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Research paper

Modelling of the Nitration of 2-Methylpyrimidine-4,6-dione (MPD) *)

Amel Belaada*, Waldemar A. Trzciński, Zbigniew C. Chyłek

Military University of Technology,
Gen. W. Urbanowicza 2 St., 00-908 Warsaw, Poland
**E-mail: amelbelaada1@gmail.com*

Abstract: The conditions and kinetics of nitration of 2-methylpyrimidine-4,6-dione (MPD), which leads to the formation of 1,1-diamino-2,2-dinitroethene (DADNE, FOX7) *via* 5,5-dinitro-2-(dinitromethylene)pyrimidine-4,6-dione, are presented. An analysis of literature data enabled us to propose a simple model of the nitration of MPD. The model was verified on the basis of literature data and our own experimental data. The influence of the rate of addition of nitric acid, into a model reactor, on temperature and composition of the reaction mixture was investigated numerically. The proposed nitration model could be useful in a study of the MPD nitration process on a large scale.

Keywords: 2-methylpyrimidine-4,6-dione, modelling of the nitration, kinetics

1 Introduction

1,1-Diamino,2,2-dinitroethene (DADNE, FOX-7) is usually synthesized by nitration of 2-methylpyrimidine-4,6-dione (MPD) [1-5]. MPD is initially nitrated with mixed acids (HNO_3 and H_2SO_4) to obtain 5,5-dinitro-2-(dinitromethylene) pyrimidine-4,6-dione (TNMPD). FOX-7 is then produced by hydrolysis of TNMPD (Figure 1). This method of obtaining FOX-7 has also been used in the present work.

*) Part of this paper was presented at the 20th Seminar on New Trends in Research of Energetic Materials, held in April 2017, Pardubice, Czech Republic

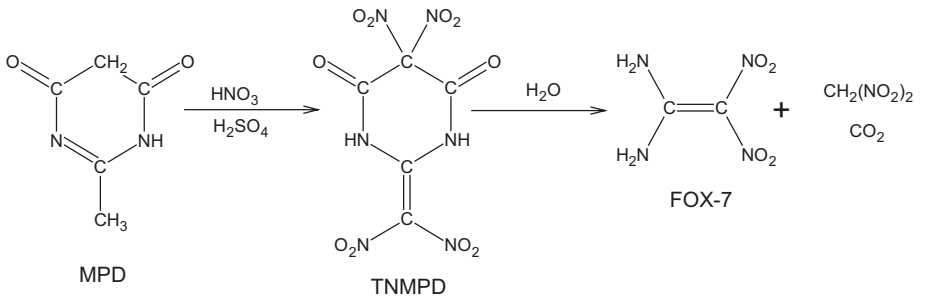

Figure 1. Scheme for the synthesis of FOX-7 [4, 5]

The kinetics of the nitration of MPD has been considered in a few studies [4-8]. The kinetic parameters of this reaction were obtained in [4] on a small scale (500 mL capacity reactor). The order of reaction shown in Figure 1 was determined from the nitration yield at different times and was equal to 2.2 (pseudo-second order). The activation energy and the pre-exponential factor were determined from the dependence of the reaction rate on temperature, and were equal to 42 kJ/mol and 44.24×10^4, respectively. The activation energy was found to be only 9% of the heat generated from the reaction of MPD (460 kJ/mol), so the reaction is sensitive to temperature. The rate of heat generated increased exponentially with temperature, so the nitration of MPD requires efficient mixing and cooling systems on a large scale. The optimum temperature determined during the nitration was 15 °C, and the maximum yield of FOX-7 was equal to 85%.

The kinetic parameters of the MPD nitration were also measured in [5] for a 1 dm^3 capacity reactor. The order of reaction with respect to MPD was determined as 1.65. The activation energy as determined from the Arrhenius law was 61 kJ/mol. The heat generated during the reaction of MPD was measured in [6] using a differential reaction calorimeter. The heat of dissolution of MPD in sulfuric acid was 95 kJ/mol, while the total heat effect was 392 kJ/mol.

In Ref. [7], the kinetics of the reactions allowing FOX-7 to be obtained as the product were analyzed. In one of them, MPD was a starting reactant. The nitration kinetics were studied using HPLC and UV spectrophotometry. According to a scheme of the reaction proposed in [7], the product of nitration of MPD is 2-methyl-5-nitropyrimidine-4,6-dione (MNMPD) and compound TNMPD is a product of its nitration. This latter product is capable of relatively rapid change giving a mixture of further nitration products. The nitration process of TNMPD forms 5,5-dinitro-2-(trinitromethyl)pyrimidine-4,6-dione (PNMPD), which subsequently decomposes giving a mixture of 5,5-dinitrobarbituric acid

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and trinitromethane.

