${\rm d}n^{(a)}/{\rm d}t$ refers to the mole change due to the addition of mixed acid whereas ${\rm d}n^{(r)}/{\rm d}t$ stands for the production or consumption by chemical reaction.

Using experimental data from different authors [6–8] the values of $L_{\rm k}$'s were correlated as a function of molar percentages using a polynomial equation of type,

$$L_{\rm k} = \prod_{i=1}^{3} \left(\sum_{j=1}^{3} a_{\rm kij}\cdot x_{\rm i}^{j-1} \right) \qquad (4)$$

where the x_i's are the molar percentages of the three components: water, nitric and sulphuric acids. The $a_{k_{ij}}$ parameters (Tables 1–3) were estimated by conjugate gradient methods [9] minimising the objective function:

$$\text{Error} = \sum_{l=1}^{m} \left(H_{d_l}^{\text{exp.}} - H_{d_l}^{\text{calc.}} \right)^2 \tag{5}$$

where m is the total number of experimental points (m=311).

Table 1 $a_{k_{ij}}$ parameters in the polynomial expression of the L_k for the water

$i \setminus j$	1	2	3
1	–23.646	3.861E–1	–1.491E–3
2	430.578	–13.675	1.396E–1
3	1.360E–3	9.780E–5	–9.678E–7

Table 2 $a_{k_{ij}}$ parameters in the polynomial expression of the L_k for the nitric acid

$i \setminus j$	1	2	3
1	–26.721	–2.666E–1	–1.951E–2
2	–214.103	–3.163	4.9226E–2
3	–5.500E–4	–8.859E–6	–9.495E–8

Table 3 $a_{k_{ij}}$ parameters in the polynomial expression of the L_k for the sulphuric acid

$i \setminus j$	1	2	3
1	–24.125	–5.786E–1	–1.530E–2
2	–284.162	3.189	–1.921E–2
3	–1.110E–3	1.155E–5	–7.325E–9

   A comparison between the experimental data from McKinley and Brown (1942) and the enthalpy–concentration diagram that was calculated using Eq. 4 and the estimated parameters is given in Fig. 2. In general, a good agreement is obtained over the whole range of concentrations.
   Equation 4 can be differentiated to be used in the calculation of Eq. 3 applying the chain rule:

$$\frac{dL_k}{dt} = \left(\frac{\partial L_k}{\partial x_1}\right)_{x_2, x_3} \frac{dx_1}{dt} + \left(\frac{\partial L_k}{\partial x_2}\right)_{x_1, x_3} \frac{dx_2}{dt} + \left(\frac{\partial L_k}{\partial x_3}\right)_{x_1, x_2} \frac{dx_3}{dt} \tag{6}$$

hence,

$$\frac{dL_k}{dt} = \sum_{i=1}^{3}\left[\left(a_{ki2} + 2\cdot a_{ki3}\cdot x_i\right)\prod_{j=1,j\neq i}^{3}\left(\sum_{l=1}^{3}a_{kil}\cdot x_j^{l-1}\right)\right]\frac{dx_i}{dt} \qquad (7)$$
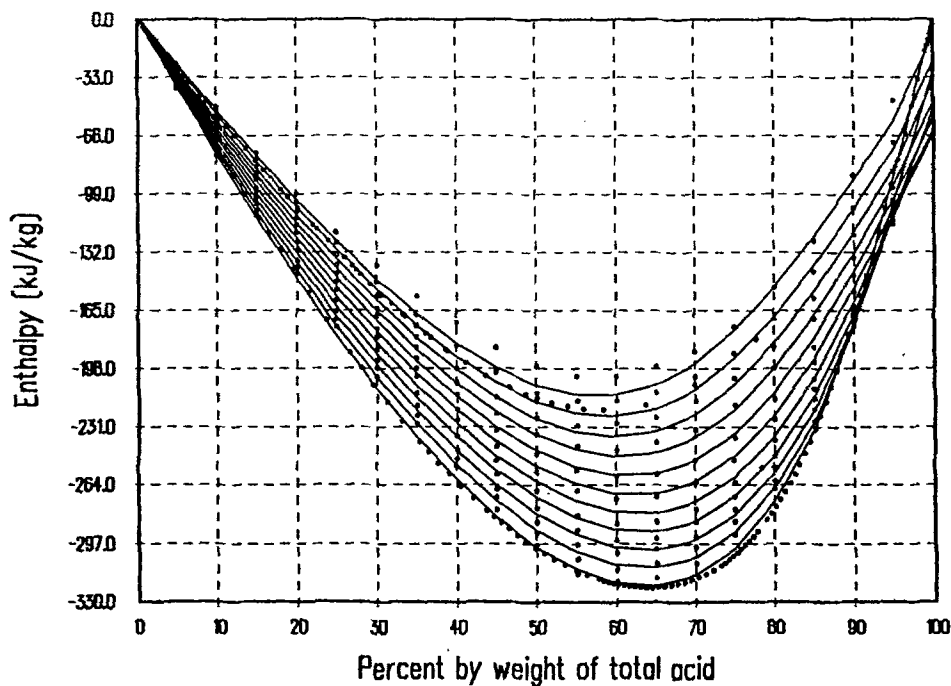

