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Modelling of the Effect of Concentrated Nitration Conditions on the Efficiency of the Production of 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT)

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Abstract: 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is one of the most important intermediates in the synthesis of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). A suitably modified Bachmann process, nitrolysis of solid hexamine in the presence of ammonium nitrate-nitric acid and acetic anhydride on a laboratory scale, is introduced to increase the efficiency, production capacity and purity of the DPT produced. Various quantitative and qualitative analytical methods were used for the identification and quality control of the product. A central composite design (CCD) of experiments was used to optimize the production process, increasing the production capacity, reducing the amount of acetic acid as the reaction medium to a suitable limit, and examining the effects of the main factors impacting on the efficiency of the nitration, *e.g.* the volume of ammonium nitrate-nitric acid solution, nitration temperature reactor addition time and volume of acetic anhydride. The overall results indicated that DPT was obtained with an efficiency of 64.58% and a production capacity of 20.77 (100 g·mL^{-1}).

Keywords: DPT, CCD, optimization, production capacity, efficiency

Supplementary material (SI)
Tables S1 to S11 and Figures S1 to S20 are available as SI at: http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2018/vol-15-no-1.html

1 Introduction

3,7-Dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) is an intermediate for the commercial explosives octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)

and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) [1, 2]. It is an unstable secondary explosive, which has a lower impact sensitivity than 2,4,6-trinitrotoluene (TNT) (Figure S1, Table 1). Due to the importance of production capacity and efficiency of DPT formation, different synthetic methods for DPT were developed, which are summarized in Table 2. Among these different methods, the Bachmann process is important for the production of DPT on an industrial scale, where the nitration of hexamine is performed under mildly acidic conditions [3]. Since DPT has a high sensitivity with respect to different external stimuli, such as impact sensitivity [4], electric spark sensitivity [5], shock sensitivity [6], friction sensitivity [6] and heat sensitivity [7], it is important to improve the current synthetic methods on the laboratory, pilot and industrial scale.

Table 1. Basic physico-chemical properties of the DPT

Chemical formula	$C_5H_{10}N_6O_4$
Molecular weight [g·mol^{-1}]	218.1707
Appearance and form	White rhombic crystalline substance (crystallized from acetone) [18]
Oxygen balance [%]	−80.67 [19]
Detonation pressure (P), [GPa]	21.8 [19]
Heat of explosion (Q_{max}), [kJ·kg^{-1}]	4299 [19]
Volume of gaseous products of detonation, [dm^3·kg^{-1}]	771 [19]
Theoretical maximal density (ρ_{TMD}), [kg·m^{-3}]	1680 [20]
Melting point [°C]	203-206 [21]
Heat of formation (ΔH_f), [kcal·mol^{-1}]	–18.14 [19]
Heat of combustion (ΔH_c), [kcal·mol^{-1}]	3793 [19]
Heat of decomposition (ΔH_d), [kJ·mol^{-1}]	671.5 [22] , 537.2 [23]
Toxicity	Medium [19]
Impact sensitivity (detection by noise), [J]	50.0 [18]
Stability	Very good
Solubility	Good solubility in low concentration mineral acids (precipitation at pH=3.4) [21]; Slightly soluble in organic solvents (*e.g.* in acetone) [21]; Practically insoluble in cold water, decomposed in hot water [24]

Table 2. Different production methods for DPT

No.	Raw material	Efficiency [%]	Production capacity (100 g·mL^{-1})	Melting point [°C]
1	Hexamethylenetetramine (Hexamine) [11, 16, 21, 25-27]	48-57	12.76-15	198-203
2	Hexamethylenetetramine dinitrate (Hexamine Dinitrate, HEXADI) [21]	-	-	-
	Hexamine Dinitrate with Acetic anhydride [29]	30.6	30.6	205-206
	Hexamine Dinitrate with Sulphuric acid [30]	31	-	199-201
3	Urea [31]	67.4	2.4	209-210
	Urea with Task-Specific Ionic Liquids (TSIL) [32]	72	-	209-210
4	N,N'-Dinitrourea (DNU) [33]	52	9.67	-
5	Dimethylolnitramide [21]	-	-	-
	Dimethylolnitramide and Formaldehyde-Ammonia [21]	83	8.66	206-208
	Dimethylolnitramide and Methylenediamine [21]	48	1.11	206-208