A model was proposed in [8] for the synthesis of FOX-7 in the manner described in [7]. The assumption of three consecutive reactions was taken into account. Among others, the influence of the nitric acid addition time on changes in temperature and composition of the reaction mixture was investigated.

The model proposed in [8] requires the designation of twelve parameters in the kinetic equations (constants in the Arrhenius equations and orders of reactions). Therefore, the present work proposes a simpler model, which corresponds to the reaction scheme shown in Figure 1. The model was verified by using experimental data contained in [4, 5] and the results from the present research.

2 Model of the Nitration of MPD

We assumed that TNMPD synthesis proceeds according to the scheme shown in Figure 1. The reaction is carried out in the reactor with a rate constant k.

$$\mathrm{MPD} \xrightarrow[k]{NO_2^+} \mathrm{TNMPD} \tag{1}$$

Concentrated nitric acid is added at a rate of s [dm^3/min] (n_s [mol/min]). Four moles of nitric acid are needed to obtain one mole of TNMPD from the nitration of one mole of MPD. The changes in reactant concentrations are described by the following equations:

$$\frac{dc_1}{dt} = -k\, c_1^n\, c_2^m - c_1 \frac{1}{V}\frac{dV}{dt} \tag{2}$$

$$\frac{dc_2}{dt} = \frac{n_s}{V} - 4\, c_1^n\, c_2^m - c_2 \frac{1}{V}\frac{dV}{dt} \tag{3}$$

where V is the volume of the reaction mixture, t is time, c_1 and c_2 are the molar concentrations of MPD and nitric acid, respectively, n and m are the orders of reaction with reference to MPD and nitric acid, respectively.

The rate constant is described by the Arrhenius equation:

$$k = A \exp\left(\frac{-E_a}{R\,T}\right) \tag{4}$$

where A is the pre-exponential coefficient of the reaction, E_a is the activation energy, and T is the temperature of the reaction mixture.

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We assumed that the volume of the reaction mixture changes due to the addition of nitric acid:

$$\frac{dV}{dt} = s \tag{5}$$

$$\text{and } n_s = \frac{dV}{dt}\frac{\rho_s}{M_s} \tag{6}$$

where ρ_s, M_s are the density and molecular mass of nitric acid, respectively.

The heat balance in the reactor can be described by the following equation:

$$(c_{pi} + \rho\, c_p\, V)\, \frac{dT}{dt} = \rho_s c_{ps}\, s\, (T_0 - T) + r_Q\, V + r_{Qm}\, V + UA\, (T_a - T) + UA_i\, (T_e - T) \tag{7}$$

where ρ and ρ_s are the densities of the reaction mixture and added nitric acid, respectively, c_p and c_{ps} are their specific heats, c_{pi} is the specific heat of elements, T_0, T_e, and T_a are the temperatures of the nitric acid, the surroundings and at the surface of the reactor, respectively, r_Q is the rate of the heat released from the reaction of MPD during the synthesis, r_{Qm} is the rate of the heat released from mixing nitric acid and sulfuric acid, UA is the coefficient of the heat transfer to the surface of the reactor (the cooling system), and UA_i is the coefficient of the heat transfer to the surroundings by uncooled elements.

The volume, mass and density of the reaction mixture change only due to the nitric acid addition:

$$V = V_{p0} + \int_0^t s\, dt \tag{8}$$

$$m = m_{p0} + \rho_s \int_0^t s\, dt \tag{9}$$

$$\rho = \frac{m_{p0} + \rho_s \int_0^t s\, dt}{V_{p0} + \int_0^t s\, dt} \tag{10}$$

where m_{p0} and V_{p0} are the initial values of mass and volume of the reaction mixture.

The specific heat of the reaction mixture was assumed to be additive:

$$c_p = \alpha_p c_{p0} + \alpha_s c_{ps} \tag{11}$$

$$\alpha_s = \frac{m_s}{m_{p0} + m_s} \tag{12}$$

$$\alpha_p = \frac{m_{p0}}{m_{p0} + m_s} \tag{13}$$

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$$m_s = p_s V_s \tag{14}$$

where V_s and m_s are the current volume and mass of the nitric acid added, respectively.

The rate of heat released during mixing nitric acid and sulfuric acid is described as follows:

$$r_{Qm} = \frac{q_r\, n_s}{V} \tag{15}$$

where q_r is the heat of mixing of nitric acid and sulfuric acid.

The rate of the heat output in 1 dm^3 of the reactants is described by the relationship:

$$r_Q = k\, c_1^n c_2^m\, q \tag{16}$$

where q denotes the reaction heat *per* unit mass of MPD.

The solution of Equations (2)-(16) allowed us to determine the changes in the concentrations of individual reactants and the reaction temperature. The system was solved by the Runge-Kutta method of fourth order.

