



Article

The Impact of Activated Carbon–Me_xO_y (Me = Bi, Mo, Zn) Additives on the Thermal Decomposition Kinetics of the Ammonium Nitrate–Magnesium–Nitrocellulose Composite

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Abstract: This research investigates the impact of additives such as activated carbon (AC) combined with metal oxides (Bi₂O₃, MoO₃, and ZnO) on the thermal decomposition kinetics of ammonium nitrate (AN), magnesium (Mg), and nitrocellulose (NC) as a basic AN–Mg–NC composite. To study the thermal properties of the AN–Mg–NC composite with and without the AC–Me_xO_y (Me = Bi, Mo, Zn) additive, a differential scanning calorimetry (DSC) analysis was conducted. The DSC results show that the AC–Me_xO_y (Me = Bi, Mo, Zn) additive catalytically affects the basic AN–Mg–NC composite, lowering the peak decomposition temperature (T_{max}) from 534.58 K (AN–Mg–NC) to 490.15 K (with the addition of AC), 490.76 K (with AC–Bi₂O₃), 492.17 K (with AC–MoO₃), and 492.38 K (with AC–ZnO) at a heating rate of β equal to 5 K/min. Based on the DSC data, the activation energies (E_a) for the AN–Mg–NC, AN–Mg–NC–AC, and AN–Mg–NC–AC–Me_xO_y (Me = Bi, Mo, Zn) composites were determined using the Kissinger method. The results suggest that incorporating AC and AC–Me_xO_y (Me = Bi, Mo, Zn) additives reduce the decomposition temperatures and activation energies of the basic AN–Mg–NC composite. Specifically, E_a decreased from 99.02 kJ/mol (for AN–Mg–NC) to 93.63 kJ/mol (with addition of AC), 91.45 kJ/mol (with AC–Bi₂O₃), 91.65 kJ/mol (with AC–MoO₃), and 91.76 kJ/mol (with AC–ZnO). These findings underscore the potential of using AC–Me_xO_y (Me = Bi, Mo, Zn) as a catalytic additive to enhance the performance of AN–Mg–NC-based energetic materials, increasing their efficiency and reliability for use in solid propellants.

Keywords: ammonium nitrate; magnesium; activated carbon; metal oxides; activation energy; thermal decomposition; Kissinger method



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1. Introduction

Ammonium nitrate (AN) has recently attracted attention as an environmentally sustainable and chlorine-free oxidizer for solid propellants [1,2], despite facing some challenges associated with its polymorphic characteristics [3,4]. However, AN is limited by factors such as low ignitability, slow burning rate, and high hygroscopicity, which restrict its exclusive application in energetic materials (EMs) [5]. Several studies have focused on enhancing AN-based formulations by integrating organic compounds, metallic powders, and aqueous solutions [6,7]. Currently, researchers are investigating the impact of various additives, including metal oxides, on the combustion properties of AN-based composites to enhance their combustibility [8].

Recent research on magnesium (Mg) in EMs highlights its potential for enhancing reactivity and energy release. For example, Mg nanoparticles demonstrated exceptional reactivity due to enhanced vaporization and accelerated energy release kinetics [9]. In addition, composites of boron, aluminum, and magnesium (BAM) showed improved oxidation and heat release compared to boron alone [10]. In another research study, the interaction between magnesium and 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) resulted in favorable, exothermic composite formation with increased sensitivity to impulse stimulus [11].

Moreover, surface modification of magnesium with silicon through non-thermal plasma processing significantly reduced ignition temperature, enhancing combustion kinetics [12]. These studies demonstrate the versatility of Mg in EMs, offering opportunities for improved performance through strategic design and the composition of nano-energetic materials with tunable energy release properties.

Nitrocellulose (NC) is an energetic polymer which is widely used in propellants and explosives [13]. As a binder, NC plays a crucial role in triple-base propellant formulations, influencing mechanical properties and energy content [14]. Recent research has focused on enhancing NC's performance through various methods. Incorporating manganese oxide nanoparticles into NC matrices has shown promising results, increasing decomposition enthalpy by 150% and enhancing the reaction propagation index by 261% [15]. Another approach involves blending NC with polyurethane (PU) to create energetic binders for composite solid propellants, potentially overcoming the performance drawbacks of conventional PU binders [16]. These advancements in NC-based compositions offer improved energy performance and decomposition kinetics, making them suitable for various high-energy applications.

