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Synthesis Optimization of High Purity HMX Using Polyphosphoric Acid by the Surface Response Method

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ABSTRACT

1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) is one of the most powerful explosives of which the purity may have a significant effect on increasing the performance of rocket engines. In this research, the synthesis of high purity HMX is presented using the nitration of 1,5-diacetyl-3,7-dinitrooctahydro-1,3,5,7-tetrazocine (DADN) with a mixture of nitric acid and polyphosphoric acid. The nitration parameters including temperature, time, and the concentration of nitric acid, and polyphosphoric acid were optimized for the desirable purity and efficiency using the response surface method and central composite method (CCD). Based on the optimization, HMX was obtained with a purity of 99% and an efficiency of 92.9% at a temperature of 70°C and the time duration of 70 minutes with a molar ratio of polyphosphoric acid to nitric acid of 1:1:6.

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1. Introduction

1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX) is known as one of the most powerful nitramine explosives, which has high density, high detonation rate and high potential for explosion [1,2]. HMX is the most powerful industrial non-nuclear explosive in the world. Nowadays, HMX is known as one of the most advanced and widely used explosives. With the progress and development of human knowledge, the need for this high-purity material has been increased in both the defense and non-defense industries. The Beckman method is the most common method of producing HMX. This method has disadvantages such as: the excessive use of acetic anhydride and acetic acid, difficult production steps and high cost, low purity of the product. These reasons have caused researchers to try to find new methods of HMX synthesis. [3]. In addition to Beckman's method, various methods have been used to synthesize HMX, of which all either had low purity or low efficiency. For example, the synthesis of HMX from 3,7-Diacetyl-1,3,5,7-Tetraazabicyclo[3.3.1] nonane (DAPT) is one

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of the used methods [2]. However, with the use of ultrasonic radiation, the reaction proceeds slowly and the efficiency of HMX synthesis will not exceed 67% [4]. On the other hand, DAPT can be converted to 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane (DADN), 1,5-diacetyl-3-nitroso-7-nitro-1,3,5,7-tetraazacyclocyanate (DANNO) and 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (TAT) [5]. Although the nitrolysis of DADN, DANNO or TAT can produce HMX with higher yields, vigorous conditions such as stronger nitration systems, higher reaction temperatures and longer reaction times are required [6]. Other nitration agents have similar problems too. For this reason, finding other nitration agents can be a vital parameter in the synthesis of this valuable compound. Accordingly, in this research, an attempt was made to consider a method for the synthesis of HMX with the ability of scaling-up and low cost. Therefore, in order to achieve a method to produce pure HMX, the following parameters should be considered: 1) choosing a method which does not have RDX as by-products; 2) selecting and optimizing stable tetrazonium derivatives suitable for the scale-up step 3) using suitable nitration agents to convert selected tetrazonium derivatives into HMX with high purity.

Nitric acid is the most well-known environment for nitration reactions, which generally facilitates the conditions for nitration by adding a series of reagents. Today, N_2O_5 is one of the best reagents used in nitration reactions, but due to the lack of its commercial access, the methods in which N_2O_5 can be produced during the reaction are generally used. A common method is the use of strong water-absorbing agents such as phosphorus pentoxide or polyphosphoric acid, which have the ability of absorbing water from nitric acid [5,7,8]. This nitrolysis system is the most promising among the nitration systems. Polyphosphoric acid (PPA) and hypophosphoric acid ($H_4P_2O_6$) act as good dehydrating agents in the presence of HNO_3 and absorb water for N_2O_5, which is the best reagent used in nitration reactions [9,10].

In the present work, the synthesis of HMX with high purity and efficiency was performed using DADN and polyphosphoric acid. The factors affecting nitration were also optimized with the Minitab 18 software using the response surface methodology and central composite design (CCD) (Figure 1).

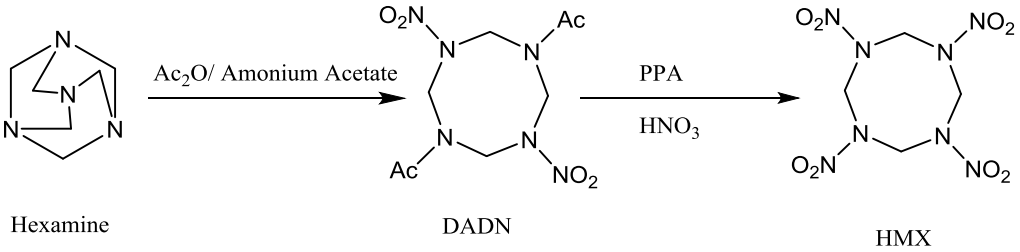

Figure 1. Synthesis of HMX from DADN

2. Materials and methods

2.1. Materials and equipment

Hexamine (Merck, 99%), ammonium acetate (Merck, 99%), acetic anhydride (99%), sulfuric acid (98%, Dr Mojallali), nitric acid (98%) and polyphosphoric acid (Dr Mojallali) were purchased and were used without purification. The equipment used to identify the synthesized compounds is the melting point determination device (Electro thermal). The purity of the synthesized substances was determined using an HPLC equipped with a UV-Vis detector (Water 486) with a C18 column.