3 Verification of the Model

3.1 Constant temperature nitration

The experimental data of MPD nitration described in [4] and [5] were used to verify the model proposed. The authors of these papers studied the kinetics of nitration at different temperatures by indirectly determining the degree of transformation of MPD to TNMPD and finally to FOX-7 at specified times from the start of the reaction.

In [4], the nitration of MPD was performed on a small scale using a reactor of 0.5 dm^3 capacity (about 64.76 mL of reaction mixture), using a mixture of acids (98% sulfuric acid and 98% nitric acid) as nitrating agent. MPD was added slowly to the mixture of acids in order to maintain a desired temperature during the nitration process. The process was stopped many times at specified times and the yield of FOX-7 was determined at each time.

In paper [5], the nitration was studied in the same way with a reactor of 1 dm^3 capacity (about 617 mL of reaction mixture). The mixture of acids (95% sulfuric acid, and 65% nitric acid) was cooled at 0 °C, then MPD was added. The process was conducted at an established temperature.

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To adapt the theoretical model to the conditions of the experiments conducted in [4] and [5], we assumed that the temperature in the reaction mixture was kept constant. Since MPD was added to the mixture of acids it was assumed that at time $t = 0$ all of the substrates were located in the reactor and that their total volume in the process remained constant ($s = 0$ and $dV/dt = 0$). With these assumptions, the MPD nitration is described by the system of Equations (2)-(4), with the initial conditions:

$$c_1(0) = c_{1,0} \tag{17}$$
$$c_2(0) = c_{2,0} \tag{18}$$

The different values of the activation energy, pre-exponential coefficient and order of reaction n with respect to MPD are given in [4] and [5] (Table 1). The order of reaction with respect to nitric acid was not determined. Therefore, the calculations were performed for values of m equal 0.5, 1 and 1.5. The calculation results are a basis for determining the order of reaction with respect to nitric acid.

Table 1. Published activation energies and pre-exponential coefficients for MPD nitration

Parameters	Reference	
	[5]	[4]
E_a [kJ/mol]	61	42
log A	8.9	5.65
n	1.65	2.2

The initial molar concentrations of MPD and nitric acid in the reaction mixture used in the synthesis of FOX-7 in [5] were as follows: $c_{1,0} = 0.46$ mol/dm^3, $c_{2,0} = 2.18$ mol/dm^3. The kinetic parameters described in [5] (Table 1) were used for the calculations. The results of the concentrations of TNMPD obtained from modelling and that obtained experimentally at various temperatures are presented in Figures 2-5.

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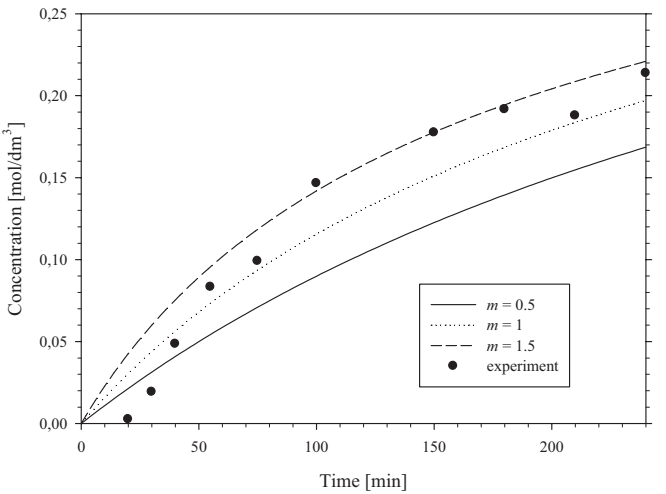

Figure 2. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [5] for a temperature inside the reactor equal to 5 °C

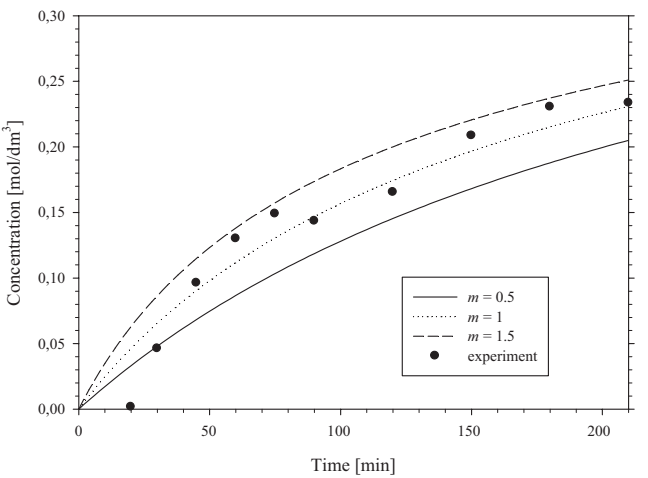

Figure 3. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [5] for a temperature inside the reactor equal to 10 °C

