



Increasing the Efficiency of the Production of 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX)

Azadeh AFZALI,* Karim ESMAEILPOUR, Sajad DAMIRI,
Zoleikha HADI, Mohammad Hossein KESHAVARZ **

*Department of Chemistry, Malek-ashtar University of Technology,
Shahin-shahr P.O. Box 83145/115, Islamic Republic of Iran*

*E-mail: *afzali.azin@yahoo.com; **mhkeshavarz@mut-es.ac.ir*

Abstract: This work introduces a suitable method for the optimization of selective synthesis of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), as one of the most well-known high explosives, from the aspects of production capacity and efficiency, by nitration of 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT). The effective factors in the productive capacity of HMX and the synthesis of a product from raw DPT with high capacity, purity, and efficiency have been identified. The required qualitative and quantitative analyses were performed for the identification and confirmation of the product quality. In order to optimize the process of increasing the capacity of HMX production and evaluation of the effects of different factors on the production capacity, a series of experiments were designed and performed by using central composite design (CCD). Practical studies and statistical analyses showed good conformity between the model presented and the actual results, allowing the selective production of HMX with an efficiency of greater than 70% and a high production capacity.

Keywords: design of experiment, efficiency, production capacity, 1,3,5,7-tetranitro-1,3,5,7-tetrazocane, 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane

1 Introduction

HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) is one of the high performance explosive materials with many applications in different types of chemical industry [1-6]. It is a non-dehumidifier, which exists in different crystal forms, α , β , γ and δ , with different densities and sensitivities to stimuli [7]. Of these polymorphs,

only β -HMX has favorable high performance [7]. Due to the desirable properties of β -HMX, it has been widely studied to improve its applications in recent years, such as nanocomposites [8], core-shell [9], polar precursors [10], nano co-crystals [11] and microcapsules [12]. Since the four modifications of HMX have high sensitivity with respect to different external stimuli such as impact sensitivity [13], electric spark sensitivity [14], shock sensitivity [15], friction sensitivity [16] and heat sensitivity [17], it is important to improve the current synthesis methods at laboratory, pilot and industrial scale. Some conventional methods have been developed to synthesize β -HMX, *e.g.* the nitrolysis of hexamine (HA) [18], 3,7-dinitro-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DPT) [19], 1,3,5,7-tetraacetyl-1,3,5,7-tetrazocane (TAT) [20] and 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetrazocane (DADN) [21]. Moreover, several new methods have been introduced in recent years to synthesis β -HMX under safe conditions, *e.g.* ionic liquids and solid acid catalysts [22-25]. The use of the precursor DPT is especially important for the chemical industry because DPT can be obtained in high yield from inexpensive urea via nitrourea and/or dinitrourea [18], and then directly nitrolysed to produce β -HMX. One of the restrictions of this process is that traditional nitrolysis of DPT by $\text{HNO}_3\text{-NH}_4\text{NO}_3$ only gave β -HMX in low yield (45%) even when more than 30 equiv. of HNO_3 were used [26]. In order to increase the yield β -HMX, some other $\text{HNO}_3\text{-NH}_4\text{NO}_3$ -based systems have been introduced. Moderate yields were obtained when MgO [27], P_2O_5 [28], SO_3 [29] and a mixture of acetic acid with acetic anhydride in the presence of $\text{HNO}_3\text{-NH}_4\text{NO}_3$ have been used [30, 31]. A comparison of some of the different methods is given in Table 1. These methods have also some disadvantages, such as a tedious workup.

In the present research, a suitable pathway will be introduced to improve the yield of β -HMX through using pure DPT as the intermediate. The major factors for increasing the efficiency of β -HMX synthesis have been investigated. This method may be attractive for scientists and the chemical industry to produce high yields of β -HMX with good safety. To accomplish the study, a suitable experimental design was prepared by using a central composite design (CCD) and MINITAB version 16 (Minitab Inc., Coventry, UK) [32]. Then, by determining the experimental values, the required optimal conditions and the effective factors were specified to increase the HMX production efficiency.