2.2. Synthesis of DADN

DADN was synthesized according to the reported procedure [9]. 14 g of hexamine (0.1 mol), 6.2 g of ammonium acetate (0.08 mol) and 7 mL of distilled water were added to a 100 ml three-necked flask equipped with a stirrer and thermometer. 30.6 g of acetic anhydride (0.3 mol) was drop by drop added to the mixture while stirring for 60 minutes at a temperature of 5-10 °C. Then the resulting mixture was stirred for 30 minutes at 10 °C. Then, the mixture of the previous step was drop by drop added to the contents of a three-necked flask equipped with a stirrer, condenser and a thermometer, which contained 63 g of nitric acid (98%) (1 mol) and 221 g of sulfuric acid (98%) (2.2 mol), during 80 minutes and at a temperature of 20-18 °C. Then the resulting mixture was stirred for 20-30 minutes at 30 °C and added to 1000 g of crushed ice. The resulting mixture was filtered and 27 g of DADN (0.093 mol) with 95% efficiency and the melting point of 265°C was obtained.

2.3. HMX synthesis

HMX was synthesized according to the reported procedure [9]. 18 g of fuming nitric acid (0.286 mol) and 30 g of polyphosphoric acid (0.089 mol) were added to a three-necked flask equipped with a condenser, stirrer, and thermometer. Then, 1.5 g of DADN (0.005 mol) was added at room temperature gradually. Then, the reaction temperature was raised up to 70°C and stirred at the same temperature for 70 minutes. The prepared mixture was added to 100 g of water-ice mixture. The mixture was washed with 50 ml of distilled water for 5 times and then dried at 70°C. Finally, 1.423 g of HMX (0.0048 mol) was obtained with 92.9% efficiency and 99% purity.

3. Results and Discussion:

According to performed researches, a number of suitable nitration catalysts and agents have been identified which have the ability to dehydrate or nitrify in the synthesis of HMX from DADN. It is cleared that the desired reagent must have the necessary stability and efficiency in the nitric acid medium as a nitration medium. Based on the mentioned qualifications, a series of compounds was selected and the initial reactions have been carried out to select the best reagent [5]. The PPA reagent has two major advantages over the other reagents in the nitration reaction of DADN to HMX, which produces a pure product with higher efficiency.

The Minitab18 software and the response surface method can make optimization easier by reducing the number of experiments [11-13]. In this research, Pure HMX was synthesized as a cyclic nitramine, and the synthesis method of HMX was studied and optimized by examining the effective parameters such as temperature, time, and the concentrations of nitric acid and PPA. This optimization was done by the central composite design method and four input factors. Based on the experimental design, 31 tests were carried out for optimization.

3.1. Analysis of the optimization outputs of the HMX synthesis from DADN by the CCD method

Experimental design is one of the best methods in optimizing the synthesis of organic compounds. Response surface, Taguchi, etc. are among the best methods that can significantly save money and time. Meanwhile, the response surface method is superior compared to other methods due to the better analysis and outputs. The response surface method itself has two central composite design (CCD) and Box-Behnken methods, from which the central composite

method is more accurate and precise due to the larger number of tests. For this reason, response surface and central composite design methods were used for optimization.

According to Table 1, the experiment was designed by the CCD method with four input factors including nitric acid, PPA, temperature and time in two upper and lower limits.

Table 1
Factors and optimization levels for the synthesis of HMX from DADN by CCD method

	Level	
Factors	**Lower limit**	**Higher limit**
HNO_3 (g)	7.5	18
PPA (g)	18	30
Temperature (°C)	70	30
Time (min)	70	40

In Table 2, the experiments resulted from the optimization and the results are shown.