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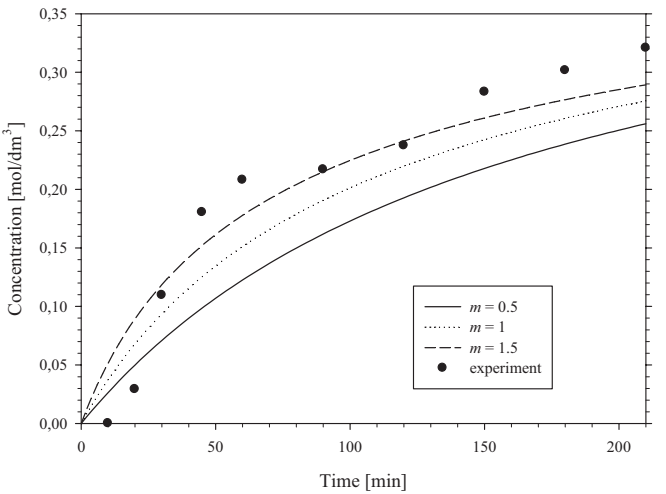

Figure 4. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [5] for a temperature inside the reactor equal to 15 °C

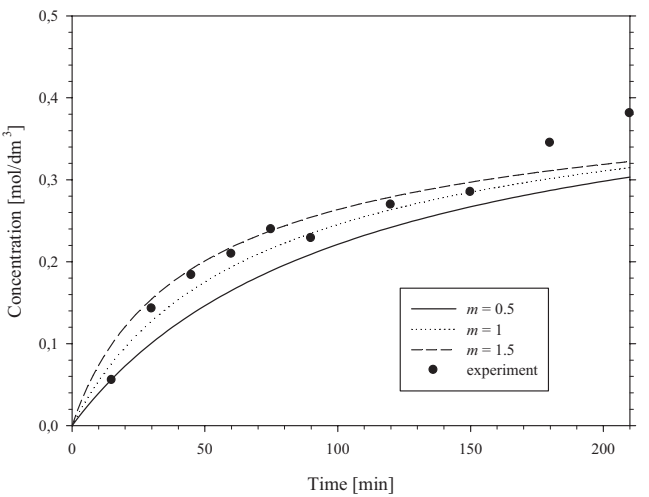

Figure 5. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [5] for a temperature inside the reactor equal to 20 °C

By analyzing the data for the synthesis of FOX-7 in [4], it follows that the initial molar concentrations of MPD and nitric acid in the reaction mixture were $c_{1,0}$ = 1.23 mol/dm^3 and $c_{2,0}$ = 6.17 mol/dm^3. The kinetic parameters used in the

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calculations are shown in Table 1. The variation of calculated concentrations of TNMPD are compared with experimental data in Figures 6-8. In the same figures, the results that were obtained experimentally at various temperatures are also shown.

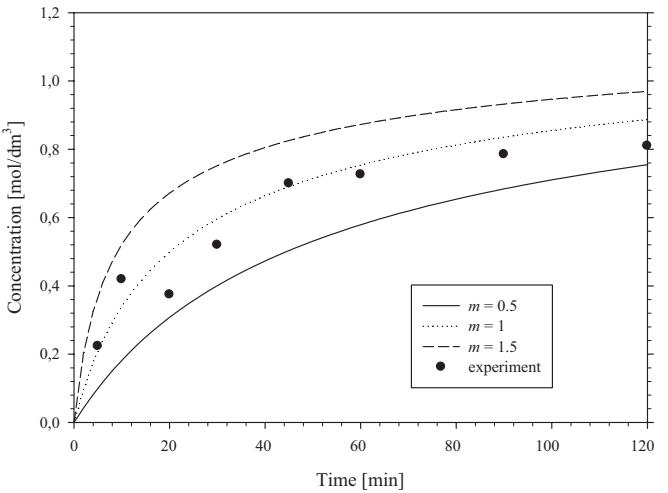

Figure 6. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [4] for a temperature inside the reactor equal to 5 °C

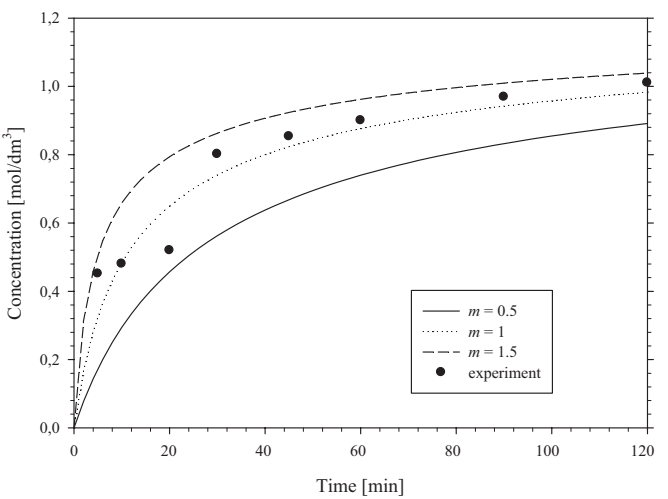

Figure 7. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [4] for a temperature inside the reactor equal to 15 °C

