

Study on Synthesis and Characterization of Primary Explosive KDNBF with Different Morphologies

Jin-Shuh Li,*^[a] Fu-Jen Chen,^[b] Hsiu-Wen Yang,^[c] and Kai-Tai Lu^{+,[a]}

Abstract: Traditional primary explosives are usually heavy metal salts, especially salts of lead, such as lead azide (LA) and lead styphnate (LS), which can cause environmental pollution problems. The potassium salt of 4,6-dinitrobenzofuroxan (KDNBF) has attracted more and more attention due to its advantages of no heavy metal pollution to the environment and appropriate sensitivity. There are many reports on the thermal properties and applications of KDNBF, but few reports on the morphological properties. In addition, little is known about the optimal synthesis conditions of KDNBF with different morphologies in the preparation process. In this study, Taguchi's experimental design method was used to determine the optimal experimental conditions for obtaining the maximum yields of KDNBF with different morphologies. The synthesized KDNBF was identified by means of SEM, NMR, FTIR, EA, and TG-DSC,

and its sensitivity was measured using BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester. The experimental results indicated that the maximum yields of flaky and spherical KDNBFs could reach 85.6% and 82.6% after purification under the optimal experimental condition, respectively. The spherical KDNBF powder had a relatively denser structure than the flaky KDNBF powder. The thermal analyses showed that the activation energies of the decomposition reaction of the flaky and spherical KDNBF powders calculated by the Kissinger method were 171.5 and 188.5 kJ mol^{-1} , respectively, and the Ozawa method were 170.7 and 186.9 kJ mol^{-1} , respectively. The thermal stability of spherical KDNBF powder was higher than that of flaky KDNBF powder. In addition, the sensitivity tests showed that the spherical KDNBF powder was less sensitive than the flaky KDNBF powder.

Keywords: Lead-free primary explosive · KDNBF · Morphology · Yield · Taguchi experimental design method

1 Introduction

Traditional primary explosives are often heavy metal salts, especially salts of lead, such as lead azide (LA) and lead styphnate (LS), which can cause environmental pollution problems, particularly in shooting ranges. Therefore, a clear need exists for the successful development and replacement of these two aforementioned primary explosives. Recently, many heterocyclic compounds have been developed to replace lead-containing primary explosives [1]. In addition, energetic materials containing potassium have also attracted more and more attention due to their advantages of no heavy metal pollution to the environment and appropriate sensitivity properties [2–4]. 4,6-Dinitrobenzofuroxan (4,6-DNBF) was first prepared in 1892 and can be used as an important intermediate for the synthesis of other energetic materials. The most important member of these energetic materials is potassium salt of 4,6-DNBF (KDNBF), which has been used in primary explosives and initiating compositions [5–6], with the recent emphasis on its environmental protection advantages over other energetic materials containing heavy metals. KDNBF has the potential to be further used as a green alternative to LA and LS in primary explosive compositions [3].

KDNBF was first prepared by Drost in 1899 and its structure was determined by Brown et al. in 1965 [7]. There are

two methods to synthesize KDNBF: the direct method and the indirect method. The direct method is mentioned in U.S. Army MIL-P-50486 [8] that DNBF is suspended in a 20–50% ethanol or acetone aqueous solution, and the KHCO_3 solution is dropped. The reaction is carried out at a temperature of about 40°C or lower. Thin and irregular shaped KDNBF crystals with low bulk density are obtained. The indirect method is to first synthesize the sodium or magnesium salt of DNBF, and then replace the sodium ion or magnesium ion with potassium ion to synthesize KDNBF [9]. McGuchan [10] has used the indirect method to obtain granular KDNBF. The morphology of energetic materials has

[a] J.-S. Li, K.-T. Lu⁺

Department of Chemical and Materials Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC

Tel.: +886-3-3891716

Fax: +886-3-3892494

*e-mail: lijinshuh@gmail.com

[b] F.-J. Chen

Master Program of Chemical Engineering, Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan, ROC

[c] H.-W. Yang

System Manufacturing Center, National Chung Shan Institute of Science and Technology, New Taipei, Taiwan, ROC

[+] Adjunct professor

a great influence on thermal stability and energetic properties, especially the density and free-flowing property [11]. Therefore, it is very important to adjust the shape of the crystals during the synthesis process. Feng et al. [12] have synthesized spherical products of KDNBF by adding different crystal modifiers into the reaction solution. There are many reports on the thermal properties and applications of KDNBF [13–17], but few reports on the morphological properties [12, 18]. In addition, little is known about the optimal synthesis conditions of KDNBF with different morphologies during preparation.

This study mainly explored the optimal synthesis parameters of KDNBF with different morphologies. KDNBF was prepared by the indirect method, and the morphology of the product was changed by the crystal modifier. Taguchi L₉ (3⁴) orthogonal array with four control factors and three levels of each control factor was adopted to design the experimental conditions. The obtained experimental data were used to analyze and evaluate the experimental conditions with optimal parameters combination for the maximum yield of KDNBF with different morphologies. Furthermore, the synthesized KDNBF was identified by means of scanning electron microscopy (SEM), nuclear magnetic resonance spectrometer (NMR), Fourier transform infrared spectrometer (FTIR), elemental analyzer (EA) and thermogravimetry-differential scanning calorimetry (TG-DSC), and then its sensitivity was determined using BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester. The DSC data were also used to calculate the activation energies by the Kissinger and Ozawa methods and then to further assess the thermal stability of KDNBF.

2 Experimental

There are some cautionary statements regarding the synthesis experiments of KDNBF. KDNBF and its synthetic raw material DNBF are sensitive to impact, friction, and electrostatic discharge, and must be handled with care during synthesis and analysis. In addition, fuming nitric acid and fuming sulfuric acid used for synthesizing DNBF are corrosive and can cause irritation to the eyes, skin, and mucous membrane, and must be handled with care during synthesis.

2.1 Materials

4,6-Dinitrobenzofuran (4,6-DNBF) was used as the starting material. It was prepared by nitrating benzofuran (BF) with mixed nitric/sulfuric acid according to the method reported by our research group [19] and then was recrystallized from ethanol to obtain high purity 4,6-DNBF. Its crystal morphology and particle size are shown in Figure 1. Sodium hydrogen carbonate (NaHCO₃, 99.9%) and potassium sulphate (K₂SO₄, 99.9%) were reagent grade and purchased from Sigma-Aldrich. Polyacrylamide [PAM, (C₃H₅NO)_n], Polyvinyl alcohol [PVA, (C₂H₄O)_x] and Polysorbate 20 (Tween 20, C₂₆H₅₀O₁₀) were employed as crystal modifiers, the former two were purchased from Sigma-Aldrich, and the latter was purchased from J.T. Baker. Ethanol (C₂H₅OH, 99.9%) was purchased from Sigma-Aldrich and used in washing and filtering processes. All solutions were prepared using deionized water.

