Research on optimizing the synthesis of ammonium dinitramide

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ABSTRACT

Ammonium dinitramide (ADN) is one of the potential oxidants in solid propellant formulations because it is environmentally friendly, has a high specific impulse, and has minimum signature exhaust gases. ADN was synthesized through the nitration reaction of potassium sulfamate salt with a mixture of sulfuric acid and nitric acid. The optimal conditions for the synthesis were studied, such as the ratio of components, reaction temperature, and reaction time. Specifically, the nitration reaction temperature was -40 ^oC, the ntration reaction time was 30 minutes, the molar ratio of potassium sulfamate, sulfuric acid, and nitric acid was 1, 2.5, and 9, respectively, and the molar ratio of potassium dinitramide to ammonium sulfate of 1: 1.1.

Keywords: Ammonium dinitramide; Potassium dinitramide; ADN; KDN; KS.

1. INTRODUCTION

Ammonium dinitramide (ADN), $NH_4N(NO_2)_2$, is a relatively newly discovered energetic ionic salt, which is of considerable interest as a potential eco-friendly oxidizing component of the future solid propellant formulation. On the other hand, ammonium perchlorate (AP) is the standard, widely used oxidizer in composite solid propellants. The disadvantage of AP is that its chlorinated exhaust products are harmful to the environment and produce a distinct signature behind missiles that can be easily detected. In addition, perchlorate may cause thyroid cancer by contaminating soil and water [1]. AP produces the toxic HCl acidic plume (generated during AP combustion), an acid known to be detrimental to the earth's ozone layer [2].

ADN mainly consists of nitrogen (N), oxygen (O), and hydrogen (H) in its molecular structure. Hence, the combustion products of ADN are harmless to the environment. Further, the presence of dinitramide anion [$N(NO_2)_2^-$] imparts high density, high heat of formation, high oxygen balance, and high oxygen content. Therefore, ADN is one of the capable oxidizers with high specific impulse (Isp) and high burning rate [3, 4]. From the above issues, ADN has thus been considered a potential replacement oxidizer for AP in propellant formulations. Thus, ADN has created significant interest in recent years. However, synthesizing energetic, halogen-free materials like ADN in high yield and purity is one of the challenging tasks.

There are many ways of synthesizing ADN, but the synthesis method through the intermediate compound is potassium dinitramide (KDN, $KN(NO_2)_2$) for high efficiency, convenience, and economic savings [5, 6]. This way, KDN is synthesized from the nitration of potassium sulfamate salt with a mixture of sulfuric acid and nitric acid at temperatures lower than -25 ^oC. The reactions take place according to the following equation:

$$KOH + H_2NSO_3H \longrightarrow K[NH_2SO_3] + H_2O$$

$$KSO_3 + NH_2 + HNO_3 \xrightarrow[< -25^oC]{H_2SO_4} HN(NO_2)_2 + KHSO_4 + H_2O$$

$$HN(NO_2)_2 + KHSO_4 + 3KOH \xrightarrow[< -10^oC]{} 2KN(NO_2)_2 + K_2SO_4 + 3H_2O$$

$$2KN(NO_2)_2 + (NH_4)_2SO_4 \longrightarrow NH_4N(NO_2)_2 + K_2SO_4$$

In this paper, we studied the modulation of ADN under domestic conditions. The research results aim to establish the optimal synthesis process conditions for the highest performance under laboratory conditions.

2. EXPERIMENTAL SECTION

2.1. Materials

The chemicals used include sulfamic acid, potassium hydroxide, ethanol, sulfuric acid, fuming nitric acid, ammonium sulfate, isopropanol, and acetone. All chemicals used were of AR grade.

2.2. Equipments and tools

IKA's reactor system consists of a double walled reactor vessel made from SUS316 stainless steel, connected to a Julabo deep negative cooling system to regulate temperature (figure 1); Heidolp vacuum rotary evaporator; Infrared spectrometer: Perkin Elmer's FT-IR Spectrum Two; Ultraviolet-Visible (UV-Vis) spectrophotometer: Perkin Elmer Lambda 365; Nuclear magnetic resonance (NMR) spectrometer: Brucker Avance 600 MHz spectrometers; X-ray diffraction spectrometer: Panalytical X'pert Pro MRD.