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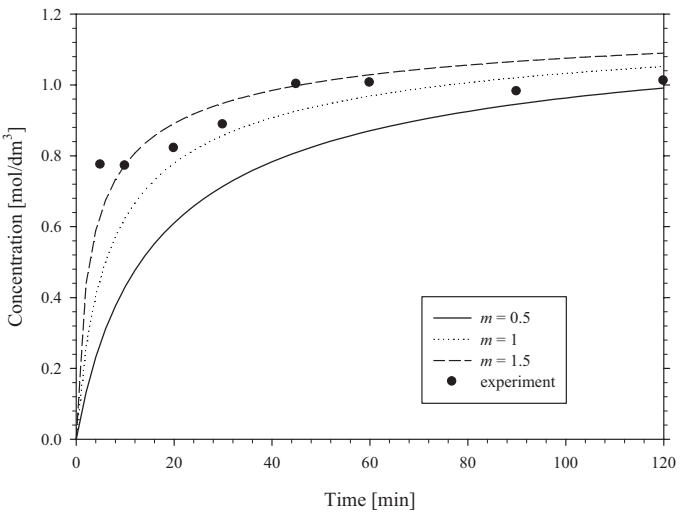

Figure 8. The concentrations of TNMPD obtained from modelling and experiment under the conditions given in [4] for a temperature inside the reactor equal to 25 °C

From the comparisons shown in Figures 2-8 it follows that the model proposed gives results in reasonable agreement with the experimental data using the kinetic parameters described in [4] and [5]. It may also be inferred that the nitration of MPD with respect to nitric acid is first order. In further calculations the value of $m = 1$ was assumed.

3.2 Variable temperature nitration

To verify the nitration model under variable temperature, the results of our own research were used. In the small scale setup, the reaction was conducted in a reactor of 1 dm^3 capacity. Initially, the reaction mixture consisted of sulfuric acid (95%, 700 mL, $\rho = 1.84$ g/cm^3) and MPD (105 g) at a temperature of −5 °C. The nitric acid (99%, 175 mL, $\rho = 1.52$ g/cm^3) was then gradually added. The temperature of the cooling system was varied in a controlled manner. The volume of the nitric acid added is shown in Figure 9a.

In a similar way, the nitration of MPD was performed in a larger reactor, of capacity 10 dm^3. MPD (1050 g in mass) was added to sulfuric acid (95%, 7 dm^3, and $\delta = 1.84$ g/cm^3). Nitric acid (99%, 1.75 dm^3, $\delta = 1.52$ g/cm^3) was then added. The volume of nitric acid added was changed according to the curve shown in Figure 9b. The temperatures of the cooling system and the reaction mixture were measured.

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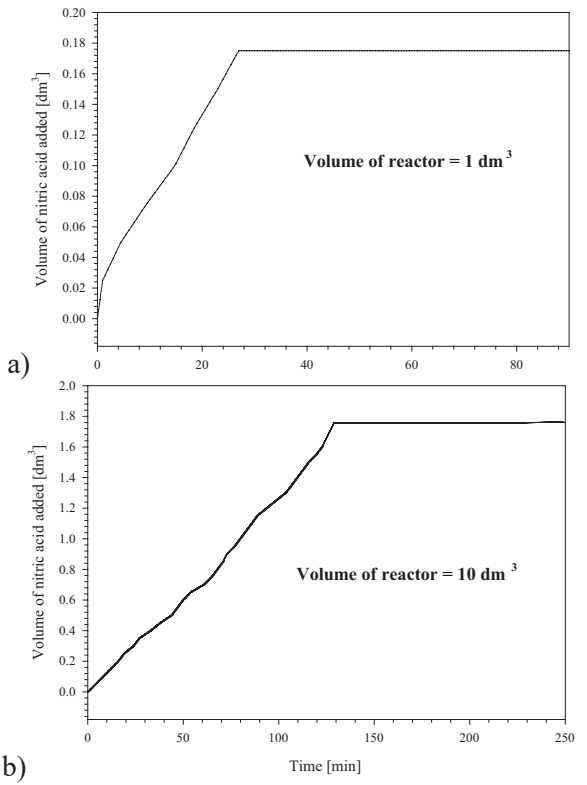

Figure 9. The volume of nitric acid added in the small (a) and large (b) reactors

The changes in the temperature of the reactants in the small (1 dm^3) and large reactors (10 dm^3) during the nitration process were determined by solving the system of Equations (2)-(16) with the following initial conditions:

$$c_1(0) = c_{10} \qquad c_2(0) = 0 \qquad T(0) = T_0 \tag{19}$$

The same initial concentration of MPD (1.11 mol/dm^3) was used in the small and large scale experiments.