Activated carbon (AC) has emerged as a versatile material in energetic applications. It can be used as a substrate for novel energetic materials by confining the oxidizers within its nanopores, potentially enhancing detonation properties [17,18]. For example, AC impregnated with TiO₂ nanoparticles has shown promise in capturing NO_x released from degrading nitrocellulose, with over 60% efficiency under UV light irradiation [19]. When doped with cupric oxide (CuO) [20] or cobalt (II, III) oxide (Co₃O₄) [21], AC acts as a catalyst in energetic composites, significantly improving thermal decomposition and combustion performance. Recent developments in AC synthesis have focused on maximizing porosity, using cheap precursors, and controlling morphology to enhance its performance in energy-related applications [22,23].

Metal oxides play a crucial role in enhancing the performance of EMs. Recent research has explored the use of metal oxides in energetic materials, focusing on their potential to enhance performance and reactivity [24,25]. Nanoscale composites of aluminum with metal oxides such as MoO₃, WO₃, CuO, and Bi₂O₃ have shown promising results in terms of pressure output and propagation velocity [26]. The incorporation of nanoscale TiO₂ particles into energetic composites has demonstrated significant improvements in burning rates [27].

This study aims to investigate the effects of activated carbon (AC), both independently and in conjunction with metal oxides—specifically bismuth oxide (Bi₂O₃), molybdenum trioxide (MoO₃), and zinc oxide (ZnO)—as additives on the thermal decomposition kinetics of the ammonium nitrate–magnesium–nitrocellulose (AN–Mg–NC) composite. The Kissinger method provides a theoretical framework for developing efficient composites and analyzing the kinetics of decomposition reactions in various composite materials. This method was applied to the AN–Mg–NC, AN–Mg–NC–AC, and AN–Mg–NC–AC–Me_xO_y (where Me = Bi, Mo, Zn) composites to calculate their activation energies based on differential scanning calorimetry (DSC) analysis results. By examining the synergistic interactions of these additives, this research seeks to enhance the understanding of the influence of metal oxides on the thermal decomposition kinetics of ammonium nitrate-based energetic materials (EMs). The findings of this study present an opportunity to advance the development of propellants by improving their efficiency and reliability for solid propellant applications, as well as for other applications that require precise control over combustion and ignition processes.

2. Materials and Methods

2.1. Materials

The ammonium nitrate (AN, NH₄NO₃, Sigma Aldrich (St. Louis, MO, USA), ACS reagent grade, ≥98%) was used in composites as an oxidizing agent. Magnesium (Mg, Sigma Aldrich (Taufkirchen, München, Germany), powder, ≥99%) with a particle size

ranging from 0.06 to 0.30 mm was used as the fuel component. Nitrocellulose (NC, $C_6H_8O_5(NO_2)_2$, Skylighted, Inc. (Round Hill, WV, USA) with a degree of nitration of 12% was served as an energetic polymer binder. The activated carbon (AC) was synthesized under controlled laboratory conditions and used as fuel component. Bismuth (III) oxide (Bi_2O_3 , Sigma Aldrich (Taufkirchen, München, Germany), nano powder 90–210 nm, 99.8% trace metals basis), molybdenum (VI) oxide (MoO_3 , Sigma Aldrich (Taufkirchen, München, Germany), nano powder < 100 nm, 99.5% trace metals basis), and zinc oxide (ZnO , Sigma Aldrich (Taufkirchen, München, Germany), nano powder < 100 nm) were used as catalytic additives and mechanically integrated into the pores of the AC through planetary milling.

Activated carbon (AC) was derived from an agricultural byproduct—rice husk (RH), carbonized at the Laboratory of Energy-intensive Nanomaterials of the Institute of Combustion Problems (Almaty, Kazakhstan). The production process involved utilizing an iron reactor in an argon atmosphere, following the methodology outlined in [28]. After carbonization, the AC underwent immersion in a KOH solution to eliminate the by-product SiO_2 . Subsequently, the solution was decanted to remove the base, and the AC-containing material was activated at 400 °C in the reactor. The synthesized AC then underwent multiple washing cycles with distilled water (approximately 20 cycles) until reaching a pH of 7.0. These procedures resulted in the production of AC with a high specific surface area of roughly 1200 m²/g (determined through BET analysis) and an absorption capacity of around 300 mL/g (measured using methylene blue).