Table 2
Optimization experiments and the results obtained by the CCD method for the synthesis of HMX from DADN

Run	HNO_3 (g)	PPA (g)	Temperature (°C)	Time (min)	Yield (%)	Purity (%)
1	7.5	30	70	40	89.59	99
2	18	30	70	40	87.29	98
3	12.75	24	50	25	79.49	96
4	18	30	70	70	92.9	99
5	18	18	70	40	84.5	99
6	12.75	24	50	55	67	87
7	7.5	18	30	70	63.45	99
8	12.75	24	50	85	86.15	96
9	18	18	30	70	73.28	99
10	18	18	70	70	88.45	99
11	18	30	30	70	84.9	99
12	12.75	24	50	55	68.43	87
13	12.75	24	50	55	67.79	87
14	23.25	24	50	55	85.46	96
15	7.5	30	30	70	79.62	99
16	18	18	30	40	69.5	99
17	12.75	24	10	55	63.2	99
18	18	30	30	40	82.66	99
19	2.25	24	50	55	78.49	95
20	7.5	18	70	70	87.42	99
21	12.75	24	50	55	66.83	87
22	7.5	18	70	40	83.23	96
23	12.75	24	50	55	66.63	87
24	12.75	36	50	55	85.65	94
25	7.5	30	30	40	78.95	99
26	12.75	24	90	55	0	0
27	12.75	12	50	55	67.98	93

28	7.5	18	30	40	61.87	99
29	12.75	24	50	55	67.79	87
30	7.5	30	70	70	90	99
31	12.75	24	50	55	65.93	87

The results of the optimization of the synthesis of HMX from DADN are reported in the form of graphs in the CCD method. The normal plot related to efficiency and purity have been shown in Figure 2, which shows an acceptable agreement between the proposed method and the tests performed in the CCD method.

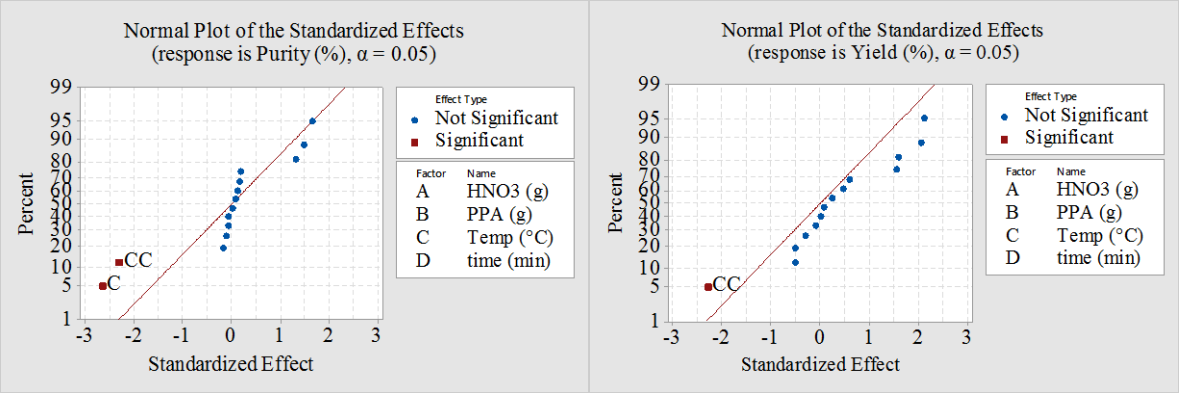

Figure 2. Normal plot related to the efficiency and purity of the synthesis of HMX from DADN

Also, Figure 3 shows the Pareto chart, which is related to efficiency and purity, in a way that temperature has the greatest effect on both purity and efficiency.

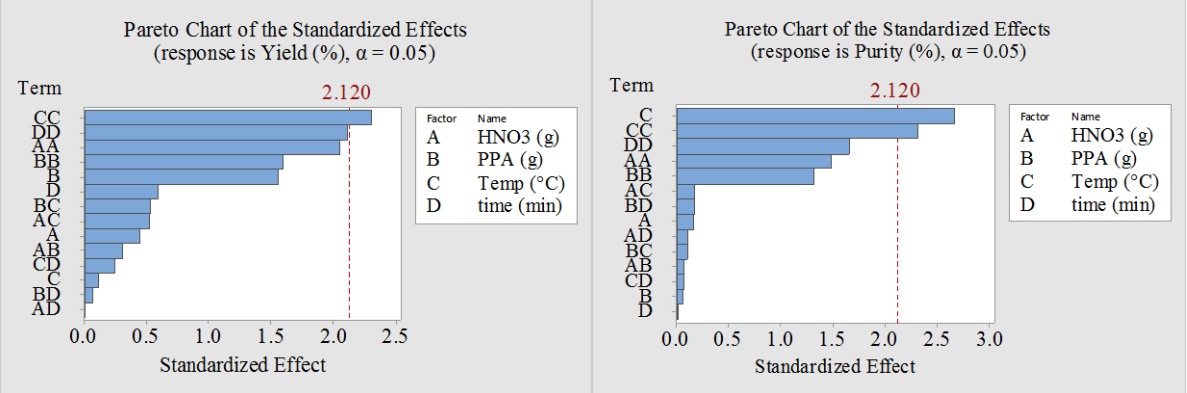

Figure 3. Pareto chart related to the efficiency and purity of the synthesis of HMX synthesis from DADN