Initially, the kinetics parameters described in [5] (Table 1) and the heat of nitration of MPD (297 kJ/mol) determined in [6] were used in the calculations. The temperature of the reactants obtained from the modelling are compared in Figures 10 and 11, with the measured temperature for the small and large scale experiments, respectively.

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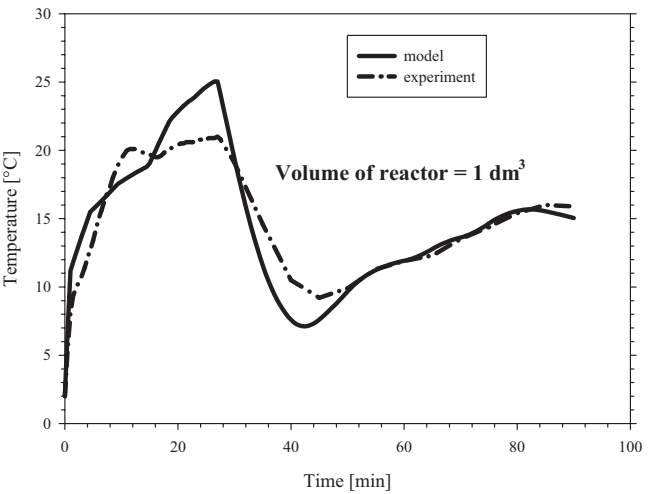

Figure 10. Temperature variation obtained from modelling with the kinetics parameters and reaction heat from [5] and [6], and the experimental variations for the 1 dm^3 reactor

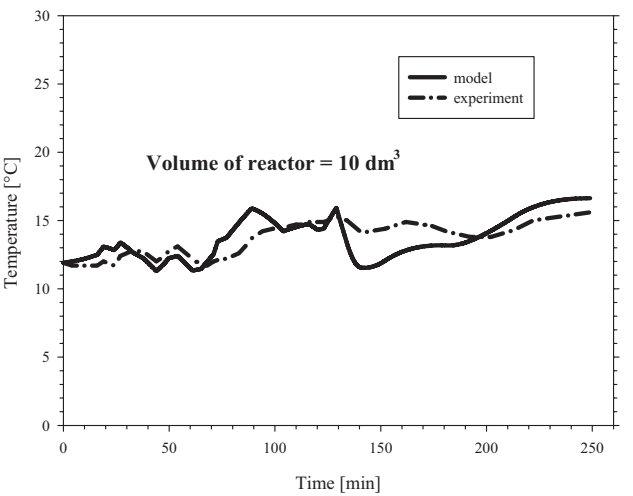

Figure 11. Temperature variation obtained from modelling with the kinetics parameters and reaction heat from [5] and [6], and the experimental variations for the 10 dm^3 reactor

The calculation of the temperature of the reaction mixture was then performed using the kinetics parameters described in [4] (Table 1). The heat of nitration of MPD used in the model was obtained by subtracting the heat released

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from the dissolution of MPD in sulfuric acid (about 95 kJ/mol) [6] from the total heat measured in [4] for the nitration of MPD (460 kJ/mol). The results of the modelling are shown in Figures 12 and 13 for the small and large scale reactors, respectively. The experimental temperatures are also shown in these figures.

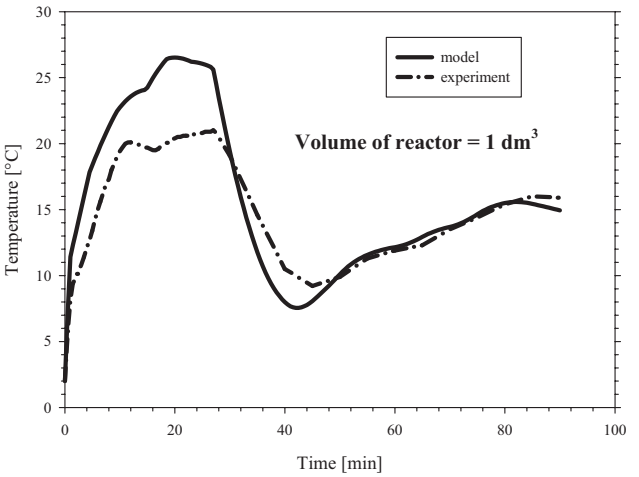

Figure 12. Temperature variation obtained from modelling with the kinetics parameters and reaction heat from [4], and the experimental variations for the 1 dm^3 reactor