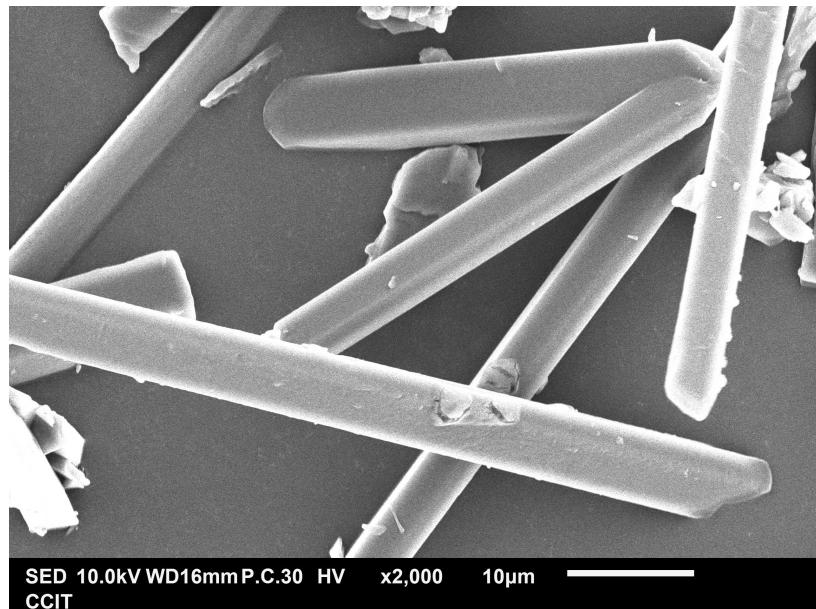


Figure 1. SEM image of high purity 4,6-DNBF crystals. [19]

2.2 Design of Experimental Conditions

Taguchi method is one of the most widely used design methods, which is making use of an orthogonal array from the experimental design to study more variables in a minimal number of experiments [20–23]. An $L_9(3^4)$ orthogonal array with four control factors and three levels was used to design the experimental conditions in this study. Four control factors were selected, including molar ratio of 4,6-DNBF to NaHCO_3 , molar ratio of 4,6-DNBF to K_2SO_4 , reaction temperature and reaction time, each at three levels, as shown in Table 1. The above four factors were assigned to the $L_9(3^4)$ orthogonal array containing nine experimental conditions as shown in Table 2, which included two series of experiments to prepare the flaky and spherical KDNBFs.

2.3 Apparatus and Procedures for Synthesis of KDNBF

KDNBF was prepared by two steps. The first step was the synthesis of sodium salt of DNBF (NaDNBF), and then the second step was the synthesis of potassium salt of DNBF (KDNBF). Firstly, 2.26 grams (0.01 mole) of 4,6-DNBF and 60 ml of deionized water were placed in a double-jacketed glass vessel with a capacity of about 250 ml, stirred and heated to 60 °C by a circulating water bath with an accuracy of ± 0.3 °C. The required amount (0.01, 0.0125 or 0.015 mole) of NaHCO_3 was then gradually added to the mixed solution under continuous stirring. After the addition, the

mixed solution was continuously stirred and kept at 60 °C for about 20 min. After cooling, the solution was filtered by vacuum suction to remove solid impurities, and a red-brown NaDNBF solution was obtained. In addition, the K_2SO_4 solution was prepared by dissolving the required amount (0.0075, 0.01 or 0.0125 mole) of K_2SO_4 in 15 ml of deionized water, and the crystal modifier was prepared by mixing 4 ml of 0.05 wt.% PAM aqueous solution, 5 ml of 2 wt.% PVA aqueous solution and 5.5 ml of 0.5 wt.% Tween 20 aqueous solution. Subsequently, the NaDNBF solution and crystal modifier were poured into the previous double-jacketed glass vessel, stirred and heated to the set reaction temperature (55, 60 or 65 °C) by a circulating water bath, and then the K_2SO_4 solution was gradually added to the solution under continuous stirring (If flaky KDNBF was to be prepared, no crystal modifier was added). After the addition, the mixed solution was continuously stirred for the set reaction time (5, 10 or 15 min), and then cooled to room temperature. Finally, the precipitate of KDNBF was collected by filtration under vacuum suction, washed twice with deionized water and once with ethanol, and dried in a vacuum oven at 50 °C for 4 hours. The schematic diagram of the experimental procedure is shown in Figure 2.

The synthesized KDNBF were characterized by means of scanning electron microscopy (SEM, Hitachi S-3000H), nuclear magnetic resonance spectrometer (NMR, Bruker AVIII 500 MHz), Fourier transform infrared spectrometer (FTIR, PerkinElmer Spectrum 100), elemental analyzer (EA, Elementar Vario EL cube), and thermogravimetry-differential scanning calorimetry (TG-DSC, Netzsch STA 449 F3). SEM was used to observe the morphology and size of the synthesized product. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and $^{15}\text{N-NMR}$ were used to determine the types and amount of hydrogen, carbon and nitrogen atoms present in the molecule, respectively, and to confirm the structure of the synthesized product. Dimethyl sulfoxide-d6 (DMSO-d6) was used as the solvent in NMR experiments because of its good solubilizing ability for KDNBF. FTIR was conducted to analyze the functional groups of the synthesized product in the 4000–500 cm^{-1} region with a spectral resolution of 4 cm^{-1} . EA was carried out

Table 1. The Control factors and levels of the Taguchi experiments.

Control factor	Level		
	1	2	3
A. Molar ratio of 4,6-DNBF to NaHCO_3	1:1	1:1.25	1:1.5
B. Molar ratio of 4,6-DNBF to K_2SO_4	1:0.75	1:1	1:1.25
C. Reaction temperature (°C)	55	60	65
D. Reaction time (min)	5	10	15

Table 2. The $L_9(3^4)$ orthogonal array of the Taguchi experiments.

Exp. No.	Molar ratio of 4,6-DNBF to NaHCO_3	Molar ratio of 4,6-DNBF to K_2SO_4	Reaction temperature (°C)	Reaction time (min)
A1, B1	1:1	1:0.75	55	5
A2, B2	1:1	1:1	60	10
A3, B3	1:1	1:1.25	65	15
A4, B4	1:1.25	1:0.75	60	15
A5, B5	1:1.25	1:1	65	5
A6, B6	1:1.25	1:1.25	55	10
A7, B7	1:1.5	1:0.75	65	10
A8, B8	1:1.5	1:1	55	15
A9, B9	1:1.5	1:1.25	60	5

Notes. A-series experiments did not add crystal modifier to prepare flaky KDNBF. B-series experiments added crystal modifier to prepare spherical KDNBF.

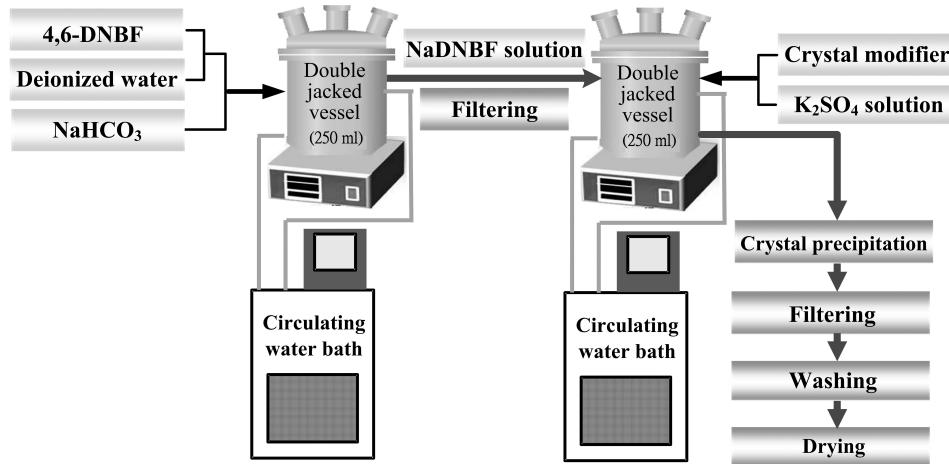


Figure 2. Schematic diagram of the experimental procedure.

to determine carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and potassium (K) contents of the synthesized product and to confirm the desired product. Simultaneous TG-DSC measurements were carried out in an argon atmosphere at heating rates of 1, 2, 5 and 10 °C min⁻¹ using the sample weight in the range of 1–2 mg to study the thermal properties of the synthesized product.