The production capacity is the weight of the product produced per unit volume. The purpose of this study was to increase the efficiency, production capacity and purity of DPT by a modified Bachmann process. A central composite design (CCD) of the experiments and MINITAB version 16 (Minitab Inc., Coventry, UK) [8] were used to identify the best conditions for the DPT synthetic process, with four important input parameters. Since DPT synthesis from hexamethylenetetramine using a solution of ammonium nitrate-nitric acid and acetic anhydride occurs in an acetic acid medium (this reagent occupied the main volume of the reactor), this study reduced the volume of acetic acid and concentrated the nitration conditions, and afforded higher production capacity, efficiency and optimal purity. Moreover, it was shown that increasing the production capacity can be achieved by increasing the efficiency and reducing the volume of acetic acid per kilogram in a batch process.

2 Experimental

2.1 Materials and methods

The starting materials consisted of hexamine (hexamethylenetetramine, HMTA), ammonium nitrate(V) (AN) (with a purity of >98%), concentrated nitric)V) acid (98%), glacial acetic acid (99%), acetic anhydride (99%) and paraformaldehyde (stabilizer) were purchased from industrial sources. A 47% solution of AN in nitric acid (NA) was prepared and used according to the industrial conditions. With regard to the density of NA (1.51 $g \cdot mL^{-1}$), it was possible to prepare the solution of 47% AN-NA by using a ratio of 400 g AN in 300 mL NA.

2.2 Preparation of DPT from hexamine

DPT was manufactured on a laboratory scale by nitrolysis of hexamine in the presence of AN-NA and acetic anhydride [9]. Glacial acetic acid (60.2 mL), acetic anhydride (7.73 mL) and paraformaldehyde (1-2 g) were added to a semi-batch jacketed glass reactor equipped with a stirring assembly (Figure S2). The temperature of the reactor was maintained in the range 32-60 °C by the simultaneous addition of solid hexamine (28.92 g), AN-NA solution (20-40 mL) and acetic anhydride (60-80 mL) to the reactor *via* a pre-calibrated dropping funnel over a period of 15-30 min. After the addition of the reactants, the reaction mixture was stirred for 20 min in the temperature range 30-46 °C. The reaction was quenched by the addition of a mixture of ice and water. The reaction product was then immediately filtered off under vacuum. The solid obtained was neutralized on the filter to pH 6-7 with 25% aqueous ammonia at 20-25 °C and washed with water several times. After drying the product at room temperature, its melting point was in the range 201-210 °C (Figure S3).

2.3 Analysis and characterization of the synthesized DPT

Various quantitative and qualitative analytical methods were applied for the identification and quality control of the synthesized DPT including:

(i) Melting point: The melting points of DPT and RDX are close to each other but lower than HMX (Table S1) [10].

(ii) ^1H NMR: The ^1H NMR of DPT shows a singlet (δ = 4.1 ppm) for the methylene bridge protons and two doublets (δ = 4.9 ppm and 5.5 ppm; gem-coupling) arising from the non-equivalence of the axial and equatorial protons of the ring methylene group that are in close agreement with reported data (Figure S4) [11, 12].

(iii) High Performance Liquid Chromatography (*HPLC):* HPLC was employed to determine the purity of DPT and the amount of RDX impurity present

in the samples. The eluent used was mixture of acetonitrile, methanol and water (5:35:60) at a flow rate of 1 mL·min^{-1}. The chromatogram of DPT (Figure S5) shows a single peak at a retention time of 4.10 min, with purity greater than 98%. The observed peak at retention time 3.03 min was due to a negligible amount of RDX impurity. The peaks present at retention times 2.31 min and 2.52 min are related to the solvent used. The chromatograms obtained for DPT containing HMX and α-HMX are shown in Figures S6 and S7, as well as Table S2.