Figure 4, shows the effect of different factors on efficiency. In Figure 4, Graph A) HNO_3, shows the effect of the concentration of nitric acid on the reaction efficiency. By increasing the amount of nitric acid from 12.75 to 18 g, the reaction efficiency also increases. As it can be seen in Graph B) PPA, the reaction efficiency also increases with the increase of the concentration of PPA from 18 to 30. Graph C) temperature shows the effect of temperature in which the efficiency of the reaction also increases with the increase in temperature from 30 to 70 °C, and Graph C) temperature has a regular upward trend. As it can be seen in Graph D) time, the efficiency decreases with the increase of time from 40 to 55 minutes, but it increases with the increase of time from 55 to 70 minutes. This event is characterized by a

positive coefficient and a low numerical value of the D factor in the Pareto chart.

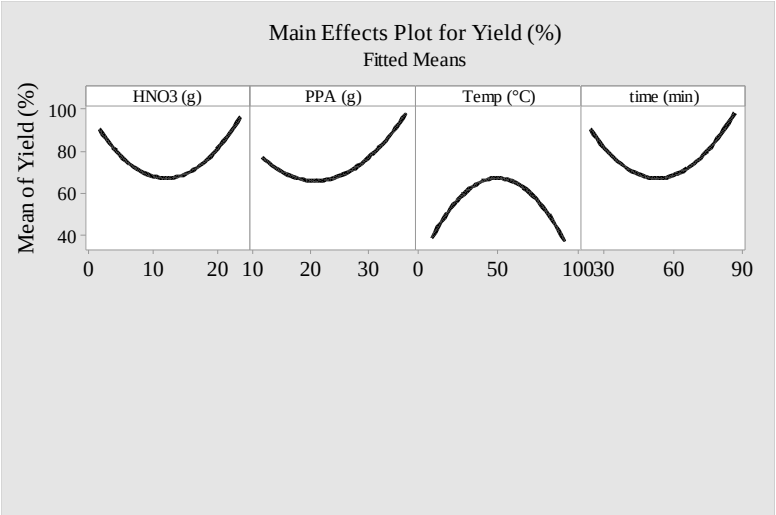

Figure 4. Effect of different factors on the yield in the synthesis of HMX from DADN: A) HNO3, B) PPA, C) Temperature, and D) time

Figure 5 shows the effect of the factors of the concentrations of nitric acid and PPA, temperature, and time on the purity percentage of the product. Graphs A) HNO_3, B) PPA, C) temperature, and D) time indicate that the curves follow a descending and ascending trend. The results show that at concentrations of above 10 g of nitric acid and 20 g PPA the curve is ascending and at temperatures of up to 55 °C and the times of more than 60 minutes, the graphs affecting purity are ascending.

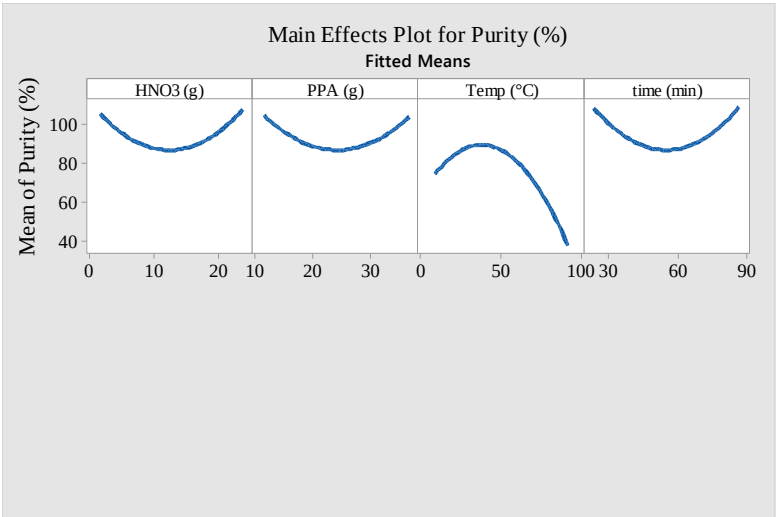

Figure 5. Effect of different factors on purity in the synthesis of HMX from DADN: A) HNO3, B) PPA, C) Temperature, and D) time

Figure 6 shows the simultaneous effects of the concentrations of nitric acid and PPA on efficiency and purity. The highest efficiency and purity were observed in the concentrations of greater than 20 g of nitric acid and greater than 30 g of PPA.