2.2. Equipment

The masses of all components were determined using an analytical balance “Shimadzu AY220” (Shimadzu Corporation, Kyoto, Japan). Thermal analysis of the prepared composites was conducted using the “NETZSCH DSC 204 F1” thermogravimetric analyzers to investigate the effects of AC–Me_xO_y (Me = Bi, Mo, Zn) additives on the thermal decomposition kinetics of the basic AN–Mg–NC composition. This analysis also aimed to calculate the activation energies and assess the effectiveness of AC–Me_xO_y (Me = Bi, Mo, Zn) as catalytic additives via the Kissinger method.

2.3. Methods

2.3.1. Oxygen Balance Calculation

Oxygen Balance (OB), a frequently employed method in the evaluation of solid propellants, was used to determine the sufficiency of oxygen within a composite for the full oxidation of all component elements [29]. The assessment of OB functions as a predictive tool to ascertain whether a substance will undergo complete combustion or yield residual products. Table 1 provides the essential data for the subsequent oxygen balance calculation of the AN–Mg–NC and AN–Mg–NC–AC–Me_xO_y (where Me = Bi, Mo, Zn) composites.

Table 1. The initial data for oxygen balance calculation.

Composite Components (n)	Mass Ratio (m_n)	Molecular Weight (MW, g/mol)	Oxygen Content (OC, g/mol)
Ammonium nitrate (NH_4NO_3)	80%	80.0	48.0
Magnesium (Mg)	5% (10% *)	24.3	0.0
Nitrocellulose (NC)	5% (10% *)	297.0	112.0
Additive (n)			
Activated Carbon (AC)	5%	12.0	0.0
Bismuth (III) oxide (Bi_2O_3)	5%	465.9	48.0
Molybdenum (VI) oxide (MoO_3)	5%	143.9	48.0
Zinc oxide (ZnO)	5%	81.4	16.0

* For oxygen balance calculation of the basic AN–Mg–NC composite.

In the context of mixed multicomponent explosives, a calculation sequence is commonly employed to ascertain the quantity of each component present in 1 kg of the composition [30]. To calculate OB [31] of a composite containing various components such as ammonium nitrate (AN), magnesium (Mg), nitrocellulose (NC), activated carbon (AC), and metal oxides (Bi_2O_3 , MoO_3 , and ZnO), specific steps need to be followed. These steps include the following: (a) Determining the molecular weights and oxygen content of each component; (b) Establishing the mass fractions (or masses) of each component in the compound. It is crucial to compute the molecular weight (MW) and the oxygen content contribution (Oxygen Content, OC) for each element.

The total oxygen content (OC_{total}) of the composite component (m_n) can be determined using Equation (1) and the information provided in Table 1:

$$\text{OC}_{\text{total}} = \frac{m_n}{100\%} \times \frac{\text{OC}_n}{\text{MW}_n} \quad (1)$$

The total fuel content (FC_{total}) of the composite component (m_n) can be determined using Equation (2) and the information provided in Table 1:

$$\text{FC}_{\text{total}} = \left(\frac{\sum m_n}{100\%} \right) \quad (2)$$

The oxygen balance (OB) calculation involves determining the total oxygen content and total fuel content in the AN–Mg–NC–AC– Me_xO_y (Me = Bi, Mo, Zn) composite, followed by calculating the oxygen balance (OB) according to Equation (3):

$$\text{OB} (\%) = \frac{1600}{\text{MW}} \left(\frac{\text{OC}_{\text{total}}}{1 \text{ kg}} - \frac{2 \times \text{FC}_{\text{total}}}{1 \text{ kg}} \right) \quad (3)$$

Oxygen balance is essential for solid propellants as it assesses the availability of oxygen to completely oxidize all elements, such as carbon and hydrogen. Determining the OB is crucial in predicting whether a compound will undergo complete combustion or leave residues, thus, providing insights into its performance and safety attributes.