2.4 Sensitivity Tests

The impact sensitivity of the synthesized KDNBF powder was determined by the BAM fallhammer (Reichel & Partner GmbH). The Bruceton method [24] was used to evaluate the impact sensitivity, which was based on a statistical analysis by determining the drop height (H_{50}) at which there was 50% probability of obtaining an ignition. Each sample was tested utilizing a 0.375 kg dropweight for 30 times to obtain a H_{50} . The impact energy (E_{50}) was calculated using the formula $E_{50}(\text{Joule}) = mgH_{50}$, where m is dropweight mass [kg], g is acceleration due to gravity [ms^{-2}], and H_{50} is drop height [m].

The friction sensitivity of the synthesized KDNBF powder was determined by the BAM friction tester (Reichel & Partner GmbH). The 1 of 6 methods was used to evaluate the friction sensitivity, which was defined as the smallest load at which an audible or visible decomposition reaction is obtained from at least one out of six trials. The measurement range of the friction load was from 0.5 to 360 N.

The electrostatic spark sensitivity of the synthesized KDNBF powder was determined by the small-scale electrostatic spark sensitivity tester (OZM Research X SPARK 10). The measurement of the electrostatic spark sensitivity was based on the principle of capacitive discharge driven through the granular bed of the test sample. If the test sample had flash, spark, burn, odor or noise other than instrument noise, it should be tested at the next lower level

until 20 consecutive failures were reported. The discharge energy was calculated using the formula $E(\text{Joule}) = 1/2 CV^2$, where C is capacitance [μF], and V is voltage [kV]. The measured discharge energy ranged from 25 μJ to 25 J.

3 Results and Discussion

3.1 Analysis and Verification of Taguchi Experiments

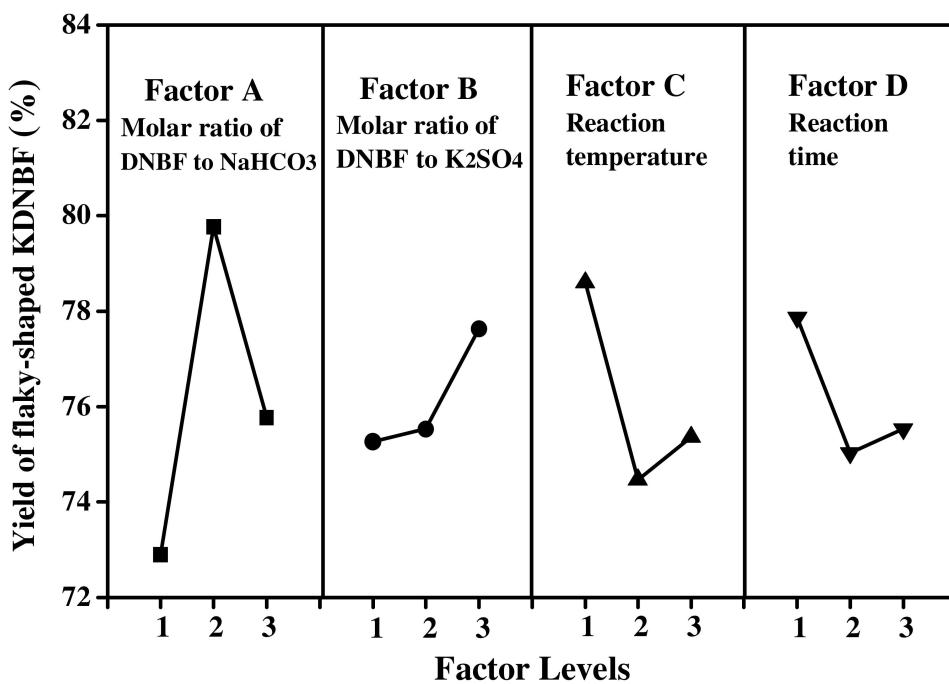
The A-series and B-series of synthesis experiments of KDNBF were carried out with different operating parameters such as molar ratio of 4,6-DNBF to NaHCO₃ (1:1, 1:1.25 and 1:1.5), molar ratio of 4,6-DNBF to K₂SO₄ (1:0.75, 1:1 and 1:1.25), reaction temperature (55, 60 and 65 °C) and reaction time (5, 10 and 15 min), and the effect of operating parameters on the yield of KDNBF with different morphologies was examined. The experimental results of the two series are listed in Table 3, which were converted into a signal-to-noise (S/N) ratio using the Taguchi method. The S/N ratio was used as the measure of the effect of noise factors on the target characteristics [22–23]. The range and contribution rank of each factor for the yield of KDNBF with different morphologies are shown in Table 4. In the table, the target values of different levels on each factor are the arithmetic average of target values corresponding to each level. The range is the difference between maximum and minimum of the target values on each factor and the rank represents the order of effect of each factor on the quality characteristic [22–23]. Figure 3 shows the trends of parameter influence for four factors on the yield of flaky KDNBF. In the figure, levels A2, B3, C1 and D1 have the largest value of yield for the factors molar ratio of 4,6-DNBF to NaHCO₃, molar ratio of 4,6-DNBF to K₂SO₄, reaction temperature and reaction time, respectively. From the above analysis, the maximum value of yield may be found on the condition that molar ratio of 4,6-DNBF to NaHCO₃ is 1:1.25, molar ra-

Table 3. Experimental results of Taguchi's orthogonal array for yield of KDNBF.

Flaky	Exp. No.	A1	A2	A3	A4	A5	A6	A7	A8	A9
	Amount after purification (g)	2.15	1.96	2.06	2.16	2.26	2.33	2.06	2.17	2.18
	Yield after purification (%)	76.2	69.5	73.0	76.6	80.1	82.6	73.0	77.0	77.3
Spherical	Exp. No.	B1	B2	B3	B4	B5	B6	B7	B8	B9
	Amount after purification (g)	2.18	2.15	2.25	1.95	1.97	2.31	1.44	2.14	1.96
	Yield after purification (%)	77.3	76.2	79.8	69.1	69.9	81.9	51.1	75.9	69.5

Table 4. Range and contribution rank of each factor for yield of KDNBF (unit: %).

	Level	Control factors			
		A (Molar ratio of 4,6-DNBF to NaHCO ₃)	B (Molar ratio of 4,6-DNBF to K ₂ SO ₄)	C (Reaction temperature)	D (Reaction time)
Flaky	1	72.90	75.27	78.60	77.87
	2	79.77	75.53	74.47	75.03
	3	75.77	77.63	75.37	75.53
	Range	6.87	2.36	4.13	2.83
	Rank	1	4	2	3
Spherical	1	77.77	65.83	78.37	72.23
	2	73.63	74.00	71.60	69.73
	3	65.50	77.07	66.93	74.93
	Range	12.27	11.23	11.43	5.20
	Rank	1	3	2	4

**Figure 3.** The trends of parameter influence for four factors on yield of flaky KDNBF.

tio of 4,6-DNBF to K₂SO₄ is 1:1.25, reaction temperature is 55 °C and reaction time is 5 min. It is also observed that the order of effect of each factor on this quality characteristic is

molar ratio of 4,6-DNBF to NaHCO₃ > reaction temperature > reaction time > molar ratio of 4,6-DNBF to K₂SO₄. The molar ratio of 4,6-DNBF to NaHCO₃ (factor A) has the great-

est influence. In addition, Figure 4 shows the trends of parameter influence for four factors on the yield of spherical KDNBF. Similar analysis shows that the maximum value of yield may be found on the condition that molar ratio of 4,6-DNBF to NaHCO₃ is 1:1 (A1), molar ratio of 4,6-DNBF to K₂SO₄ is 1:1.25 (B3), reaction temperature is 55 °C (C1) and reaction time is 15 min (D3). The order of effect of each factor on this quality characteristic is molar ratio of 4,6-DNBF to NaHCO₃ > reaction temperature > molar ratio of 4,6-DNBF to K₂SO₄ > reaction time. Similarly, the molar ratio of 4,6-DNBF to NaHCO₃ (factor A) has the greatest influence.