Table 1. Different production methods for HMX

Raw material	Maximum production efficiency	Ref.
DPT, acetic anhydride, ammonium nitrate, and nitric acid	65	[18, 39]
DPT, hexamine, acetic anhydride, ammonium nitrate, nitric acid, and paraformaldehyde	70	[31]
Acetic acid, acetic anhydride, paraformaldehyde, hexamine, nitric acid, and ammonium nitrate	95	[31]
TAT, nitric acid and phosphorous pentoxide	80	[40]
DAPT, nitric acid-phosphorous pentoxide	11	[40]
DADN, nitric acid, nitrogen pentoxide	81	[40]
DPT, nitric acid, ammonium nitrate, and PEG 200 ionic liquid	64	[37]
DADN or TAT, N ₂ O ₄ /HNO ₃ solution and nitric acid	87	[41]
Hexamine, glacial acetic acid, ammonium nitrate, nitric acid and acetic anhydride	80.4	[7]
Hexamine, acetic acid, acetic anhydride, boron tri-fluoride, diethyl ether, ammonium nitrate	90	[39]

2 Materials and Methods

Industrial grades of all materials were purchased from different chemical industries in Iran. These materials consisted of hexamine, ammonium nitrate with a purity of <98%, concentrated nitric acid 98%, glacial acetic acid 99%, acetic anhydride 99%, acetone 99% and nitric acid 65%. With regard to the density of nitric acid (1.51 g·mL⁻¹), it was possible to prepare a 47% solution of ammonium nitrate in nitric acid using ammonium nitrate (400 g) in nitric acid (300 mL). Since mixing ammonium nitrate with concentrated nitric acid is accompanied by the evolution of intense heat and the production of gas, mixing should be done with cooling. The melting points of the synthesized compounds were measured using a capillary melting point apparatus (model 600/12 H HUND). The purity of DPT was checked with high performance liquid chromatography (HPLC) (model SHIMADZU-LC6A and a wavelength of 300 nm). Elemental analysis (CHNO) was carried out using model GmbH, Vario EL III. ¹H NMR spectra were scanned at 400 MHz (model Bruker Ultrashield). The study of solid phases was performed with an X-ray diffraction device (XRD) (model D8ADVANCE-Bruker). The IR spectra were recorded on a model FT/IR-6300, JASCO Japan,

with the capability of measuring the absorption and transmission spectra within the spectral range 20-15000 cm^{-1} .

3 Experimental

3.1 DPT synthesis from hexamine

The DPT was synthesized according to the Bachmann route [18, 19, 33]. Two portions of 38% hexamine-acetic acid [36 mL each, containing hexamine (23.17 g, 0.165 mol) dissolved in acetic acid (36 mL, 0.631 mol)] and 47% $\text{NH}_4\text{NO}_3\text{-HNO}_3$ solution [17 mL, containing ammonium nitrate (22.7 g, 0.283 mol) dissolved in nitric acid (17 mL, 0.407 mol)] were prepared. Then, these solutions and 45 mL acetic anhydride were added simultaneously to the reaction solution inside the reactor over 18 min. The reaction mixture was stirred for a further 15 min at the same temperature in order to complete the reaction (shelf life). The reaction was stopped by means of an ice-water bath. The reaction product, which was cooled down to 20 °C, was immediately filtered off. The product obtained was washed with water several times. The acidity of the suspension was adjusted to pH = 6-7 (neutralized with 28% ammonia). The product was consistently obtained by this method, in about 77% (18.5 g) yield, with melting point 203-210 °C and purity over 95%.