2.3.2. Activation Energy Calculations via the Kissinger Method

The Kissinger method is a widely used technique for calculating the activation energy (E_a) of a chemical reaction, particularly within the context of thermal analysis. This method involves utilizing the peak temperature derived from differential scanning calorimetry (DSC) analysis at different heating rates to ascertain E_a . Through the construction of a graph that plots the natural logarithm of the heating rate divided by the square of the peak temperature (T_{max}) against the reciprocal of the peak temperature, a linear correlation can be established. As per the Kissinger equation, the slope of this line is directly proportional to E_a . This method offers a direct and dependable approach for evaluating the kinetic parameters of the thermal decomposition of the composites, eliminating the necessity of understanding the reaction mechanism.

3. Results

3.1. Oxygen Balance Calculations

The concept of oxygen balance (OB) is predominantly applied in the context of energetic materials to assess the potential for a composite to undergo full combustion or decomposition. To ensure the thorough oxidation of the AN–Mg–NC–AC– Me_xO_y (where Me = Bi, Mo, Zn) components to their corresponding higher oxides (if any) during the combustion process, we calculated the OB for each composite sample according to Equations (1)–(3). The results of these calculations are presented in Table 2. The objective of conducting an OB calculation is to assess the stoichiometric equilibrium of oxygen in various composites, including AN–Mg–NC, AN–Mg–NC–AC and AN–Mg–NC–AC– Me_xO_y (Me = Bi, Mo, or Zn).

Table 2. The calculated total oxygen content (OC_{total}), total fuel content (FC_{total}), and oxygen balance (OB) for AN–Mg–NC, AN–Mg–NC–AC and AN–Mg–NC–AC– Me_xO_y ($Me = Bi, Mo, Zn$) composites based on 1 kg of the material.

Composite	Total Oxygen Content (OC_{total} , kg)	Total Fuel Content (FC_{total})	Oxygen Balance (OB)
AN–Mg–NC	0.517	0.162	+3.27%
AN–Mg–NC–AC	0.499	0.150	+3.95%
AN–Mg–NC–AC– Bi_2O_3	0.504	0.150	+3.14%
AN–Mg–NC–AC– MoO_3	0.515	0.150	+4.61%
AN–Mg–NC–AC– ZnO	0.508	0.150	+3.94%

A positive oxygen balance, as illustrated in Table 2, across all composites signifies an oxygen surplus in the composite. This surplus can potentially improve combustion efficiency and mitigate the production of harmful by-products (for example, carbon monoxide (CO), soot, etc.).

3.2. Thermal Decomposition Characteristics from DSC Analysis

The thermal analysis method referred to as differential scanning calorimetry (DSC) offers a swift and efficient means of examining the thermal ignition properties of energetic materials (EMs). Each sample underwent DSC measurements three times to ensure reliability. Figure 1 illustrates the DSC curve obtained from the basic AN–Mg–NC composite when exposed to a heating rate of $\beta = 5$ K/min in a nitrogen atmosphere.

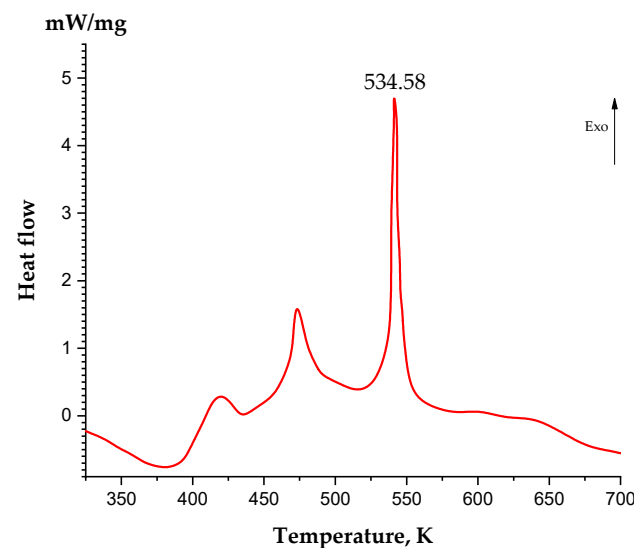


Figure 1. DSC curve of an AN–Mg–NC basic composite heated at $\beta = 5$ K/min.