Additional confirmation experiments were carried out to verify the effectiveness of the optimal parameters determined using the Taguchi method. The optimal design factors for the yields of flaky and spherical KDNBFs were A2B3 C1D1 and A1B3 C1D3 parameter combinations, respectively. Table 5 gives the results of confirmation experiments. Each experiment was repeated three times and the average value was calculated. The experimental results in-

dicate that the A2B3 C1D1 and A1B3 C1D3 parameter combinations for preparing flaky and spherical KDNBFs have higher yields than other combinations. Taguchi method successfully predicted these two optimal parameter combinations to achieve maximum yield. In this way, the maximum yields of flaky and spherical KDNBFs can reach 85.6% and 82.6%, respectively.

3.2 Identification of Synthesized Products

The morphology and size of the synthesized product crystals were observed by SEM. Figure 5 shows the SEM images of flaky and spherical KDNBF powders synthesized under the operating conditions of optimal parameter combination (A2B3C1D1 and A1B3C1D3). It can be seen from Figure 5(a) that the synthesized KDNBF powder exhibits a flaky structure and partial aggregation. In addition, from Figures 5(b) and 5(c), it can be observed that the synthesized KDNBF

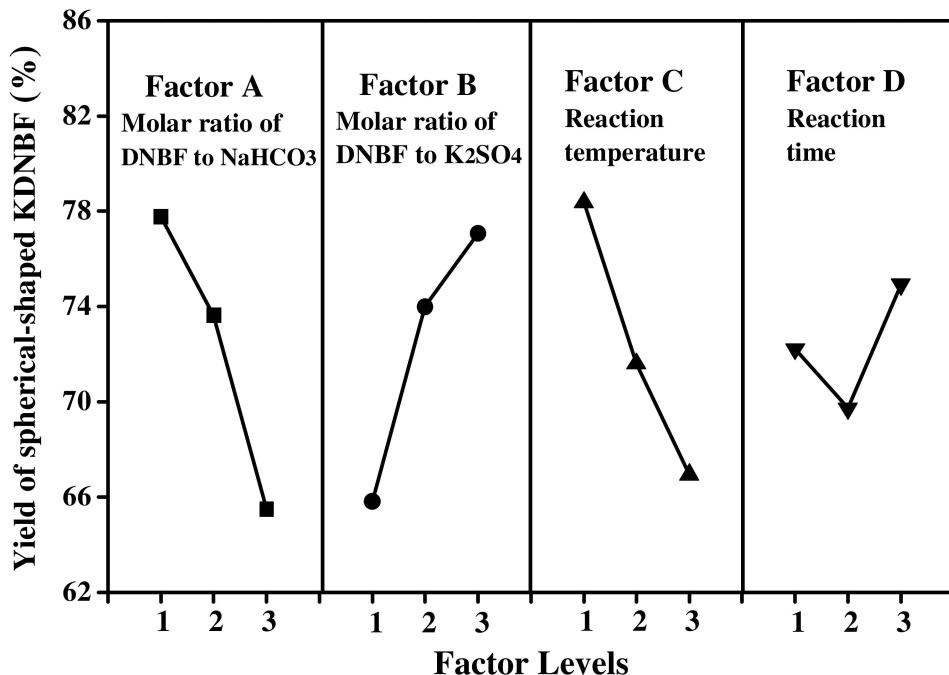


Figure 4. The trends of parameter influence for four factors on yield of spherical KDNBF.

Table 5. Results of confirmation experiments.

Faky KDNBF Optimal parameter combinations	Exp. No.	Amount after purification (g)	Yield after purification (%)	Spherical KDNBF Optimal parameter combinations	Exp. No.	Amount after purification (g)	Yield after purification (%)
A2B3C1D1	F1	2.37	84.0	A1B3 C1D3	S1	2.34	83.0
	F2	2.43	86.2		S2	2.32	82.3
	F3	2.44	86.5		S3	2.33	82.6
Average value		2.41	85.6	Average value		2.33	82.6

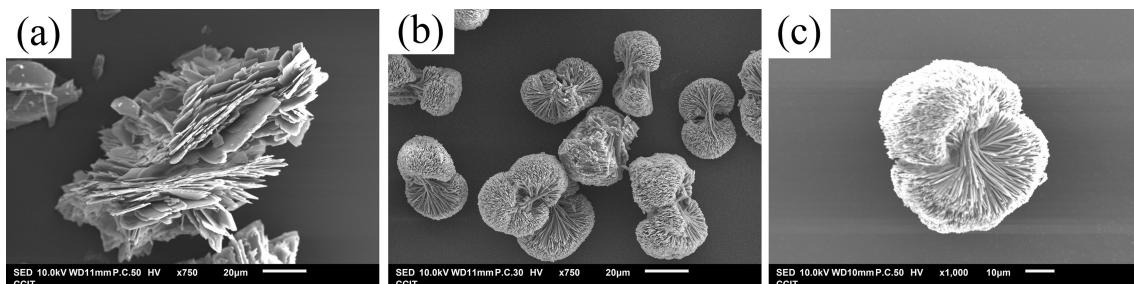


Figure 5. SEM images of synthesized flaky (a) and spherical (b, c) KDNBF powders.

powder shows a spherical structure aggregated by needle-like crystals. It is obvious that spherical KDNBF powder has a relatively denser structure than flaky KDNBF powder.

3.2.1 NMR Spectrum

The structure of the synthesized product was confirmed by NMR spectroscopy. Figures 6–8 show the ^1H -NMR, ^{13}C -NMR and ^{15}N -NMR spectra of the synthesized spherical KDNBF in DMSO-d6. ^1H -NMR spectrum shows that two signals at 5.8 (H7) and 8.5 (H5) ppm correspond to the hydrogen atoms in the benzene ring, and one signal at 6.3 (OH) ppm corresponds to the hydrogen atom on the hydroxyl group. The other two signals at 2.5 and 3.7 ppm are attributed to DMSO-d6 solvent and H_2O , respectively. ^{13}C -NMR spectrum shows six signals at 57.5 (C7), 109.8 (C8), 113.4 (C4), 128.1 (C6), 130.6 (C5) and 148.6 (C9) ppm in the 57–149 ppm re-

gion, representing the six carbon atoms on the benzene ring. Another strong signal in the 39–40 ppm region is due to the DMSO-d6 solvent. In addition, ^{15}N -NMR spectrum shows four signals at 352.8 (N10), 359.0 (N1), 360.8 (N11) and 369.3 (N3) ppm, which correspond to the nitrogen atoms in the molecule. The above NMR analysis can be used to confirm that the synthesized product is KDNBF. Sebban et al. [25] have also presented a similar analysis and results. Furthermore, the ^1H -NMR, ^{13}C -NMR and ^{15}N -NMR spectra of the synthesized flaky KDNBF are similar to that of the synthesized spherical KDNBF.