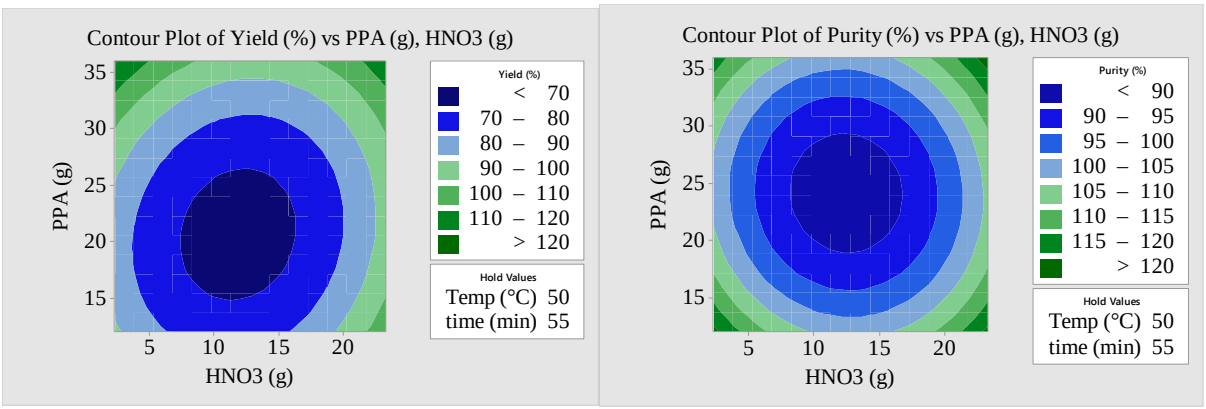

Figure 6. Two-dimensional diagram of the simultaneous effects of nitric acid and the PPA concentration on efficiency and purity in the synthesis of HMX from DADN

Figure 7 shows the simultaneous effects of temperature and the concentration of nitric acid on efficiency and purity. As it can be seen in Figure 7, the highest efficiency and purity were observed in the concentrations of nitric acid of more than 20 g and the temperature range of 40 to 70 °C.

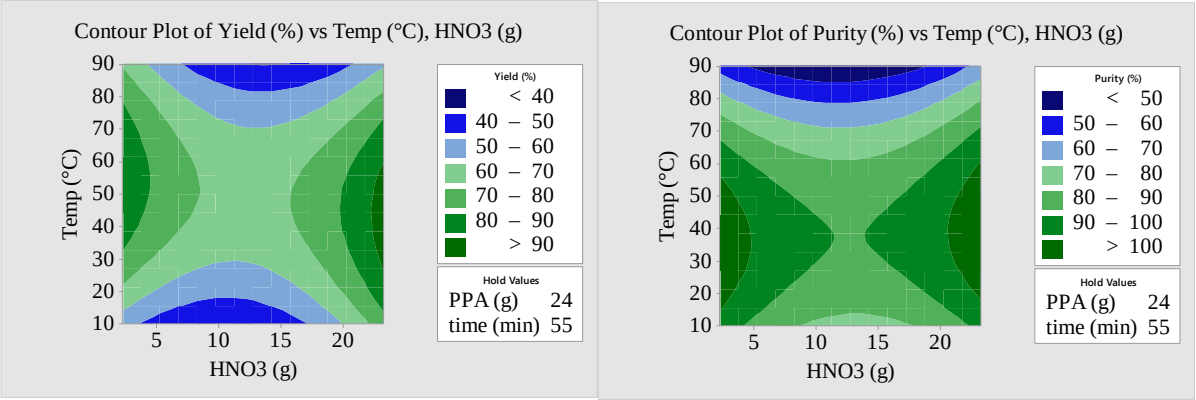

Figure 7. Two-dimensional diagram of the simultaneous effects of the concentration of nitric acid and temperature on efficiency and purity in the synthesis of HMX from DADN

Figure 8 illustrates the three-dimensional diagram of the simultaneous effects of the two factors of the concentrations of nitric acid and PPA on efficiency and purity. The highest efficiency and purity were observed in the concentrations of greater than 20 g of nitric acid and greater than 20-30 g of PPA.