3.2 Optimal method for increasing the production capacity of DPT to HMX (high capacity and desirable purity)

Acetic acid (35 mL), acetic anhydride (11 mL), and DPT (10.45 g) were added to the reactor, and a thermometer was placed inside. While stirring, the temperature of this mixture was adjusted to 49 ± 1 °C. After adjusting the temperature, $\text{NH}_4\text{NO}_3\text{-HNO}_3$ solution (8 mL) and acetic anhydride (12 mL) were added to the reactor over 20 min at a constant rate. Care should be taken to keep the temperature constant throughout the experiment. After termination of the reaction, the reaction mixture was stirred for a further 30 min. The mixture was poured into ice/water (250 g) and the product was filtered off under vacuum. The product obtained was thoroughly washed with water (500 mL). In order to remove linear nitramine impurities in the mixture, a mixture of acetic acid and water, in the ratio of 70 mL to 30 mL, was added and boiled within the range 90-100 °C for 45 min so that emission of the brown vapour resulting from the disintegration of the unstable linear nitramines was complete. Then, by adding ice/water (300 mL) to the container, its temperature was rapidly reduced. The product obtained was filtered off and washed thoroughly with water (1 L). The

product was dried at 70 °C for 24 h. After drying, 12.79 g of the product with a melting point of 285 °C was obtained.

3.3 Analysis and characterization of the synthesized HMX

The XRD technique was used to identify the nature of the synthesized HMX product. In addition, HPLC was employed to determine the purity of the HMX and to measure the amount of RDX impurity present in the samples. To perform the analysis, suitable conditions for the separation of RDX from HMX were obtained with the UV detector within a wavelength of 3000 nm. For this purpose, a mobile phase of water and methanol in a ratio of 1:1 and a flow of 1.0 mL·min⁻¹ was employed. The linear region of the calibration curve was obtained, with a regression index of 0.9994, for the analysis of the amount of RDX in the explosive material. To analyze the actual samples, samples of HMX (0.02 g) were dissolved in acetone (5 g), and after injection into the HPLC, the area under the RDX peak was recorded. The concentration of RDX in the sample was calculated from the calibration curve.

4 Results and Discussion

4.1 Presentation of the CCD for modelling and optimization of the reaction

A suitable design should be specified for all of the factors influencing the reaction. Then, the effect of these parameters on each other and the level of the selected factors should be determined. The general design can be presented at the end of all of these stages. The effective factors in the HMX synthesis, based on a specific quantity of DPT, were: (a) the amount of NH₄NO₃–HNO₃, (b) the amount of acetic acid (dilution of the system), (c) the anhydride present in the reactor (materials present in the reactor), (d) reaction temperature, (e) addition time or the input discharge of the raw materials to the reactor, (f) speed of stirring, (g) residence time and (h) the initial pH. Of these factors, four initial factors, viz. (a)–(d), influence the production capacity and efficiency. Thus, the other factors were considered constant with regard to the conditions and process for the industrial production of HMX. For example, a solution of NH₄NO₃–HNO₃, with equal percentage weights suitable for the operational conditions in industry, was prepared and the effect of different volumes of this solution on the nitration was investigated. The influencing factors, areas, and the related quantities are presented in Table S1. The levels selected for the time (α') when the model was obtained as a full doublet model according to Equation 1 [32]:

$$\alpha'=[2^k]^{1/4} \quad (1)$$

where k is the number of factors selected for the design of the experiments. The full doublet model is a model including three models of linear, linear and square, and linear and doublet interactions. The direct effects of each factor on the experimental process, the second order of the same factors as well as the mutual effect of each factor with the other factors were investigated. The CCD for the performance of the tests and experimental, as well as the modelled results, are presented in Tables S2 and S3.

4.2 HMX synthesis from DPT

The process of DPT nitration to HMX is rather exothermic. The reaction temperature should be precisely controlled because this material ($\text{NH}_4\text{NO}_3\text{-HNO}_3$ and hexamine-acetic acid solutions) and can be changed to different compositions under different reaction conditions. At the beginning of the addition of the raw materials to the suspension of DPT in acetic acid, the latter became a transparent solution. This can be attributed to the formation of the intermediate material 1-hydroxymethyl-3,5,7-trinitro-1,3,5,7-tetrazocane, and then to the formation of 1-acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazocane in the reaction environment [34]. 1-Acetoxymethyl-3,5,7-trinitro-1,3,5,7-tetrazocane is changed to HMX by nitration [34]. Analysis of the synthesized product, by XRD, HPLC, FT-IR, and ^1H NMR, confirmed the efficiency of the synthesis.