(iv) Fourier transform infrared spectroscopy (FT-IR): The FT-IR spectrum of the synthesized DPT is shown in Figure S8, in which two peaks at 1508 cm^{-1} and 1546 cm^{-1}, correspond to the asymmetric stretching vibrations, as well as a single peak at 1289 cm^{-1}, are related to the symmetric stretching vibrations of the nitro group. IR absorptions at 2965 cm^{-1} and 3052 cm^{-1} are assigned to the asymmetric and symmetric vibrations of the methylene groups of DPT. The FT-IR spectrum is in conformity with the reference spectrum [11].

3 Results and Discussion

3.1 Methodology

The Response Surface Methodology (RSM) is a statistical method that is useful for the optimization of chemical reactions and industrial process. It is widely used for the Design of Experiments (DOE) [13]. In this article, the use of CCD for DOE was used to determine the settings of the factors that would result in the optimum value of the response.

3.1.1 Identification of the inputs and responses of the system

The volume of ammonium nitrate-nitric acid solution (x_1), nitration temperature (x_2), reactor addition time (x_3) and the volume of acetic anhydride (x_4) were considered as the input parameters. Meanwhile, the efficiency (E) and the production capacity (Pr) were specified as the responses, as shown in Figure S9.

3.1.2 Selecting the appropriate levels for the process parameters

Selection of the operating range of the process parameters is important because too wide a selection may form an infeasible range for the response surface, while a narrow range can result in poor information regarding sensitivity [14]. The levels for each process parameter were decided on the basis of information provided by industry, initial experiments and consulting the literature (Table S3). The CCD was used to optimize the levels of the four selected input parameters for obtaining the maximum response.

3.1.3 Experimental design

In statistics, RSM explores the relationships between several exploratory variables and one or more response variables, where the second order polynomial response surface mathematical models can be developed as [15]:

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{i<j} \sum \beta_{ij} x_i x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \epsilon \quad (1)$$

where y is the corresponding response (E or Pr) for the various DPT synthetic process variables, the x_i $(1, 2, \ldots, k)$ are the coded levels of k quantitative process variables, the terms β_0, β_i, β_{jj} and β_{ij} are the second order regression coefficients and ϵ is a random error term. The second, third and fourth terms in Equation 1 correspond to the linear effect, the interactive effects of the process parameters and the higher-order effects, respectively.

3.1.4 Experimental data collection

The suggested 31 experiments were different combinations of the four different parameters consisting of five levels (Table S4). The sets of combinations of the input operating parameters, as suggested by the MINITAB 16 software, are listed in Table S4.

3.1.5 Developing the statistical models, statistical analysis and testing of the models

Experiments were conducted to determine the E and Pr values for DPT using different combinations of the variables. The non-linear regression model was developed using the data collected as per the CCD of experiments. The analysis of variance (ANOVA) technique was used to evaluate the statistical significance of the constructed models. ANOVA consists of determining which factors significantly affect the response by the Fisher statistical test (F-test). A significance test was conducted to determine the influence of the various input process parameters and their interaction terms on E and Pr values of the DPT synthetic process. The results of the significance test are listed in Table S5. P-values lower than 0.05 indicate that the developed model and the terms are statistically significant, which confirms the significance of E and Pr as well as the other terms (Table S6). If the model is a good predictor of the experimental results, the F-value should be equal to or greater than the tabulated value of the F-distribution for a certain number of degrees of freedom in the model at a level of significance α (the standard 95% confidence limit) [15].

4 Results and Discussion

The data for the experimental runs (Table S4) were used to find the coefficients of the response surface equation suggested in Equations 2 and 3.

4.1 Response-*E* and response-*Pr*

The results of the significance test for the reduced non-linear model for *Pr* are shown in Table S5; the F-value and P-value suggested that the individual, second order and some interaction terms, such as x_1, x_2, x_3, x_4, x_1x_2, x_2x_3, x_3x_4, x_1^2, x_2^2 and x_4^2 are significant, whereas all other terms are insignificant. The P-value of this reduced model was 0.029, which clearly confirms an excellent fit of the experimental data. The suggested reduced non-linear model in un-coded form is given by:

$$Pr = -496.993 + 6.325x_1 + 5.607x_2 + 2.828x_3 + 7.531x_4 - 0.050x_1x_2 + 0.017x_2x_3 - 0.050x_3x_4 - 0.071x_1^2 - 0.047x_2^2 - 0.047x_4^2 \quad (2)$$