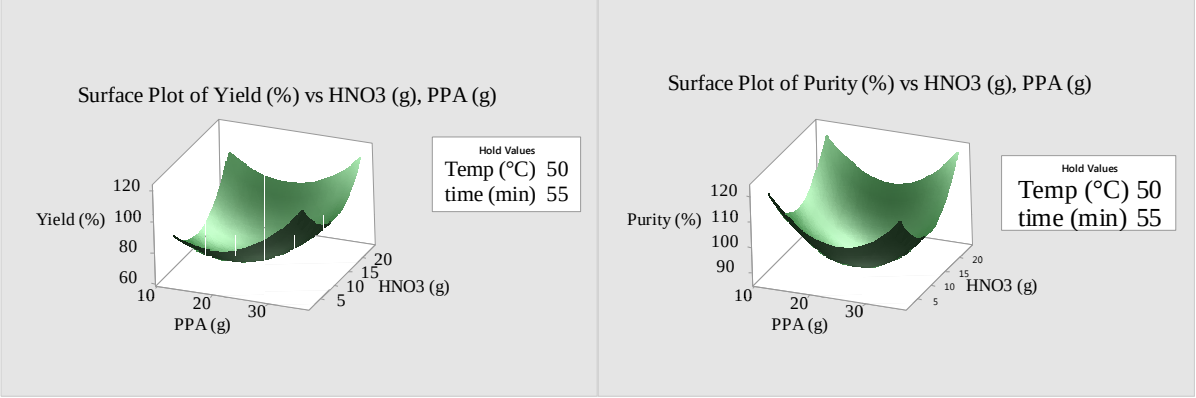

Figure 8. Three-dimensional diagram of the simultaneous effects of the concentrations of nitric acid and PPA on efficiency and purity in the synthesis of HMX from DADN

Figure 9 shows the three-dimensional diagram of the simultaneous effects of temperature and the concentration of nitric acid on efficiency and purity. As it can be seen, the highest efficiency and purity were observed in the concentration more than 20 g of nitric acid and temperatures of 40 to 70 °C.

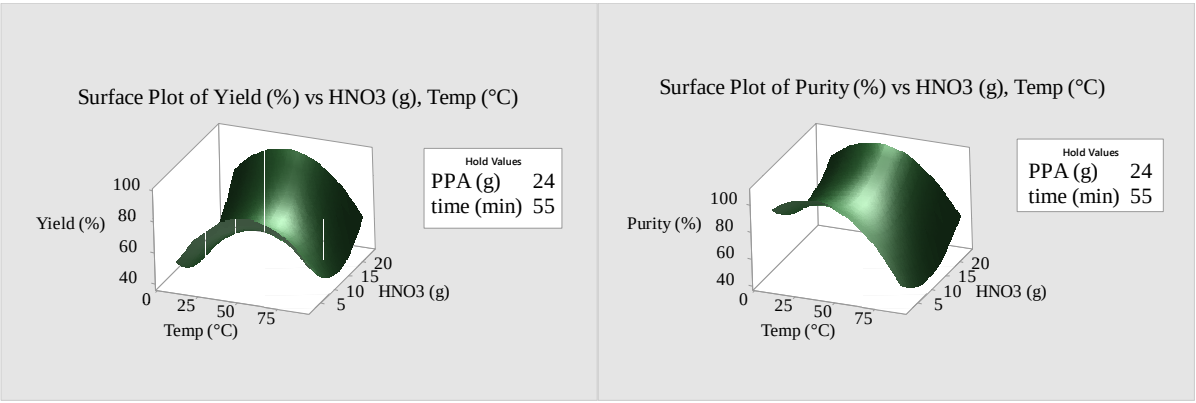

Figure 9. Three-dimensional diagram of the simultaneous effects of the concentration of nitric acid and temperature on efficiency and purity in the synthesis of HMX from DADN

Figure 10 shows the three-dimensional diagram of the effect of two factors, the concentration of nitric acid and time on yield and purity. The highest yield and purity were observed at a concentration of 20 g of nitric acid and after more than 60 minutes from the start of the reaction.