4.2.1 ^1H NMR

With regard to the structure drawn in Figure S1, HMX has one type of hydrogen and one single chemical shift at 6.02 ppm for the methylene protons; $\delta=6.02$ ppm (8H, singlet).

4.2.2 HPLC

The purity of the HMX was tested by HPLC with reverse phase micro C_{18} column and a mobile phase composed of methanol:water (50:50). At a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$, the chromatogram obtained for HMX exhibited one single peak at a residence time of 2.31 min, with purity greater than 98% for HMX. The chromatogram was in conformity with the reference spectrum [35].

The peak observed in point 4 and at residence time 5.8 min (Figure S2), is related to a negligible amount of RDX as an impurity. The peaks present in points of 2 and 3 are consistent with the solvent used.

4.2.3 FT-IR

The FT-IR spectrum of the synthesized HMX is shown in Figure S3. As indicated, the IR spectrum shows two specific peaks at 1542.77 cm^{-1} and 1263.15 cm^{-1} resulting from the symmetrical and asymmetrical stretching vibrations of the nitro group. Additionally, there is a small peak at 3050.83 cm^{-1} indicative of the symmetrical vibrations of the HMX methylene groups. β -HMX exhibits only one strong transmission peak in the fingerprint region, while α and γ -HMX have three weak transmission peaks in the fingerprint region [23]. One strong peak in 764.637 shown in Figure S3 shows that β -HMX was obtained by this method.

4.2.4 XRD

The XRD overlapped and pure diffraction patterns of the raw HMX that is crystallized in acetone solvent are shown in Figures S4 and S5, respectively. As shown, the raw HMX sample contains more β -HMX polymorph because the XRD diffraction pattern of the sample have more overlapping with the XRD diffraction pattern in a β -HMX sample. However, these samples contain the β -HMX polymorph and RDX as well. Figure S6 shows an industrial sample containing the β -HMX polymorph along with α -HMX polymorph and RDX whose crystalline image conforms to the XRD data with an hexagonal structure. Figure S7 shows the suggested HMX synthesis mechanism from DPT. As seen, acetic anhydride absorbs water and changes to acetic acid through acetolysis followed by hydrolysis. During this process, formaldehyde is also produced, which can be converted to hexamine by reacting with the ammonia present in the system. In turn, hexamine is nitrolyzed to produce DPT and subsequently HMX. The residence time not only allows complete DPT nitrolysis but also contributes to this issue. The reaction equation is given as follows [7]:



In general, the balanced equation for the production of HMX from DPT is:



The calculated efficiency observed in this research was based on this reaction while considering the change in the number of hexamine methylene groups to the product [36].

4.3 Efficiency behaviour modelling and HMX production capacity

4.3.1 Modelling and efficiency behaviour

Table S4 shows the coefficients of the parameters and quantities of the P-values related to the first model for predicting the production efficiency (PE) of HMX. Since a confidence level of 95% was considered for the construction of the model, the parameters containing P values greater than 0.05 were deleted. However, the mathematical relationship between PE and the different variables containing X_1 to X_4 are given as follows:

$$\text{PE} = 224.682 + 6.091 X_1 + 8.421 X_3 + 0.477 X_4 + 0.085 X_3^2 + 0.395 X_1X_2 + 0.118 X_2X_3 \quad (4)$$

Table S5 shows the P values for all of the factors in Equation 4 which are smaller than 0.05. Therefore, all of them have a significant effect on the production efficiency of HMX. The model has 4 first-order effects, 3 second-order effects, and 2 second-order interactions at the confidence level of 95%.