The decomposition of the AN–Mg–NC basic composite is depicted in Figure 1, showing a three-stage exothermic reaction. The maximum exothermic peak occurs at $T_{max} = 534.58$ K, corresponding to the decomposition of AN, with a heat release of 4.7 mW/mg. Additionally, an initial minor heat absorption peak at ~ 420 K is likely associated with the polymorphic transition of AN, accompanied by an endothermic peak at ~ 475 K that could be attributed to water evaporation.

Figure 2 depicts the DSC curves derived from the AN–Mg–NC–AC and AN–Mg–NC–AC– Me_xO_y (where $Me = Bi, Mo, Zn$) composites when subjected to heating at a rate of $\beta = 5$ K/min in a nitrogen environment.

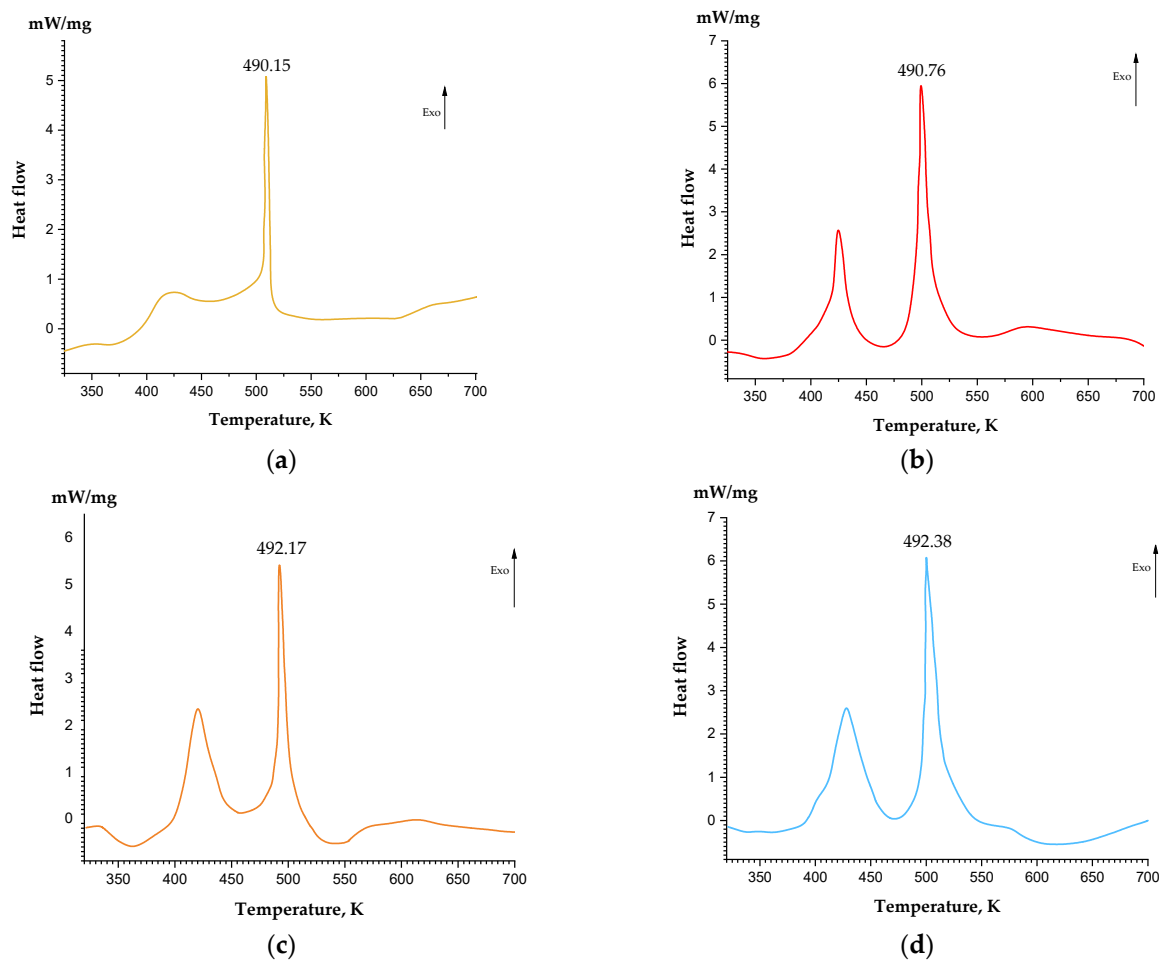


Figure 2. DSC curves of (a) AN-Mg-NC-AC; (b) AN-Mg-NC-AC-Bi₂O₃; (c) AN-Mg-NC-AC-MoO₃; (d) AN-Mg-NC-AC-ZnO composites heated at $\beta = 5$ K/min.