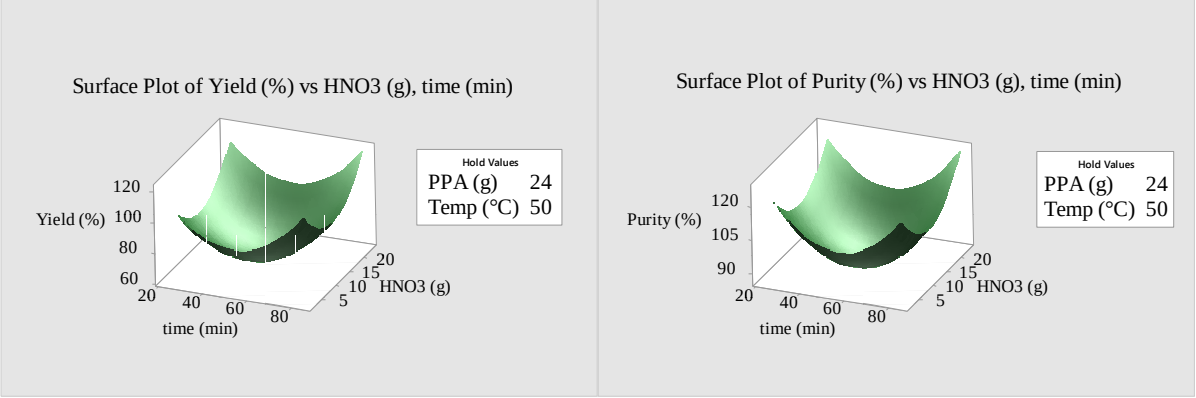

Figure 10. Three-dimensional diagram of the simultaneous effects of the concentration of nitric acid and time on efficiency and purity in the synthesis of HMX from DADN

Figure 11 shows the effect of the concentration of PPA and temperature on yield and purity respectively. The highest yield and purity were observed at a concentration of 30 g of PPA and a temperature in the range of 40-70 °C.

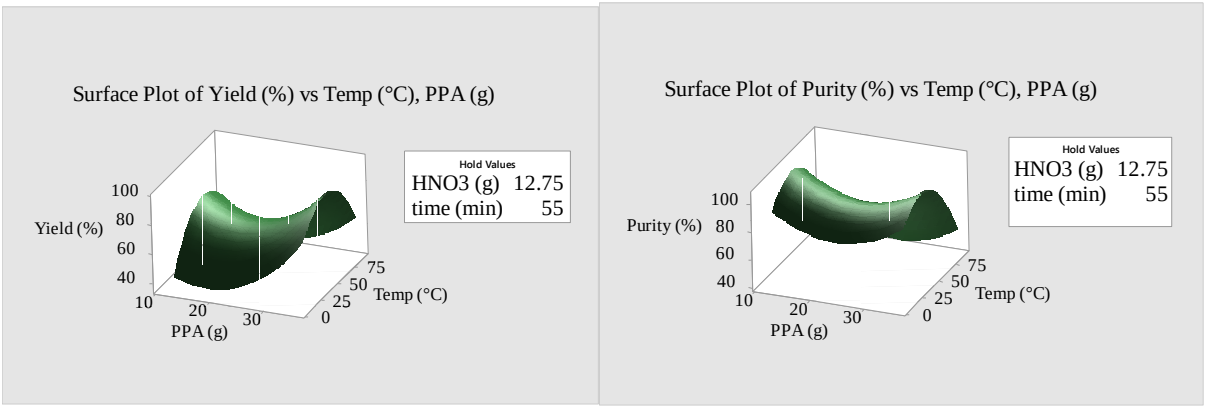

Figure 11. Three-dimensional diagram of the simultaneous effects of the concentration of PPA and temperature on efficiency and purity in the synthesis of HMX from DADN

Finally, with the help of software and according to the results of CCD, the optimal conditions can be predicted, which are shown in Figure 12.