4.3.2 Behaviour modelling of the production capacity

Tables S6 and S7 show the initial and final coefficients of the parameters and P values related to the first model for the estimation of the production capacity (PC) of HMX and second-order combinations of four parameters. After deleting the factors which have no effect on the production capacity, a new model was derived:

$$\text{PC} = 47.5274 + 1.2417 X_1 + 1.5097 X_2 + 1.7608 X_3 + 0.0972 X_4 + 0.0179 X_2^2 + 0.179 X_3^2 + 0.0805 X_1X_2 + 0.0242 X_2X_3 \quad (5)$$

A linear correlation exists between the experimental results obtained by this test and the quantities predicted (fitted), as presented in Figure S8.

4.4 Prediction of optimal conditions by modelling

4.4.1 Presentation of suitable and optimal conditions for an increase in HMX production efficiency

The goal of optimization is to reach the maximum response [32], which is shown in Figure S9. As seen, the maximum efficiency is 69.9994 with a desirability degree (d) of 0.99998. To reach the efficiency of 69.9994 with regard to the optimal diagram plotted, the values of X_1 to X_4 were 8.276, 53 °C, 14.39 mL and 19.81 min, respectively. Moreover, the optimal temperature was 49.5 °C to 53 °C;

the addition time was in the range 14-18 min; the quantity of $\text{NH}_4\text{NO}_3\text{-HNO}_3$, was 8.27 mL; and the quantity of acetic anhydride was selected to be 14.39 mL.

4.4.2 Optimal instruction for the production of HMX with high efficiency from DPT

To study the degree of agreement between the theoretical values presented by the software and the experimental values at the optimal point of the parameters, an optimal method was selected among the tests performed and the purity of the HMX was specified. In this regard, to be sure of the conditions, the test was performed several times. The optimal method and its results are reported in Table 2 and compared with two previous studies [37, 38], where their experimental data were available. Care should be taken that the temperature is kept constant during the tests. Stirring was kept at a constant temperature for 30 min during the completion of the reaction. The reaction mixture was then poured into ice/water mixture (250 g), and the product was filtered off under vacuum. It was thoroughly washed with water (500 mL). In order to remove the linear nitramines impurities, the product mixture was added to a mixture of acetic acid and water (ratio of 70 mL to 30 mL) and boiled for 45 min at a temperature of 90-100 °C. The product was dried during 24 h to give pure HMX. Therefore, the efficiency was 64.29%.

Table 2. Comparison of the efficiency and production capacity of the current work with two methods mentioned in HMX synthesis

No.	DPT [g]	NH_4NO_3 [g]	HNO_3 [mL]	$\text{NH}_4\text{NO}_3\text{-HNO}_3$ [mL]	Ac_2O [mL]	AcOH [mL]	T [°C]	Efficiency	Production capacity [g/100mL]	Melting point [°C]	Ref.
1	5	-	-	4	17	35	52±1	74.61	10.93	279	[38]
2	2	1.9	9.21	-	46.2	-	60-65	61	11.15	-	[37]
3	10.45	7	5.2	9	12	35	51±1	72.09	20.24	285	This work

4.4.3 Presentation of suitable and optimal conditions for an increase in the HMX production capacity

We can determine the optimal values for the parameters to reach the maximum production capacity for HMX. The goal of the optimization was to reach the maximum response. The optimal values presented by the software [32] are shown in Figure S10. As indicated, the maximum production capacity was 19.51 with a desirability degree (d) of 0.813. Thus, the values of X_1 to X_4 were 7.750, 52.22 °C, 15 mL and 20 min, to reach a production capacity of 19.505 g/100 mL.