Fig. 2 Comparison between the data recompiled by McKinley and Brown (1942) and the values calculated using the correlation's for L_k. In this enthalpy-concentration diagram the enthalpy in kJ/kg for a specific composition of solution is obtained by interpolation between the lines of indicated nitric acid composition (starting from the top that refers to pure HNO_3 and decreasing at 10% intervals up to pure H_2SO_4), based on anhydrous acid ($HNO_3+H_2SO_4$)

and dx_i/dt can be expressed on function of n_i as,

$$\frac{dx_i}{dt} = \frac{100}{n_{Tot}}\left(\frac{dn_i}{dt} - \frac{n_i}{n_{Tot}}\cdot\frac{dn_{Tot}}{dt}\right) \qquad (8)$$

## Experimental model validation

In order to check the validity of the dynamic model to predict the heat evolution due to dilution during an aromatic nitration, different experiments were car-
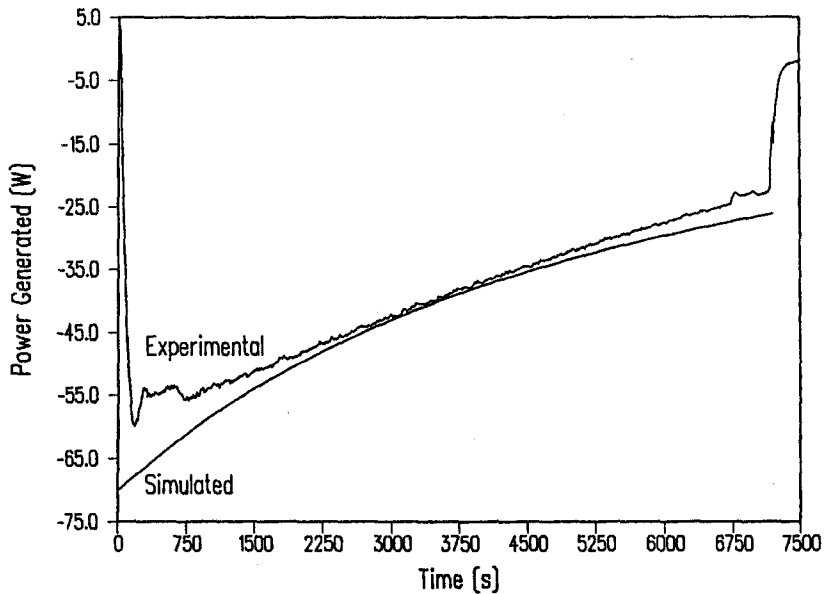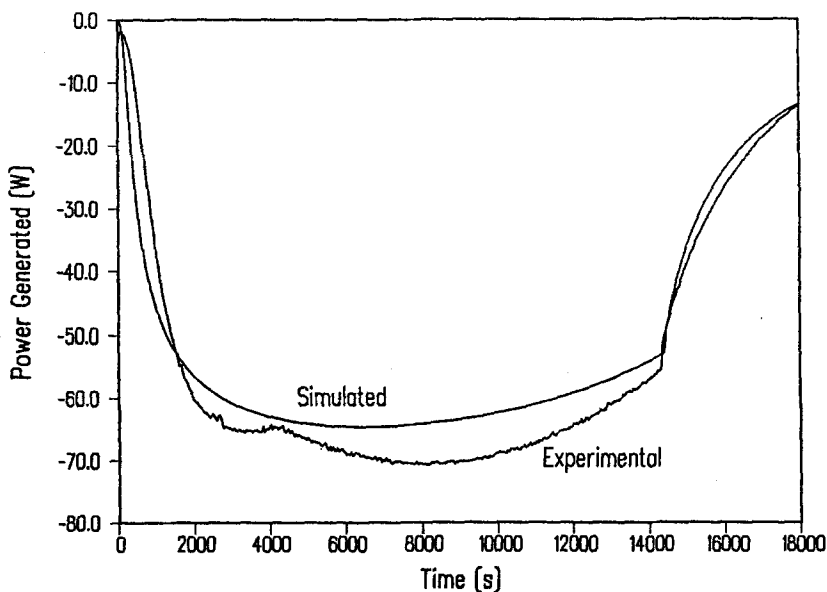
Fig. 3 Experimental and simulated rates of heat generation during the preparation of mixed
acid in the RC1. 1592 g of H_2SO_4 (96 wt.%) added to 1200 g of HNO_3 (70 wt.%) in 2 h
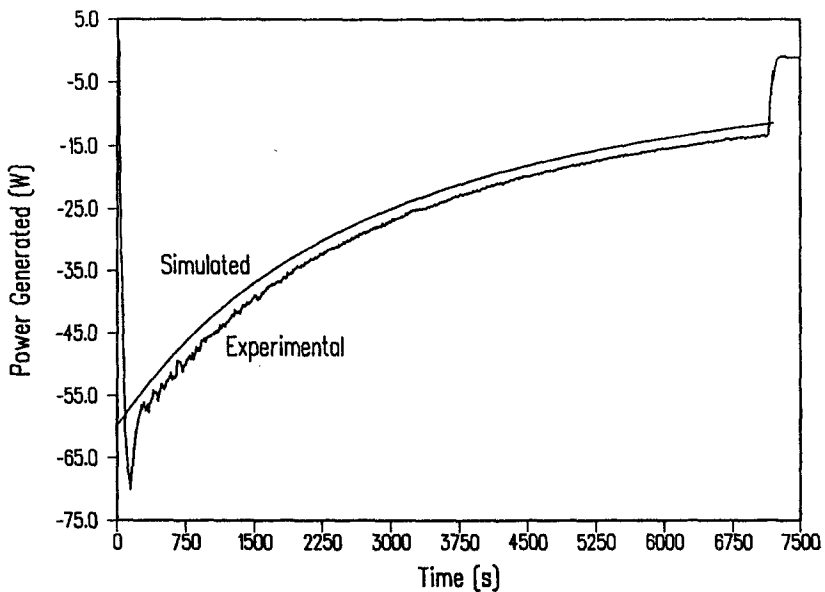
Fig. 4 Experimental and simulated rates of heat generation during the preparation of mixed
acid in the RC1. 1754 g of H_2SO_4 (96 wt.%) added to 740 g of HNO_3 (43.5 wt.%) in
2 h
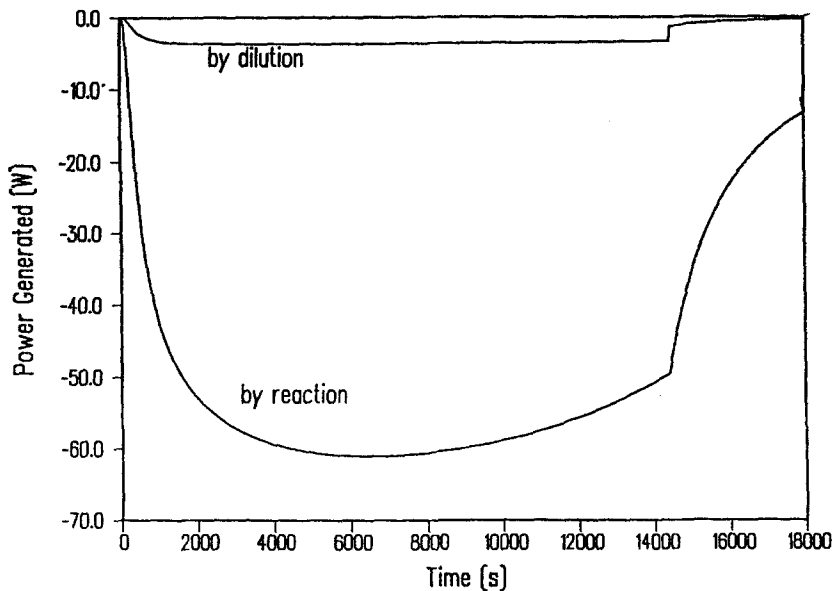
Fig. 5 Simulated rates of heat generation of reaction and dilution during the mononitration of toluene in semibatch RC1 experiments. $T_{m_{set-point}}$=298 K. 1363 g of mixed acid (comp.: 56.2 wt% H_2SO_4 and 28.8 wt% HNO_3) added to 600 g of toluene in 4 h. N_a=13.33 s^{-1}