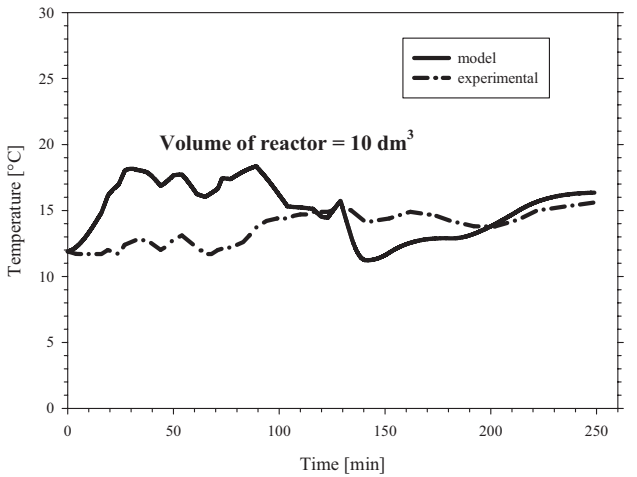

Figure 13. Temperature variation obtained from modelling with the kinetics parameters and reaction heat from [4], and the experimental variations for the 10 dm^3 reactor

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The calculations performed using the kinetic parameters and the heat of nitration described in [5] and [6] gave results reasonably close to those obtained experimentally, so these data will be used for the parametrization of a model reactor for the nitration of MPD.

4 Parametric Study of a Model Reactor

The study of the influence of the rate of addition of nitric acid and the temperature of the cooling system on changes of the temperature of the reaction mixture and the concentrations of the components was performed numerically. We assumed that the reaction substrates were the same as used in the experiments in the large reactor (7 dm^3 95% sulfuric acid, 1.75 dm^3 99% nitric acid, and 1050 g of MPD). The kinetic parameters from [5] and the heat of nitration from [6] were chosen for the calculations. It was assumed that nitric acid was added at a constant rate during 60 min, 90 min, 120 min or 150 min, and that the temperature at the surface of the reactor T_a was constant and equal respectively 0 °C, −5 °C, −10 °C or −15 °C.

The volume of nitric acid added is shown in Figure 14. The calculated temperatures in the reaction mixture during the nitration of MPD are shown in Figure 15 for the lowest and highest temperatures T_a.

Nitration of MPD was tested in paper [4] in a temperature range from 5 °C to 35 °C. During the reaction, hazardous products such as dinitromethane or nitroform can be formed at higher temperatures. Therefore, due to the high reaction heat, it can be assumed that a temperature of 35 °C is the maximum safe temperature. From the graphs shown in Figure 15 it follows that a dosing time of 60 min is too short and the temperature of the reactants exceeds the safe temperature. A similar case is observed for t_{dos} = 90 min and the temperature of the cooling system of 0 °C and −5 °C.

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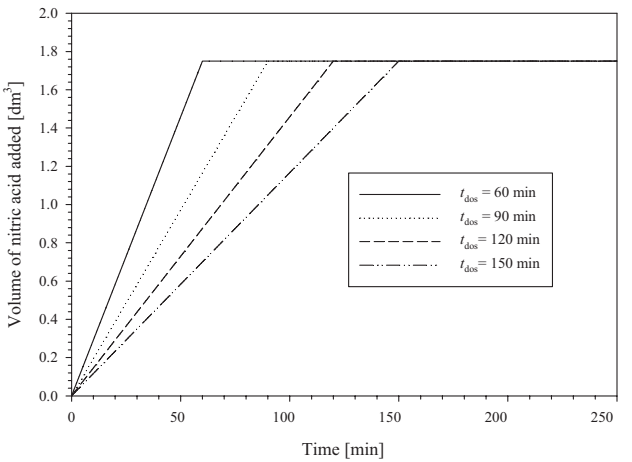

Figure 14. Volume variation of the nitric acid added to the reactor of volume 10 dm^3

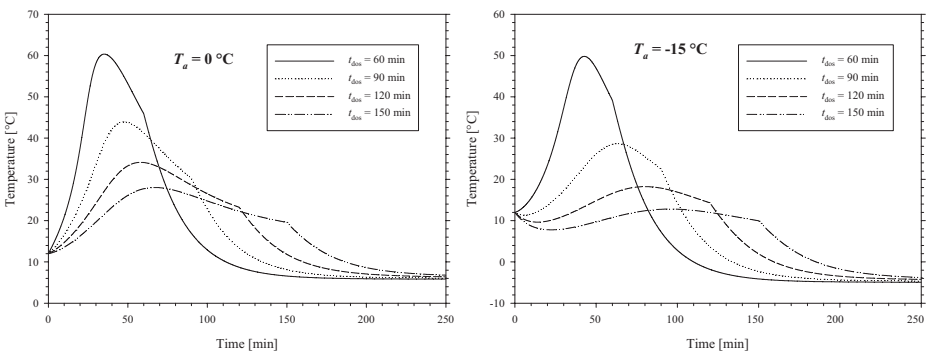

Figure 15. Temperature variations obtained from modelling with different temperatures at the reactor surface