Figure 1. *IKA's reactor system.*

2.3. Analytical methods

2.3.1. FTIR spectroscopy method

The FTIR spectroscopy method was used to determine the characteristic functional groups of the synthesized products. Synthetic products were mixed with KBr, compressed into pellets, and measured on a Perkin Elmer FT-IR Spectrum Two infrared spectrometer.

2.3.2. UV-Vis spectroscopy method

The UV-Vis spectroscopy method was used to determine the characteristic wavelengths of the ADN product. The ADN synthesis product was dissolved in water at a concentration of 10 mg/l and measured on a UV-Vis spectrophotometer Perkin Elmer Lambda 365.

2.3.3. NMR spectroscopy method

The NMR spectroscopy method was used to determine the structure of the synthesized compounds. ^{1}H NMR spectra: δ (H) are given in ppm relative to tetramethylsilane (TMS), using δ (acetone-d_6) = 2.05 ppm as the internal reference.

2.3.4. Powder X-ray diffraction

The powder X-ray diffraction (PXRD) patterns of ADN and KDN were determined based on Cu-Kα radiation using a Panalytical X'pert Pro MRD, which operated at 40 kV and 35mA. The data of samples were collected at a scan rate of 0.5 s per step over the range of 10°–80° (step size: 0.03°).

2.4. Preparation of potassium sulfamate (KS)

100 g of sulfamic acid and 50 ml of water were suspended in a 500 ml beaker. 60 g of potassium hydroxide was dissolved in 50 ml of water. Then the potassium hydroxide solution was added slowly to the beaker containing sulfamic acid and the suspension until pH = 7 was reached. The solution was then poured into a beaker containing 100 ml of ethanol. A white precipitate appeared and was filtered off with a Buchner funnel, washed with alcohol and dried at 70 °C to obtain a white salt (KS). After drying, the salt was ground, and crushed into a fine powder in a porcelain mortar. M.p: 218.4 - 220 ^{o}C, yield: 95.7%.

2.5. Preparation of potassium dinitramide (KDN)

110 ml of fuming nitric acid (98%) and 40 ml of sulfuric acid (98%) were placed into the IKA reactor system reactor vessel. As soon as the reaction vessel temperature reached -40 ^{o}C, 40 g of potassium sulfamate was placed slowly into the acid mixture for 15 minutes. After adding the potassium sulfamate, stir the mixture vigorously for 30 minutes. The mixture's viscosity increased as the reaction occurred, and a white precipitate appeared. The reaction mixture was then poured into a beaker containing 400 g of finely ground ice. The reaction mixture was neutralized by slowly adding a solution of potassium hydroxide (50%) to maintain the mass reaction temperature between -10 ^{o}C and 0 °C. When approaching the neutral point, the color of the mixture turned into a specific yellow-green color. When the pH of the reaction solution reached the point between 7 and 8, the neutralization process stopped. The formed precipitate was then filtered off with a Buchner funnel and washed with 80 ml of water. The filtered solution was then evaporated to a quarter of its volume by the evaporator and was allowed to cool to room temperature. The precipitated salts were filtered off and washed with 50 ml of water. The filtrate was evaporated to dryness to obtain a solid mixture. The mixture of these salts was extracted with 150 ml of acetone. The extract was evaporated using a rotary evaporator until obtaining a pale-yellow solid (KDN). The obtained KDN was dried at 60 ^{o}C to constant weight. Mp: 128.1 - 129.3 ^{o}C, yield: 50.4%.

2.6. Synthesis of ammonium dinitramide (ADN)

10 g of potassium dinitramide and 11.5 g of ammonium sulfate were each dissolved separately into 10 ml of water. The solutions were mixed and stirred for 30 minutes. 100 ml of isopropanol was added to the mixture, then a white precipitate appeared and was filtered off with a glass funnel. The filtrate was evaporated on a rotary vacuum evaporator until a white solid (ADN) was obtained. This solid was dried at 50 ^{o}C until the mass remained constant. Mp: 92.1 - 93.5 ^{o}C, yield: 92.1%.

3. RESULTS AND DISCUSSION

3.1. Effect of reaction temperature on KDN synthesis yield

To determine the optimum temperature during the nitration of potassium sulfamate with a mixture of nitric and sulfuric acids. The research team performed the nitration reaction at different temperatures in a reaction time of 30 minutes. The results of the dependence of KDN yield on reaction temperature are presented in table 1 and figure 2.