3.2.2 FTIR Spectrum

The functional groups of the synthesized product were analyzed by FTIR. Figure 9 shows the FTIR spectrum of the synthesized spherical KDNBF. The aromatic C=C stretching is

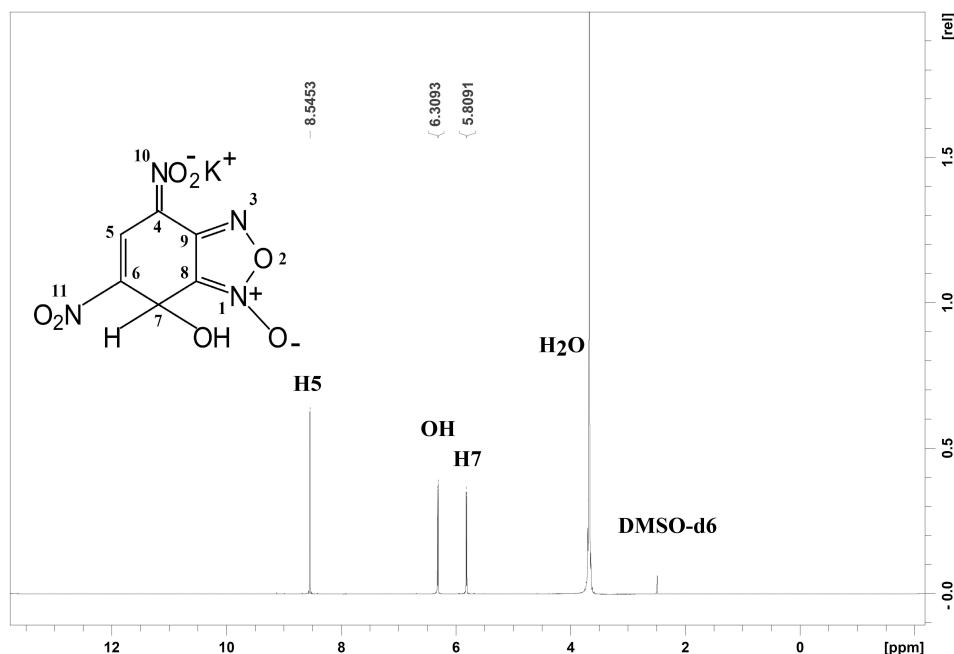


Figure 6. ^1H -NMR spectrum of synthesized spherical KDNBF in DMSO-d6.

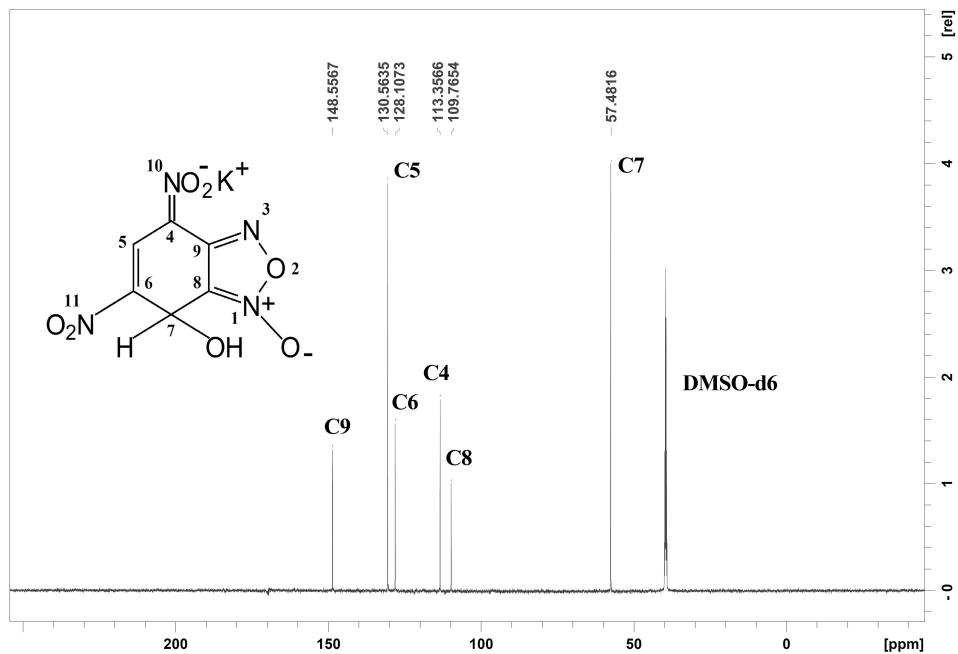


Figure 7. ^{13}C -NMR spectrum of synthesized spherical KDNBF in DMSO-d6.

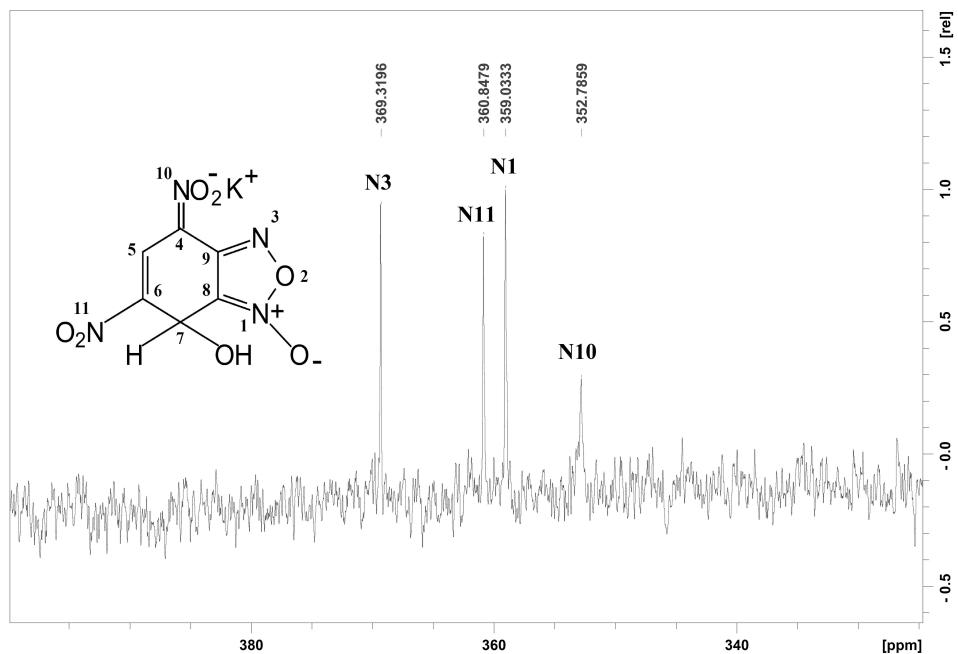


Figure 8. ^{15}N -NMR spectrum of synthesized spherical KDNBF in DMSO-d6.

observed at 1618 cm^{-1} , indicating the presence of a ring structure. Two adjacent Ar–H and Ar–OH stretchings are found at 3082 and 3435 cm^{-1} , respectively. In addition, Ar– NO_2 symmetric and asymmetric stretchings are respectively seen at 1398 and 1547 cm^{-1} , and – ONO stretching is found at 1477 and 1590 cm^{-1} . Therefore, the FTIR spectrum can further verify that the synthesized product is KDNBF. Spear

et al. [6] have also reported similar results in their study. Furthermore, the FTIR spectrum of the synthesized flaky KDNBF is similar to that of the synthesized spherical KDNBF.