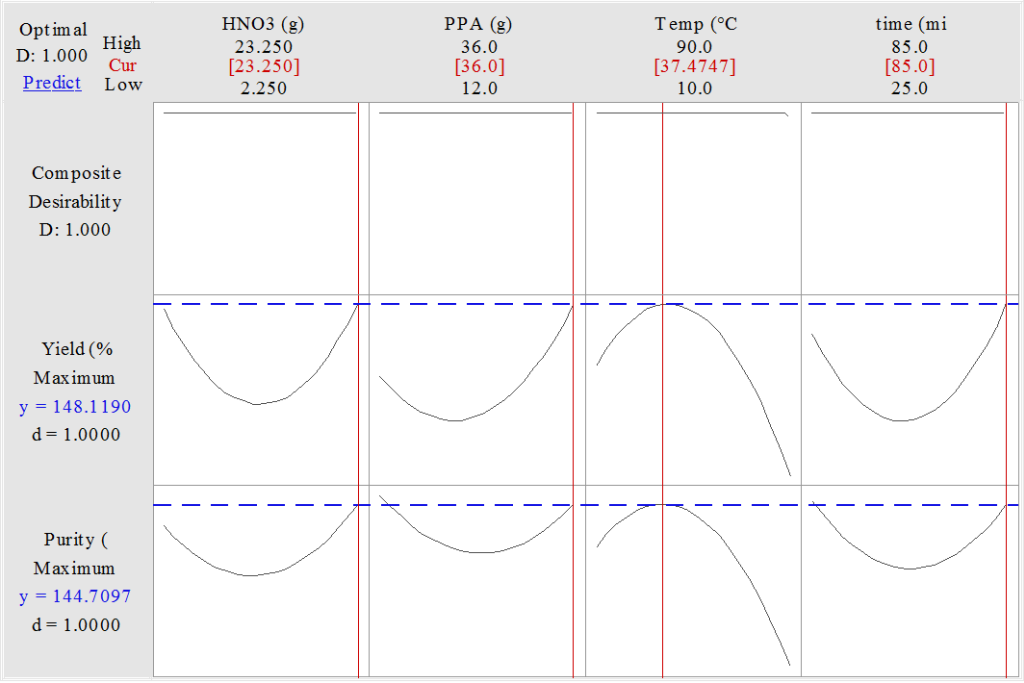

Figure 12. Prediction curves of the optimal conditions for the synthesis of HMX from DADN by CCD method

3.2. Determination the purity of HMX by HPLC

The use of the HPLC analysis is one of the best methods to determine the purity of organic materials. Figure 13 shows the HPLC curve of the HMX sample. As shown in Figure 13, the synthesized sample has a purity of more than 99%. The HPLC analysis showed that by using polyphosphoric acid, HMX with high purity can be synthesized.

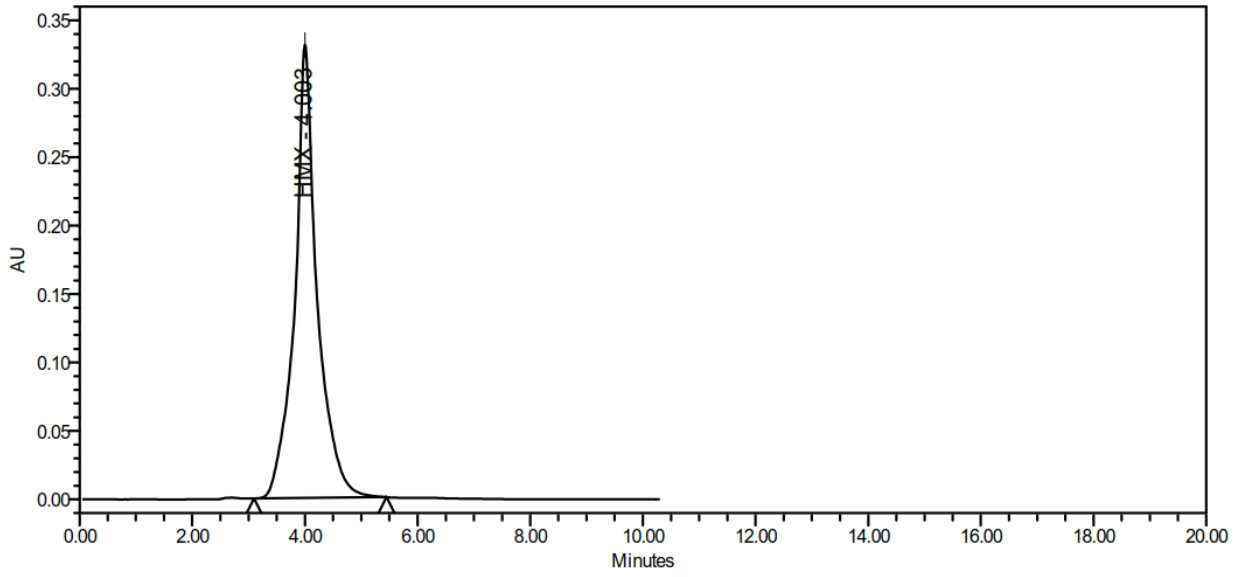

Figure 13. HPLC curve of HMX synthesized using polyphosphoric acid

4. Conclusion

HMX is an energetic and efficient nitramine with high performance in engines and PBXs. The purity of explosives can have a significant impact on their performance and application, and obtaining high purity products is always a

challenge for researchers. Polyphosphoric acid along with nitric acid is an important nitration agent for the conversion of DADN to HMX. The results indicate that PPA has two major advantages over other reagents in the nitration reaction of DADN to HMX, which produces a pure product with higher efficiency, while in other nitration agents, both of these advantages cannot be achieved at the same time. The response surface method can make it easier to achieve this goal by reducing costs and time. In this research, HMX with high purity and high efficiency was obtained by optimizing various factors using the central composite method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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