In order to check the influence of the reactants' temperature on the yield of TNMPD we chose a nitric acid addition time t_{dos} = 120 min and an initial temperature at the reactor surface T_a = −10 °C, but the latter was set after the completion of dosing at −10 °C, 0 °C, 10 °C or 20 °C. The calculated temperature and the concentrations of MPD and nitric acid in the reaction mixture are shown in Figures 16 and 17, respectively.

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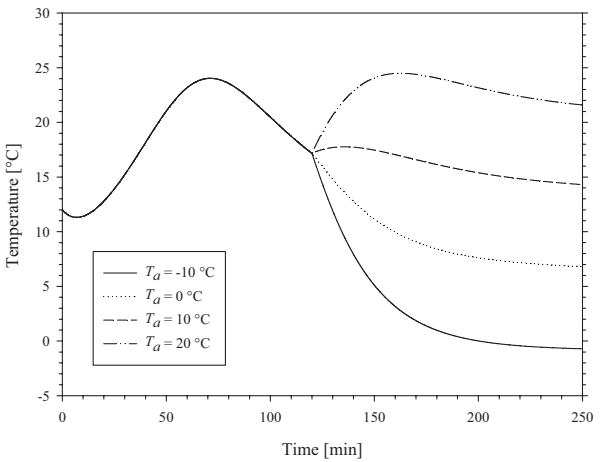

Figure 16. The temperature of the reaction mixture obtained from modelling

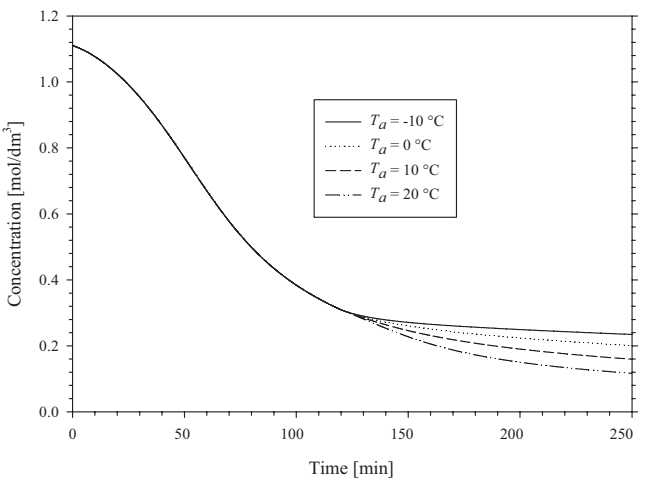

Figure 17. The concentrations of MPD obtained from modelling

The results in Figure 16 show that the temperature in the reactor depends on the cooling jacket temperature during the second stage of the MPD nitration, but it does not exceed 25 °C. The jacket temperature also influences the final degree of nitration. The concentration of MPD at 250 min was equal 0.2346 and 0.1168 for jacket temperatures of −10 °C and 20 °C, respectively (Figure 17). This means that the degree of nitration is 79% and 89%. The model of MPD nitration makes it possible to choose the parameters of the reactor in such a manner that the temperature will be maintained at an optimal level from the point of view

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of the efficiency of nitration, with the nitration time as short as possible. This will ensure maximum efficiency of the nitration and minimize the production of harmful by-products of the reaction.

5 Conclusions

The present work provides a theoretical model for the investigation of the influences of various factors on both the increase in temperature in the reactor, and the efficiency of the MPD nitration. The model was verified using experimental data from the nitration at various scales. The kinetic parameters for nitration given in the literature were checked by simulations. The calculations of the temperature in the reactor during nitration of MPD, obtained using the kinetic parameters and the heat of nitration described in [5] and [6] are in a good agreement with that obtained experimentally in both small and large scale experiments. Moreover, the nitration of MPD was established as a first order reaction with respect to nitric acid.

The verified nitration model was applied to optimize the parameters of the process in such a way that the temperature was maintained at an optimal level from the point of view of nitration efficiency, with the nitration time as short as possible. For the model reactor, the temperature inside the reactor did not exceed a safe temperature of 25 °C when the nitric acid addition time was 120 min, the initial temperature at the reactor surface was −10 °C during dosing and this temperature was changed to 20 °C after dosing. The theoretical degree of nitration was 89% at the end of the nitration process (250 min).

The model used is less complex than the model proposed in [8] and requires a smaller number of parameters of the nitration kinetics that should be determined experimentally.

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