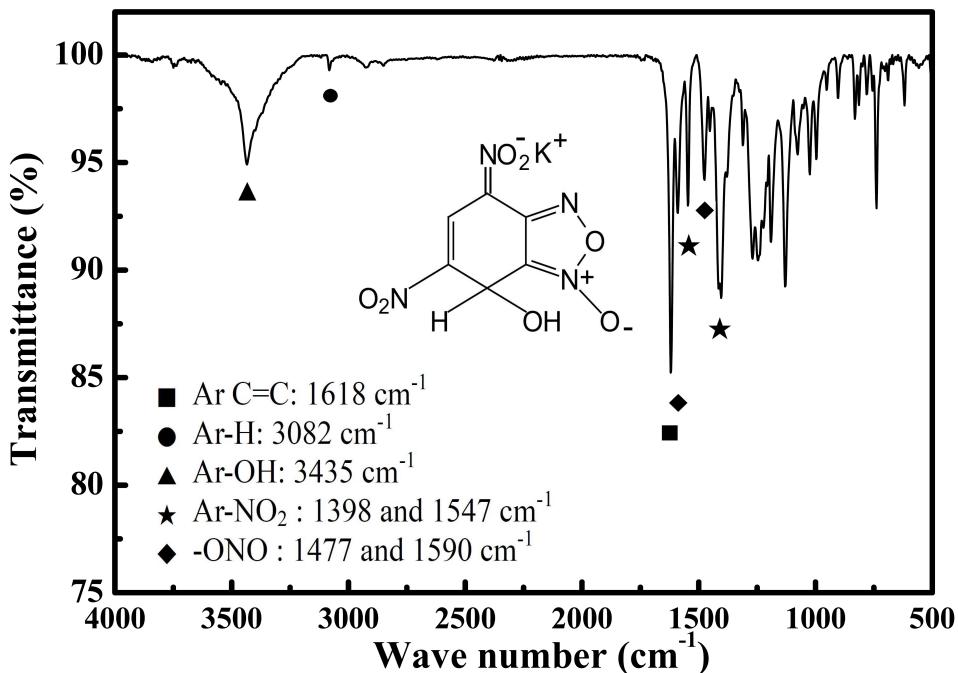


Figure 9. FTIR spectrum of synthesized spherical KDNBF powder.

3.2.3 EA Analysis

The elemental composition of the synthesized product was analyzed by EA. The experiment was run three times and the average value of each element content was calculated as shown in Table 6. The analysis result shows that the synthesized spherical KDNBF contains 13.86% potassium, 25.51% carbon, 1.30% hydrogen, 19.76% nitrogen and 39.58% oxygen, which are very close to the theoretical values of KDNBF composition. The elemental analysis of the synthesized flaky KDNBF also has similar results.

3.2.4 TG-DSC Thermogram

The thermal properties of the synthesized product were studied by simultaneous TG-DSC analysis. Figure 10 shows the TG-DSC curve of the synthesized spherical KDNBF. It is found that the DSC curve exhibits three exothermic peaks

including one strong initial peak at 213 °C and two much weaker subsequent peaks at 242 °C and 270 °C. These three peaks can reasonably be attributed to the primary and secondary decomposition stages of KDNBF because the TG curve shows continuous weight loss. The TG-DSC curve of the synthesized flaky KDNBF is similar to that of the synthesized spherical KDNBF. Jones et al. [26] have also reported similar experimental results. In addition, Figures 11 and 12 present the DSC curves of the synthesized spherical and flaky KDNBFs at heating rates of 1, 2, 5 and 10 °C min⁻¹, respectively. The activation energies of the decomposition reaction were calculated by the Kissinger and Ozawa methods [27] and are listed in Table 7. The activation energy for the decomposition of spherical KDNBF is higher than that of flaky KDNBF. Therefore, the thermal stability of spherical KDNBF is higher than that of flaky KDNBF.

Table 6. Elemental analysis of synthesized spherical KDNBF.

Element	Molecular formula KC ₆ H ₃ N ₄ O ₇ (Molecular weight 282.2 g/mol)			Average value	Theoretical value
	Test 1	Test 2	Test 3		
K (wt.%)	13.72	14.01	13.84	13.86	13.85
C (wt.%)	25.65	25.27	25.60	25.51	25.54
H (wt.%)	1.32	1.29	1.29	1.30	1.07
N (wt.%)	19.84	19.64	19.80	19.76	19.85
O (wt.%)	39.47	39.79	39.47	39.58	39.69

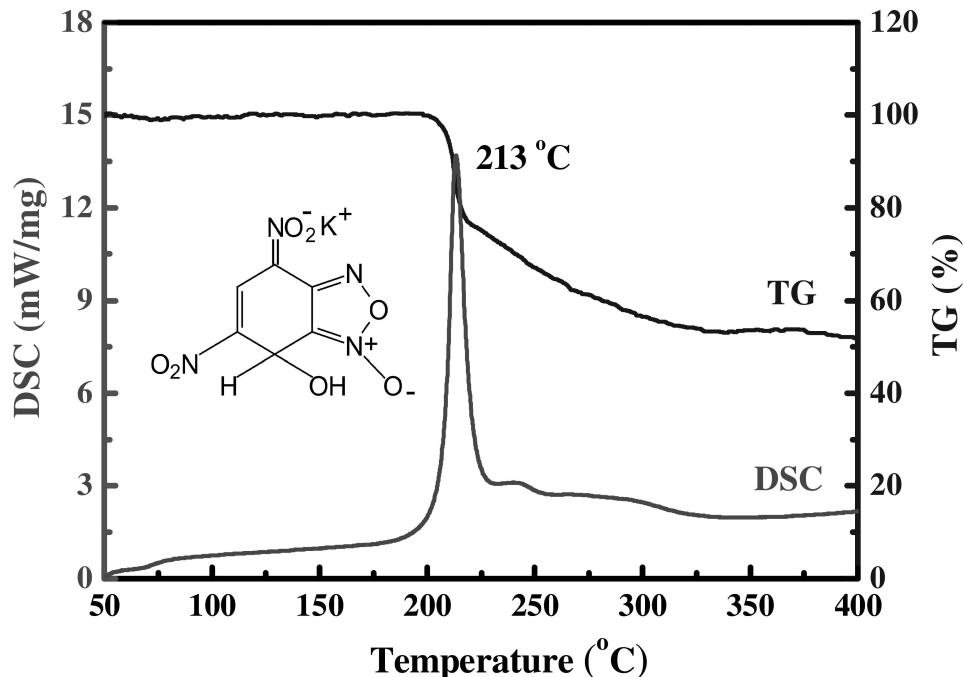


Figure 10. TG-DSC curves of synthesized spherical KDNBF.

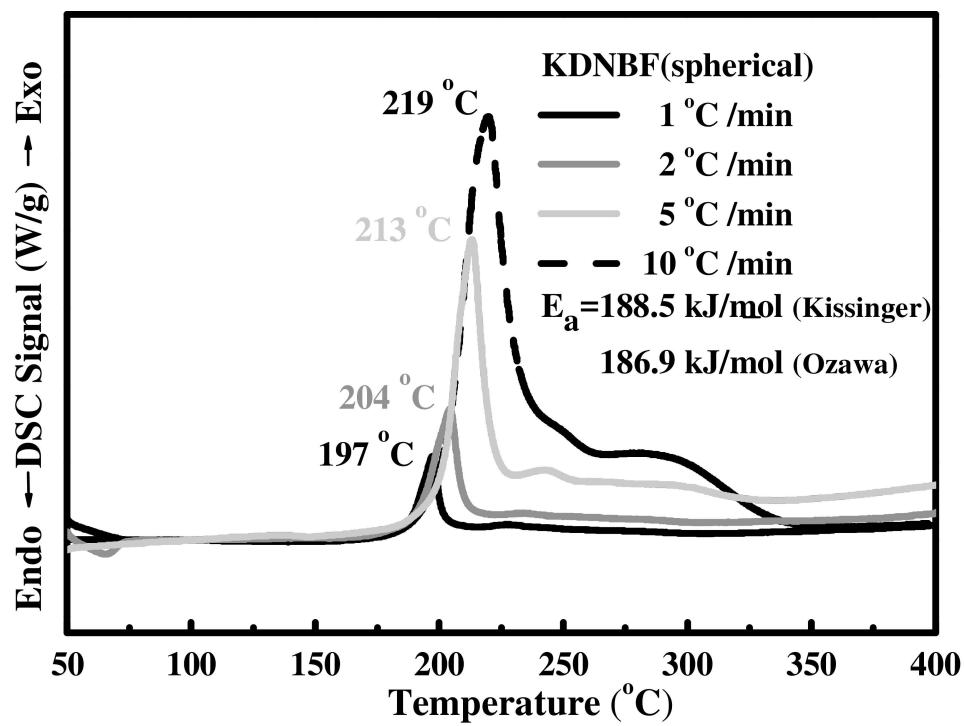


Figure 11. DSC curves of synthesized spherical KDNBF at different heating rates.