Figure 2 illustrates the DSC curves for AN-Mg-NC-AC, AN-Mg-NC-Bi₂O₃, AN-Mg-NC-AC-MoO₃, and AN-Mg-NC-AC-ZnO composites. The inclusion of AC (Figure 2a) significantly altered the thermal behavior of the AN-Mg-NC-AC composite. The second peak experiences a decrease to $T_{\max} = 490.15$ K (with a heat release of 5.1 mW/mg) in comparison with the basic AN-Mg-NC composite with $T_{\max} = 534.58$ K (with a heat release of 4.7 mW/mg).

The inclusion of the AC-Bi₂O₃ additive (Figure 2b) brought about a notable change in the thermal characteristics of the AN-Mg-NC composite. The second peak exhibited a reduction to $T_{\max} = 490.76$ K (accompanied by a heat release of 6.0 mW/mg) compared to the basic AN-Mg-NC composite, which had $T_{\max} = 534.58$ K and a heat release of 4.7 mW/mg.

The incorporation of the AC-MoO₃ additive (Figure 2c) into the basic composite AN-Mg-NC leads to an accelerated decomposition rate of the AN-Mg-NC-AC-MoO₃ composite. The decomposition temperature decreases to 492.17 K (accompanied by a heat release of 5.5 mW/mg) compared to 534.58 K for the initial AN-Mg-NC composite, with a heat release of 4.7 mW/mg.

The incorporation of the AC-ZnO additive (Figure 2d) into the basic composite AN-Mg-NC leads to an accelerated decomposition rate of the AN-Mg-NC-AC-ZnO composite. The decomposition temperature decreases to 492.38 K (accompanied by a heat release of 6.1 mW/mg) compared to 534.58 K for the initial AN-Mg-NC composite, which has a heat release of 4.7 mW/mg.

The absence of endothermic peaks, which are typically indicative of water evaporation, observed in Figure 2a–d, in contrast to the basic AN–Mg–NC composite presented in Figure 1, may be attributed to the adsorption characteristics of AC.

The DSC analysis demonstrates that the inclusion of different additives (AC–Bi₂O₃, AC–MoO₃, and AC–ZnO) in the AN–Mg–NC composite significantly accelerates the decomposition process. This is evident from the decrease in decomposition temperature from 534.58 K to approximately 490–492 K. Furthermore, these additives amplify the heat release during decomposition, elevating it from 4.7 mW/mg to values between 5.5 and 6.1 mW/mg. This indicates that the additives facilitate quicker decomposition and contribute to a more exothermic reaction. Such enhancements could be advantageous for applications requiring controlled and efficient energy release.

3.3. Kinetics via the Kissinger Method

The Kissinger method is widely used for determining the activation energy (E_a) of thermally stimulated processes investigated through techniques such as differential scanning calorimetry (DSC). The E_a determination can be conducted via the Kissinger method, which is based on the Arrhenius equation that elucidates the relationship between the rate of a chemical reaction and temperature. By plotting the natural logarithm of the heating rate divided by the square of the peak temperature against the reciprocal of the peak temperature, a linear correlation is established. The slope of this linear relationship, as per the Kissinger equation, is directly correlated to the activation energy. This approach simplifies the determination of kinetic parameters for thermal decomposition processes, providing a reliable and effective means to analyze reactions without necessitating an in-depth understanding of the reaction mechanism.

The Kissinger method uses the following formula to determine the activation energy (Equation (4)) [32]:

$$E_a = -R \frac{d \ln \left(\frac{\beta}{T_p^2} \right)}{dT_p^{-1}} \quad (4)$$

β —heating rate (K/min); T_p —peak temperature (K) at which the reaction rate is maximum; E_a —activation energy (J/mol); R —universal gas constant (8.314 J/mol·K).