Table 1. *The dependence of KDN yield on reaction temperature.*

Reaction temperature, ^{o}C	-20 ^{o}C	-30 ^{o}C	-35 ^{o}C	-40 ^{o}C	-45 ^{o}C	-50 ^{o}C
Yield, %	10.1	30.3	40.6	50.4	35.5	20.5

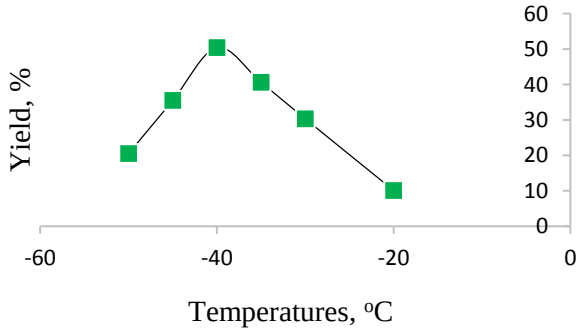

Figure 2. *The dependence of KDN yield on reaction temperature.*

It can be seen that the reaction efficiency was highest at -40 ^{o}C (figure 2 and table 1). This

can be explained as follows: during the process, two competing exothermic reactions occurred, namely the nitration of potassium sulfamate and the decomposition of the product. While conducting the reaction at -20 ^{o}C, the nitration reaction occurred quickly, but the product also decomposed fast, so the synthesis efficiency was very low. According to some studies, the decomposition temperature of the product occurred rapidly at temperatures higher than -25 ^{o}C [3]. Therefore, the yield at -30 ^{o}C was lower than at -40 ^{o}C, because the decomposition of the product occurred faster. At -50 °C, the product was also stable. However, the yield was much lower because the low temperature led to the high viscosity of the reaction mixture, thus causing difficulty separating the heat generated in the reaction [5]. This caused local overheating of the reaction mixture and rapid decomposition of the products.

3.2. Effect of reaction time on KDN synthesis efficiency

The nitration process's reaction time was calculated from when all the potassium sulfamate was added to the acid mixture. To optimize the reaction time, the authors carried out the nitration reaction at -40 ^{o}C and maintained the reaction for 5 minutes, 15 minutes, 30 minutes, 45 minutes, and 60 minutes. The results are shown in table 2 and figure 3.

Table 2. *The dependence of KDN yield on reaction time.*

Reaction time, min	5	15	30	45	60
Yield, %	15.3	30.6	50.4	45.2	40.7

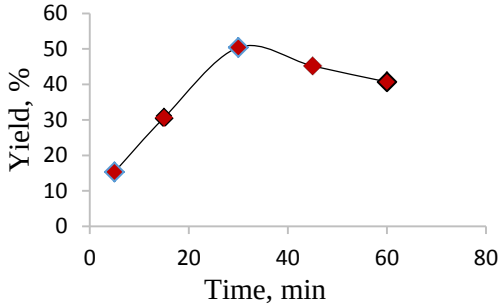

Figure 3. *The dependence of KDN yield on reaction time.*

We see that the highest efficiency achieved was 50.4%, with a reaction time of 30 minutes. When the reaction time was increased from 5 minutes to 30 minutes, the reaction efficiency increased because the nitration process took place completely. At -40 ^{o}C, the product decomposition process was slow, so when the nitration reaction occurred utterly, the product decomposition reaction started to take place strongly. As a result, the yield began to decrease when the reaction time was increased to more than 30 minutes. This decrease was entirely consistent with the effect of temperature on the synthesis performance.

3.3. Study on the effect of the ratio of acid mixture on the synthesis efficiency of KDN

The nitration of potassium sulfamate is the crucial stage in preparing potassium dinitramide. The nitration agent for KDN synthesis is a mixture of sulfuric acid and nitric acid, and the nitration mechanism of acidic mixtures is due to the formation of nitronium ions. The formation of these nitronium ions depends on the amount of sulfuric acid and nitric acid. Therefore, the nitration step was modified by varying the quantity and ratio of the acids used. Based on some published documents [5, 6], the team fixed the volume ratio of the sulfuric acid to nitric acid of 1: 2.75 ($nHNO_3$: nH_2SO_4 = 3.6 : 1) and varied the mass ratio of the acid mixture to KS to evaluate the effect of the ratio of components on the KDN synthesis efficiency. The results are presented in figure 4.