Fig. 6 Comparison between experimental and simulated rates of heat generation for the experiment described in Fig. 5

ried out in the reaction calorimeter. Unfortunately during nitration it is not pos-
sible to separate both heat effects, therefore the preparation of different mixed
acid in the reaction calorimeter was used to validate experimentally the model
developed.

Figures 3 and 4 show the comparison between experimental and simulated
rate of heat generation for two experiments in which mixed acid of different com-
positions were prepared. In Fig. 5 the simulated rate of heat generation due to
dilution of mixed acid and mononitration of toluene are shown whereas Fig. 6
shows the experimental and simulated power generated-time profiles of this ex-
periment.

Discussion and conclusions

Although the heat of dilution is approximately 7% of the heat of nitration, its
evolution is important when simulating the dynamic behaviour of a discontinuous
nitration process because it changes over time and is related to the rate of reaction
and concentration of the mixed acid. From the comparison between experimental
and model predicted results it has been demonstrated that the general approach to
the mathematical modelling of the rate of heat generation due to dilution, leads to
a satisfactory agreement when preparing different mixed acids within the range of
experimental conditions studied. Thus, the presented model can be introduced
into the general modelling for the simulation of aromatic nitration reactions.

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Zusammenfassung — Obwohl die Reaktionswärme aromatischer Nitrierungsreaktionen
verglichen mit der Lösungswärme relativ groß ist, ist das Wissen um die Geschwindigkeit der
Wärmefreisetzung beim Lösevorgang der gemischten Säuren von großer Bedeutung, um das
thermische Verhalten diskontinuierlicher Nitrierungsprozesse vorherzusagen. In vorliegender
Arbeit wird ein mathematisches Modell, dessen Anwendung und experimentelle Bestätigung
der Lösungswärme-Effekte beschrieben und diskutiert.