As indicated in Table S6, the second order and some interaction terms containing x_1, x_2, x_3, x_4, x_1x_2, x_1x_3, x_1x_4, x_2x_3, x_3x_4, x_1^2, x_2^2 and x_4^2 for *E* are significant, whereas all other terms are insignificant. The P-value of this reduced model was ≤0.004, which clearly confirms an excellent fit of the experimental data. The suggested reduced non-linear model in un-coded form is given by:

$$E = -1679.23 + 25.55x_1 + 18.48x_2 + 6.22x_3 + 24.30x_4 - 0.22x_1^2 - 0.16x_2^2 - 0.14x_4^2 - 0.19x_1x_2 - 0.04x_1x_3 - 0.05x_1x_4 + 0.10x_2x_3 - 0.13x_3x_4 \quad (3)$$

The F-value of *Pr*, 81.38, is clearly greater than the tabulated F (2.20 at 95% significance), which confirms the adequacy of the model fit. The F-value of *E*, 614.12, is also greater than the tabulated F (2.18 at 95% significance), which indicates the significance of the model.

4.2 Adequacy test of the models

ANOVA was used to check the adequacy of the CCD model of the experimental design based on the response surface [15]. Table S7 shows the ANOVA regression parameters of the predicted surface response model for *E* and *Pr*. Properties such as lack of fit, R-squared, adjusted R-squared (R_{adj}), the predicted R-squared (R_{pred}) and PRESS were examined. Since the R value always decreases when a regression variable is eliminated from the model, the R_{adj}, which takes the number of regression variables into account, is usually selected. In addition,

R_{pred}, which indicates the predictive power of the model, is chosen for the same reason. It can be seen from Table S7 that the R_{adj} is greater than 0.7 as part of the conditions for the model's adequacy. Since the difference between R_{adj} and R_{pred} is less than 0.2, the model is adequate. The PRESS statistic is a measure of how well the model will predict new data. A model with a small value of PRESS indicates that the model is likely to be a good predictor. The lack of fit test with the P-values for *E* and *Pr* shows that the model is significant and fitted well. The regression coefficients (R^2) are listed in Table S7, and quantitatively evaluate the correlation between the experimental data and the predicted responses (*E* or *Pr*). The experimental results and the predicted values are shown in Figure S10, where the experimental data in the plot is able to generate a straight line.

4.3 Confirmation test of the models

Optimization of the experiments was carried out for all of the responses (Table S8). Analysis of the confirmation of the experiments for *E* and *Pr* is listed in Table S9. The percentage error for *E* and *Pr* is computed as:

$$\text{Error}\ (\%) = \frac{\text{Predicted value} - \text{experimental value}}{\text{Predicted value}} \times 100 \qquad (4)$$

The purpose of the optimization is to reach the maximum response [15]. The optimal values obtained by the software [8] are shown in Figure S11, where the optimal parameter values can be determine to reach the maximum responses of the process (*Pr* and *E*) for DPT. As seen, the maximum *E* was 64.97% with a desirability degree (*d*) of 0.9988. In order to obtain an *E* value of 64.97% with regard to the optimal diagram plotted (Figure S11), the values of x_1 to x_4 were 30.00 mL, 46 °C, 30 min and 69.73 mL, respectively. Moreover, the maximum *Pr* was 23.00 (100 g·mL^{-1}), with $d = 0.99996$. Thus, the values of x_1 to x_4 were 30.00 mL, 47.70 °C, 30 min and 64.65 mL to obtain a *Pr* value of 23.00 (100 g·mL^{-1}).

4.4 Optimal method for increasing the *E* and *Pr* values of hexamine to DPT (high capacity and desirable purity)

An optimal method, similar to the synthetic method given in Section 2.1, was selected from among the tests in which the purity of the DPT was specified (Table S10). Sediment with a purity of over 95% was obtained through this method, where DPT was purified by recrystallization from acetone. In this regard, to be sure of the conditions, the test was performed several times (Table S11).