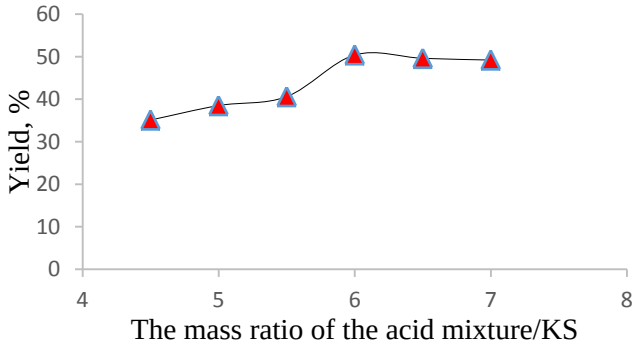

Figure 4. *The dependence of KDN yield on quantity of acid mixture.*

From the data in figure 4, we found that when the mass ratio of acid mixture to potassium sulfamate was raised from 4.5 to 6, the reaction efficiency increased from 35.1% to 50.4%. However, the efficiency was almost unchanged when increasing acid mixture. From here, it can be seen that the excess amount of acid mixture did not significantly affect efficiency. However, when the quality of acid mixture decreased to 25%, the efficiency decreased by 15.3%.

The quantity of sulfuric acid and its effect on the nitration yield at a constant molar ratio of potassium sulfamate to nitric acid ($nHNO_3$: nKS = 9 : 1) was also studied. The results of these measurements are shown in figure 5.

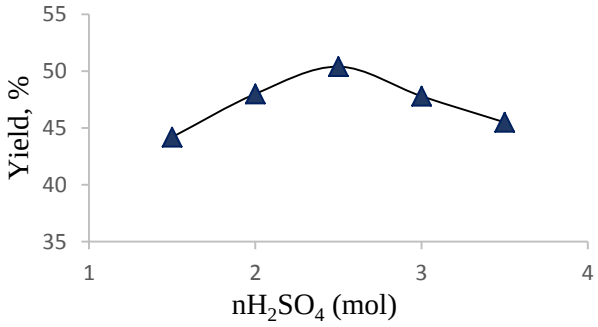

Figure 5. *The effect of sulfuric acid quantity on the yield nitration.*

The highest yield was noted with moles of sulfuric acid of 2.5 mol. When reducing the amount of sulfuric acid, the activity of the nitrate mixture was reduced, leading to a lower nitration efficiency. Conversely, a large amount of sulfuric acid also adversely affected the nitration performance because it may have increased the mixture's viscosity at low temperatures. This led to an increase in the local temperature of the reaction mixture. This increase caused the decomposition of the product to take place rapidly. Therefore, we determined that the optimal molar ratio of potassium sulfamate to sulfuric acid to nitric acid of 1 : 2.5 : 9. On the other hand, a lowered sulfuric acid quantity reduced the waste potassium sulfate formed and the amount of potassium hydroxide used to neutralize.

3.4. Study on the effect of the ratio of components on the synthesis efficiency of ADN

At room temperature, ADN was obtained from KDN and ammonium sulfate by cation exchange. To study the effect of the ratio of components on the synthesis efficiency of ADN, we carried out many reactions with the change in the molar ratio of KDN to $(NH_4)_2SO_4$. The results of the dependence of ADN yield on the ratio of components are presented in figure 6.

It was found that the reaction yield was not significantly affected by increasing the molar ratio of $(NH_4)_2SO_4$ to KDN by more than 1 (figure 6). Moreover, more unwanted products, such as

potassium sulfate, were created when increasing the amount of ammonium sulfate. Therefore, the optimal molar ratio of $(NH_4)_2SO_4$ to KS for the ADN synthesis reaction was 1.1.

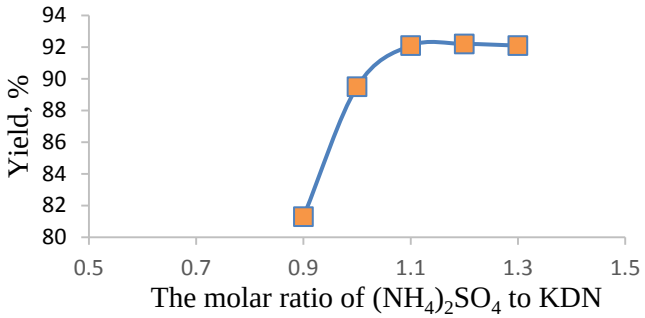

Figure 6. *The dependence of ADN yield on the ratio of components.*

3.5. Features of the product of KDN, ADN synthesis

The synthesis product (ADN) is a white solid with a melting point of 92.1 - 93.5 ^oC and a density of 1.82 g/cm^3. The synthesized products were dried and measured by FTIR, UV-Vis, ^1H NMR spectra and XRD pattern.