3.3 Analysis of Bulk Density

The bulk densities of the synthesized flaky and spherical KDNBFs were measured by the Archimedes principle and

are given in Table 7, which are 0.24 and 0.36 g cm^{-3} , respectively. It is expected that the bulk density of spherical KDNBF is higher than that of flaky KDNBF because spherical KDNBF has a relatively dense structure.

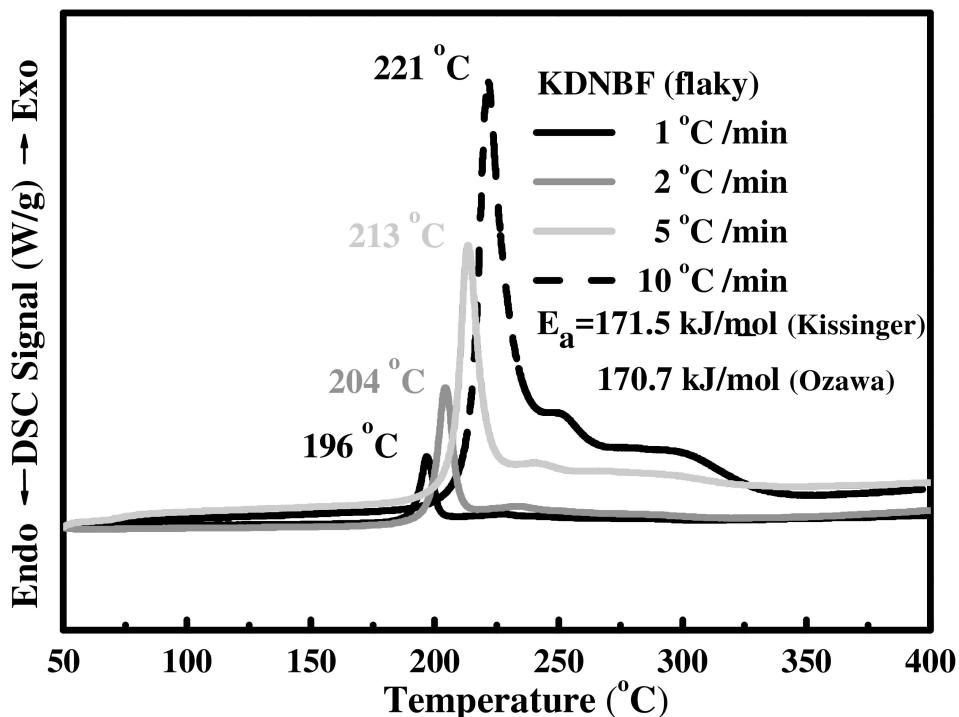


Figure 12. DSC curves of synthesized flaky KDNBF at different heating rates.

Table 7. Characteristic test results for synthesized KDNBF.

Shape	Bulk density [g cm ⁻³]	Activation energy kJ mol ⁻¹ Kissinger method	Ozawa method	Impact sensitivity H ₅₀ (cm)	E ₅₀ (J)	Friction sensitivity (N)	Electrostatic spark sensitivity (mJ)
Flaky	0.24	171.5	170.7	7.6	0.26	8.0	40.0
Spherical	0.36	188.5	186.9	14.2	0.52	9.0	62.5

3.4 Measurement of Sensitivity

The impact, friction, and electrostatic spark sensitivities of the synthesized flaky and spherical KDNBFs were determined by BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester, respectively. Each experiment was run three times and the average value was calculated as shown in Table 7. The impact, friction and electrostatic spark sensitivities of flaky KDNBF are 0.26 J, 8.0 N, and 40.0 mJ, respectively. On the other hand, that of spherical KDNBF are 0.52 J, 9.0 N and 62.5 mJ, respectively. According to the hot spot growth mechanism [28, 29], the spherical KDNBF can efficiently reduce the number of hot spots in these sensitivity tests and exhibits lower sensitivity. In addition, van der Heijden et al. [30–32] have reported several different analytical techniques to understand the difference between conventional and insensitive energetic materials. These analytical techniques can also be used to evaluate the possible causes of the reduced sensitivity of the spherical KDNBF.

4 Conclusion

This study successfully used Taguchi's experimental design method to obtain the optimal parameter combinations to achieve the maximum yields of flaky and spherical KDNBFs. The synthesized KDNBF powder was confirmed by NMR, FTIR, EA, and TG-DSC analyses. In addition, the morphology and size of the synthesized flaky and spherical KDNBF powders were observed by SEM, and the sensitivity was measured using BAM fallhammer, BAM friction tester, and electrostatic spark sensitivity tester. Based on the experimental results and analyses, the following conclusions are obtained:

- (1) The optimal synthesis parameters of flaky KDNBF powder are as follows: molar ratio of 4,6-DNBF to NaHCO₃ is 1:1.25, molar ratio of 4,6-DNBF to K₂SO₄ is 1:1.25, reaction temperature is 55 °C and reaction time is 5 mins. The maximum yield after purification can reach 85.6%. The molar ratio of 4,6-DNBF to NaHCO₃ has the greatest influence.

- (2) The optimal synthesis parameters of spherical KDNBF powder are as follows: molar ratio of 4,6-DNBF to NaHCO₃ is 1:1, molar ratio of 4,6-DNBF to K₂SO₄ is 1:1.25, reaction temperature is 55°C and reaction time is 15 min. The maximum yield after purification can reach 82.6%. Similarly, the molar ratio of 4,6-DNBF to NaHCO₃ has the greatest influence.
- (3) The SEM images indicate that the flaky KDNBF powder exhibits a flaky structure and partial aggregation, and the spherical KDNBF powder shows a spherical structure aggregated by needle-like crystals. The spherical KDNBF powder has a relatively denser structure than the flaky KDNBF powder.
- (4) The thermal analyses indicate that the activation energies of the decomposition reaction of the flaky and spherical KDNBF powders calculated by the Kissinger method are 171.5 and 188.5 kJ mol⁻¹, respectively, and the Ozawa method are 170.7 and 186.9 kJ mol⁻¹, respectively. The thermal stability of spherical KDNBF powder is higher than that of flaky KDNBF powder.
- (5) The sensitivity tests indicate that the spherical KDNBF powder is less sensitive than the flaky KDNBF powder. According to the hot spot growth mechanism, the spherical KDNBF powder can efficiently reduce the number of hot spots and exhibit lower sensitivity.

Acknowledgements

This research was financially supported by the System Manufacturing Center, National Chung Shan Institute of Science and Technology, R.O.C. under grant number of YR08112P092PE-CS.