4.4.4 Optimal instruction for an increase in HMX production capacity from DPT

In order to investigate the degree of agreement between the theoretical production capacity presented by the software [32] and the experimental production capacity at the optimal point of the parameters, the following test was performed:

Acetic acid (35 mL), of acetic anhydride (12 mL), and of DPT (10.45 g) were added to the reactor and a thermometer was placed in the solution. The temperature of this mixture, which was being stirred, was adjusted to 51 ± 1 °C. Subsequently, 47% $\text{NH}_4\text{NO}_3\text{-HNO}_3$ (9 mL) and acetic anhydride (15 mL) were added to the reactor at a constant discharge rate over 20 min. The reaction mixture, while stirring, was kept at a constant temperature for a further 30 min to complete the reaction. The reaction mixture was then poured into ice/water mixture (250 g), and the separated product was filtered off under vacuum. It was dried at 70 °C for 24 h. The pure HMX efficiency and the production capacity were 72.09% and 20.24%, respectively.

4.5 Study of the effect of different factors on the HMX production efficiency

To increase the production capacity, efficiency, and HMX purity, we should produce the DPT intermediate with high efficiency and purity. For this purpose, the reaction conditions were directed towards producing DPT with higher efficiency and purity by studying, determining and optimization the effective factors in DPT production. The effects of each factor on the efficiency were studied by plotting their 2-D and 3-D images. The surface and contour plots were plotted by keeping two variables constant and changing the other two variables. The surface plots in these studies gave a method for the prediction of the value of efficiency for different values of the effective factors and the littoral diagrams contributed to the identification of the type of interactions among these factors.

Figures S11 to S18 show the contour plots for the efficiency and production capacity in terms of the different variables, and gave the following results:

(i) *The effect of reaction temperature on efficiency and HMX production capacity (Figures S11 and S12):* If initially acetylation and then nitration are performed for the change of DPT to HMX, a product with less impurities is produced. In other words, acetylation results in controlled nitration and becomes milder. When the mixture becomes colourless, in fact the intermediates between DPT and HMX, are acetylated compounds [23]. If acetylation occurs faster at the beginning of the reaction, the acetylated intermediate compounds are certainly formed faster.

(ii) *The effect of the amount of 47% $\text{NH}_4\text{NO}_3\text{--HNO}_3$ entering the reactor (Figures S13 and S14):* An increase up to the permitted limit improves the conditions for nitration, which leads to milder conditions for nitration and more efficient production, followed by high HMX production capacity. However, if the temperature becomes higher than the permitted limit, the nitration conditions become stronger and the synthesis of RDX from DPT becomes more likely than the synthesis of HMX. Thus, the efficiency and production capacity of the product is lowered.

(iii) *The effect of increased addition time of acetic anhydride on HMX production efficiency (Figures S15 and S16):* A reduction in the amount of acetic anhydride present in the reaction environment can decrease the purity, efficiency, and production capacity of the reaction.

(iv) *The effect of the acetic anhydride value on the efficiency and HMX production capacity (Figures S17 and S18):* Since dilution of the reaction reduces the speed of nitration at high values, it has a little negative effect on the efficiency. Due to an increase in the capacity volume, production is also reduced.

5 Conclusion

A new method was used in this research to optimize HMX synthesis from DPT starting material. During this optimization, it was specified that the factors influencing efficiency and production capacity could not be studied separately because these factors have interacting effects on each other. The CCD method was used to study these effects and to obtain an optimal point for the parameters.

Four factors, temperature, addition time of the starting materials, consumption of $\text{NH}_4\text{NO}_3\text{--HNO}_3$ and acetic anhydride were important parameters. Temperature and the quantity of $\text{NH}_4\text{NO}_3\text{--HNO}_3$ had the greatest effect on the efficiency. The optimal points offered by the software, were experimentally tested in the laboratory. Ultimately, HMX with an efficiency of 67.79% and with a production capacity of over 17.48% was achieved.

Supplementary material

Tables 1S to 7S and Figures 1S to 18S are given as supplementary material (SI), available at <http://www.wydawnictwa.ipo.waw.pl/CEJEM/contents/2016/vol-13-number-4.html>.

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