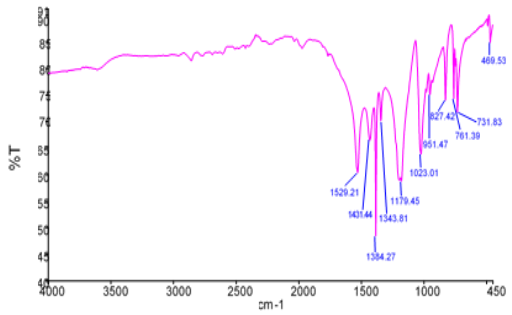

Figure 7*. FTIR spectrum of KDN.*

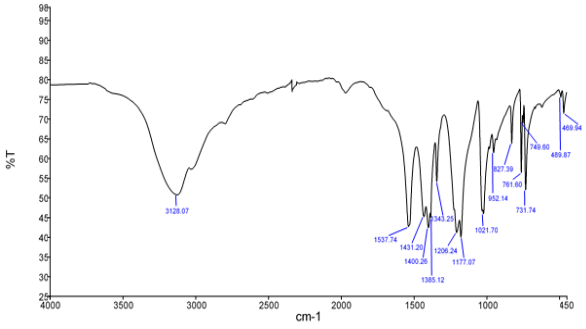

Figure 8*. FTIR spectrum of ADN.*

Table 3. *Major FTIR peaks for KDN, ADN and their assignments.*

Wavenumber (cm^{-1})[a]		Assignments[b]
KDN	**ADN**	
-	3128 b	υ s NH_4^+ in phase
1529 s	1537 s	υ as NO_2 in phase
-	1400 sh	δ sciss NH_4^+ out of phase
1344 w	1343 w	υ s NO_2 in phase
-	1206 w	υ s NO_2 in phase
1179 vs	1177 vs	υ s NO_2 in phase
1023 s	1021 s	υ as N_3
951 sh	952 sh	υ s N_3
827 mw	827 mw	δ sciss NO_2 in phase
761 m	761 m	δ sciss NO_2 out of phase
731 m	731 m	δ rock NO_2 out of phase
489 w	489 w	δ wag NO_2 out of phase

[a]: s (strong); b (broad); sh (sharp); v (various); m (medium); w (weak).
[b]: υ, δ are stretching, bending vibrations, respectively; s, as are symetric, asymestric stretch, respectively.

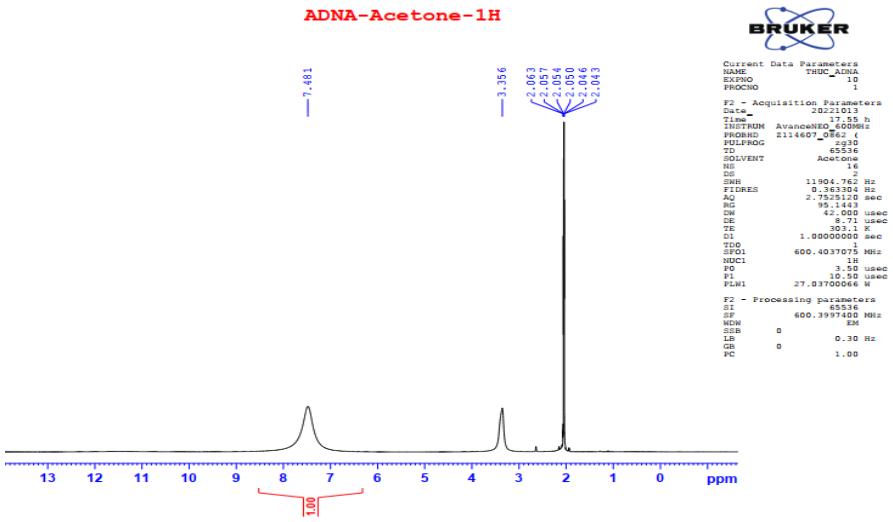

Figure 9. *^{1}H NMR spectrum of ADN.*

The ^{1}H-NMR spectrum of ADN displayed a simple at 7.48 ppm (4H) corresponding to NH_4^+ protons.