References

- [1] J. A. Joule, K. Mills, *Heterocyclic Chemistry at a Glance*, 2nd ed., John Wiley & Sons, Chichester, UK, 2012, p. 52.
- [2] P. D. Shinde, M. Mehlal, R. B. Salunke, J. P. Agrawal, Some transition metal salts of 4,6-dinitrobenzofuroxan: synthesis, characterization and evaluation of their Properties, *Propellants Explos. Pyrotech.* 2003, 28, 77.
- [3] J. Sabatini, K. D. Oyler, Recent advances in the synthesis of high explosive materials, *Crystals* 2016, 6, 5.
- [4] M. A. Il'yushin, I. V. Tselinsky, I. V. Shugalei, Environmentally friendly energetic materials for initiation devices, *Cent. Eur. J. Energ. Mater.* 2012, 9, 293.
- [5] R. Meyer, J. Köhler, A. Hombury, *Explosives*, 6th ed., Wiley-VCH Verlag GmbH, Weinheim, Germany, 2007, p. 24.
- [6] R. J. Spear, W. P. Norsis, Structure and properties of the potassium hydroxide - dinitrobenzofuroxan adduct (KDNBF) and related explosive salts, *Propellants Explos. Pyrotech.* 1983, 8, 85.
- [7] T. S. Costain, Investigation of potassium dinitrobenzofuroxan (KDNBF) to provide data necessary for the preparation of a military specification, *Picatinny Arsenal Technical report 4067*, Dover, NJ, USA, 1970, p. 4.
- [8] Potassium dinitrohydroxy hydrobenzofuroxan (For Use in Ammunition), MIL-P-50486, March 19, 1971.
- [9] T. Piechowics, Preparation of 4,6-dinitrobenzofuroxan- an useful initiating explosives, France Patent No.: 1,579,799, 1968.
- [10] R. McGuchan, Improvement in primary explosive compositions and their manufacture, *Proceedings of the 10th Symposium on Explosives and Pyrotechnics*, San Francisco, California, February 14–16, 1979.
- [11] A. K. Mehlal, P. S. Sikder, N. J. Sikder, Synthesis, characterisation, thermal and explosive properties of 4,6-dinitrobenzofuroxan salts, *Hazard. Mater.* 2002, 90, 221.
- [12] J. L. Feng, J. G. Zhang, T. L. Zhang, Z. M. Li, L. Yang, S. Z. Wang, Morphology Control and its influence on the decomposition behavior and sensitivity of KDNBF, *Acta Phys.-Chim. Sin.* 2010, 26, 2613.
- [13] S. Löbbecke, T. Keicher, H. Krause, A. Pfeil, The new energetic material ammonium dinitramide and its thermal decomposition, *Solid State Ionics* 1997, 101–103, 945.
- [14] D. E. G. Jones, H. T. Feng, R. C. Fouchard, Kinetic studies of the thermal decomposition of KDNBF, a Primer for Explosives, *Therm. Anal. Calorim.* 2000, 60, 917.
- [15] G. B. Carter, Primer compositions containing dinitrobenzofuroxan compounds, US Patent No.: 5538569, 1996, Eley Limited, Birmingham, England.
- [16] A. E. Fogelzang, V. P. Korolev, V. Y. Egorshev, V. I. Kolesov, V. D. Pochukaev, Y. M. Baskakov, A. S. Tokarev, N. M. Bibnev, V. N. Hovanskov, I. F. Evdokimova, Y. P. Voronin, Pyrotechnical percussion combustion composition for small arms ammunition primers, US Patent No.: 6165294, 2000.
- [17] U. Bley, U. Brede, Use of a microjet reactor for manufacturing a primary explosive, European Patent No.: EP1505047 A2, 2005, Dynamit Nobel AIS GmbH Automotive Ignition Systems, Fürth, Germany.
- [18] Y. F. Li, T. L. Zhang, J. G. Zhang, Thermal decomposition processes and non-isothermal kinetics of KDNBF, *Chin. J. Energet. Mater.* 2004, 4, 203.
- [19] J. S. Li, F. J. Chen, H. W. Yang, K. T. Lu, Optimization of the Process Parameters for the Synthesis of High Purity 4,6-Dinitrobenzofuroxan (4,6-DNBF), *Propellants Explos. Pyrotech.* 2020, <https://doi.org/10.1002/prep.201900413>.
- [20] S. Taguchi, *Taguchi Methods and QFD: Hows and Whys for Management*, American Supplier Institute, Michigan, 1987, p. 1.
- [21] W. G. Cochran, G. M. Cox, *Experimental Design*, 2nd ed., John Wiley & Sons, New York, 1992, p. 114.
- [22] J. S. Li, C. M. Chung, T. M. Yang, C. C. Hwang, K. T. Lu, T. F. Yeh, Combustion Rate and Light Emission of Mg/NaNO₃/Na₂C₂O₄/ Binder-Flares, *Propellants Explos. Pyrotech.* 2018, 43, 512.
- [23] T. M. Yang, C. S. Su, J. S. Li, K. T. Lu, T. F. Yeh, Recrystallization and Micronization of p-Toluenesulfonamide Using the Rapid Expansion of Supercritical Solution (RESS) Process, *Crystals* 2019, 9, 449.
- [24] J. W. Dixon, A. M. Mood, A method for obtaining and analyzing sensitivity data, *J. Am. Stat. Assoc.* 1948, 43, 109.
- [25] M. Sebban, P. Sepulcri, C. Jovene, D. Vichard, F. Terrier, R. Goumont, NMR Spectroscopy: A Useful Tool in the Determination of the Electrophilic Character of Benzofuroxans – Case Examples of the Reactions of Nitrobenzofuroxans with Dienes and Nucleophiles, in *Magnetic Resonance Spectroscopy*, Ed. D. H. Kim, InTech Europe, Rijeka, Croatia, 2012, p. 183.
- [26] D. E. G. Jones, P. D. Lightfoot, R. C. Fouchard, Q. Kwok, A. M. Turcotte, W. Ridley, Hazard characterization of KDNBF using a variety of different techniques, *Thermochim. Acta* 2002, 384, 57.
- [27] J. S. Li, J. J. Chen, C. C. Hwang, K. T. Lu, T. F. Yeh, Study on thermal characteristics of TNT based melt-cast explosives, *Propellants Explos. Pyrotech.* 2019, 44, 1270.

- [28] R. W. Armstrong, H. L. Ammon, W. L. Elban, Investigation of hot spot characteristics in energetic crystals, *Thermochim. Acta* **2002**, *384*, 303.
- [29] X. L. Song, Y. Wang, C. W. An, X. D. Guo, F. S. Li, Dependence of particle morphology and size on the mechanical sensitivity and thermal stability of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Hazard. Mater.* **2008**, *159*, 222.
- [30] A. E. D. M. van der Heijden, C. P. M. Roelands, Y. L. M. Creyghton, E. Marino, R. H. B. Bouma, J. H. G. Scholtes, W. Duvalois, Energetic materials: crystallization, characterization and insensitive plastic bonded explosives, *Propellants Explos. Pyrotech.* **2008**, *33*, 25.
- [31] A. E. D. M. van der Heijden, R. H. B. Bouma, Crystallization and characterization of RDX, HMX and CL20, *Cryst. Growth Des.* **2004**, *4*, 999.
- [32] R. H. B. Bouma, W. Duvalois, A. E. D. M. van der Heijden, Characterization of defect structure in RDX crystals, *J. Microsc.* **2013**, *252*, 263.

Manuscript received: March 8, 2020

Revised manuscript received: March 12, 2020

Version of record online: April 29, 2020