4.5 Nitrolysis of hexamine by NO_2^+

Figure S12 shows the suggested synthesis mechanism for DPT from hexamine. As with the electrophilic nitration process of aromatic compounds, a σ-complex of hexamine will form when NO_2^+ is drawn close to hexamine. The balanced equation for the production of DPT from hexamine is:

$$5C_6H_{12}N_4 + 8HNO_3 + 4NH_4NO_3 + 12C_4H_6O_3 \rightarrow 6C_5H_{10}N_6O_4 + 24C_2H_4O_2 \quad (5)$$

The calculated *E* is based on this reaction by considering the number of hexamine methylene groups converted to the product [16, 17].

4.6 Study of the effect of different factors on the *E* and *Pr* of DPT

The effects of the different parameters and their interactions on the responses in the surface (3D) and contour (2D) plots for the predicted responses can be established [15]. The surface and contour plots with two variables kept constant and the other two varying within the experimental ranges are shown in Figures S13 to S20.

(i) The effect of volume of AN–NA solution (x_1) on E and Pr of DPT (Figures S13 and S14): Generally, if the x_1 becomes higher than the permitted limit, the nitration conditions become stronger so that the synthesis of RDX and linear compounds from hexamine becomes more likely than the synthesis of DPT. Thus, the *E* and *Pr* values of DPT are lowered.

(ii) The effect of nitration temperature (x_2) on E and Pr of DPT (Figures S15 and S16): For x_2, an increasing trend was observed in the *E* and *Pr* of DPT. Increasing the temperature within the specified range can enhance the reaction rate and cause the desired reaction to compete. On increasing x_2 above a specific limit, a decrease in *E* and *Pr* of DPT was observed because the bonding of the methylene groups can be easily broken and the by-products linear nitramines, RDX and HMX were produced. Acetic anhydride can be converted to acetic acid by absorbing hydrogen from nitric acid at high temperatures, which reduces *E*, *Pr* and the purity of DPT. High temperature conditions were confirmed in laboratory scale experiments by determining the solubility in acetone and degradation in hot water. The nitrolysis of hexamine at low temperatures has led to the synthesis of a number of cyclic nitramines [18].

(iii) The effect of reactor addition time (x_3) on E and Pr of DPT (Figures S17 and S18): The reaction will go to completion because increasing the time has a positive effect on the percentage of impurity removal. Thus, it is important to optimize the x_3 simultaneously with the other parameters for obtaining the best responses.

(iv) The effect of volume of acetic anhydride (x_4) on E and Pr of DPT (Figures S19 and S20): Acetic anhydride in these mixtures acts as a dehydrating agent that reacts with water to generate acetic acid. A reduction of x_4 in the reaction environment can decrease the *E* and *Pr* as well as the purity of the DPT. Since dilution of the reaction reduces the rate of nitration at high values, it has a little negative effect on *E*. Due to an increase in the capacity volume, production is also reduced. The optimal method and its results are reported in Table 3 and compared with two previous studies, where the experimental data were available. As indicated, both *E* and *Pr* have been increased in the current work as compared to the two previous works.

Table 3. Comparison of the and values of the current work with two methods mentioned in DPT synthesis

No.	Raw material	Efficiency [%]	Production capacity (100 g·mL^{-1})	Melting point [°C]	Ref.
1	Hexamine	48	15	198	[9]
2	Hexamine	57	12.76	201-203	[34]
3	Hexamine	64.58	20.77	201-205	This work

5 Conclusions

A new method was used to optimize DPT synthesis from solid hexamine as starting material. During this optimization, it was specified that the factors influencing *E* and *Pr* could not be studied separately because these factors have interacting effects on each other. The CCD method was used to obtain an optimal point for the parameters. To optimize the production process and increase *Pr*, the amount of acetic acid as a reaction medium was reduced to a suitable limit. Four variables, x_1, x_2, x_3 and x_4, are also important, in that x_1 and x_2 have the greatest effects on the *E* and *Pr* values. The optimal points generated by the software, were experimentally tested in the laboratory. Ultimately, DPT with an *E* of 64.58% and with a *Pr* of 20.77 (100 g·mL^{-1} was achieved.

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