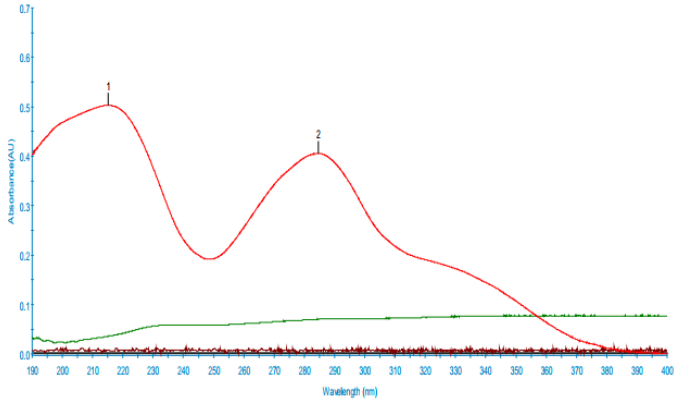

Figure 10. *UV-Vis spectrum of ADN.*

The UV-Vis spectrum of the synthesized product has two peak positions at wavelengths of 215.1 nm and 284.7 nm. These are characteristic peaks of the dinitramide ion. These peaks prove that the product contains dinitramide ions.

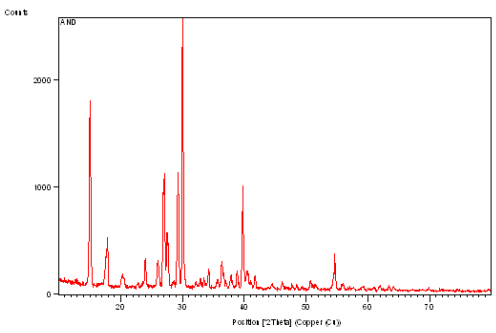

Figure 11. *XRD pattern of ADN.*

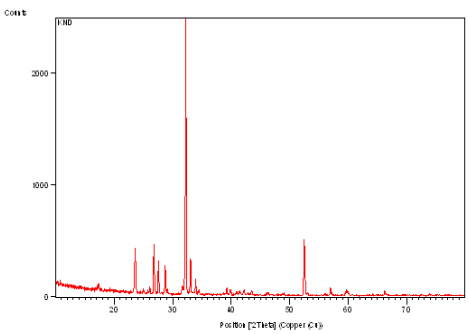

Figure 12. *XRD pattern of KDN.*

The XRD pattern of ADN has characteristic peaks at angles 2θ of 15.055, 17.845, 27.115, 30.025, and 39.745. All the data of analysis of ^{1}H NMR, FT-IR, UV-Vis, XRD agree with the reported data in the literature [7-10].

4. CONCLUSIONS

In summary, ADN was synthesized through the intermediate compound KDN with a total yield of 46%. KDN was prepared from the nitration of potassium sulfamate using a sulfuric acid/ nitric acid mixture. We have found that the optimal condition of ADN synthesis was at a nitration temperature of -40 ^{o}C, the nitration reaction time was 30 minutes, the molar ratio of KS to H_2SO_4 to HNO_3 of 1 : 2.5 : 9 and the molar ratio of KDN to $(NH_4)_2SO_4$ of 1 : 1.1.

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TÓM TẮT

Nghiên cứu tối ưu quá trình tổng hợp amoni dinitramit

Amoni dinitramit (ADN) là một trong những chất oxy hóa tiềm năng cho nhiên liệu tên lửa rắn vì nó thân thiên môi trường, có xung lực đẩy riêng cao và có ít khí thải đặc trưng. ADN được tổng hợp thông qua phản ứng nitro hóa muối kali sunfamat bằng hỗn hợp axit sunfuric và axit nitric. Các điều kiện tối ưu cho quá trình tổng hợp đã được nghiên cứu như tỷ lệ các thành phần, nhiệt độ phản ứng, thời gian phản ứng. Trong đó, nhiệt độ phản ứng nitro hóa là -40 ^{o}C, thời gian phản ứng 30 phút, tỷ lệ mol kali sunfamat, axit sunfuric và axit nitric lần lượt là 1, 2.5, 9 và tỷ lệ mol kali dinitramit, amoni sunfat là 1 : 1.1.

Từ khóa: Amoni dinitramit; Kali dinitramit; ADN; KDN; KS.