The kinetic parameters of the thermal decomposition of the basic AN–Mg–NC composite are outlined in Table 3.

Table 3. Detailed results of the activation energy (E_a) calculation for the basic AN–Mg–NC composite using the Kissinger method.

$T_{\max}$, K	$1/T_{\max}$	Heating Rate (β), K/min	$\ln (\beta/(T_{\max})^2)$
534.58	0.00187	5	−12.37
549.20	0.00182	10	−12.34
556.20	0.00180	15	−12.32
567.71	0.00176	20	−12.30
From Kissinger Plot			
Slope:			−11,910.06
Intercept:			11.36
E_a :			99.02 kJ/mol

The plot (Figure 3) effectively illustrates the application of the Kissinger method in determining the activation energy (E_a) for the reaction of the AN–Mg–NC composite. A linear regression line is fitted to the data points, representing the optimal fit line based on the least squares method. The negative slope of the line aligns with the Kissinger equation.

The calculation based on the slope yields E_a of approximately 99.02 kJ/mol. The linear correlation and the derived E_a offer significant insights into the thermal decomposition kinetics of the composite material.

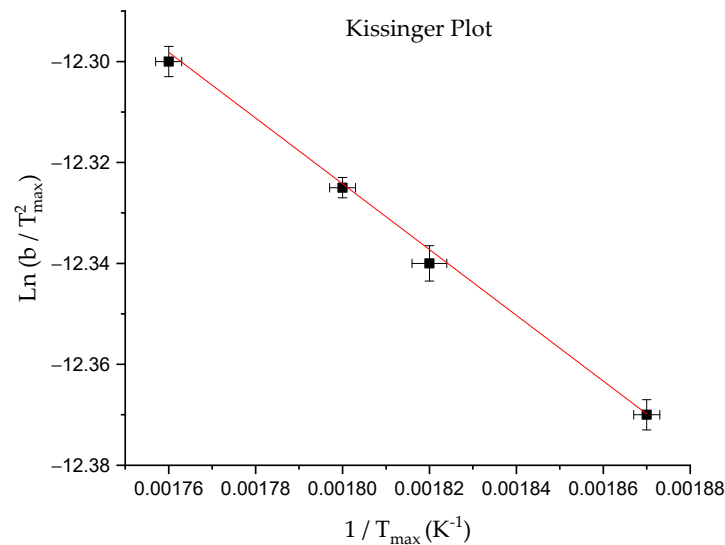


Figure 3. Kissinger plot of the basic AN–Mg–NC composite.

For the AN–Mg–NC–AC composite, the kinetic parameters of the thermal decomposition were calculated using the Kissinger method (Table 4).

Table 4. Detailed results of the activation energy (E_a) calculation for the AN–Mg–NC–AC composite using the Kissinger method.

$T_{\max}$, K	$1/T_{\max}$ (K ^{−1})	Heating Rate (β), K/min	$\ln(\beta/(T_{\max})^2)$
490.15	0.00204	5	−10.78
512.17	0.00197	10	−10.17
514.12	0.00194	15	−9.77
522.18	0.00191	20	−9.52
From Kissinger Plot			
Slope:			−9818.63
Intercept:			9.21
E_a :			93.63 kJ/mol

The plot (Figure 4) successfully demonstrates the use of the Kissinger method to determine E_a for the reaction of the AN–Mg–NC–AC composite. The negative slope of the line is expected according to the Kissinger method. From the slope of the line, E_a was calculated to be approximately 93.63 kJ/mol. The linear relationship and the calculated E_a provide valuable insights into the thermal decomposition kinetics of the composite material.

For the AN–Mg–NC–AC–Bi₂O₃ composite, the kinetic parameters of the thermal decomposition were calculated using the Kissinger method (Table 5).

The plot (Figure 5) successfully demonstrates the use of the Kissinger method to determine E_a for the reaction of the AN–Mg–NC–AC–Bi₂O₃ composite. The negative slope of the line is expected according to the Kissinger method. From the slope of the line, E_a was calculated to be approximately 91.45 kJ/mol. The linear relationship and the

calculated E_a provide valuable insights into the thermal decomposition kinetics of the composite material.

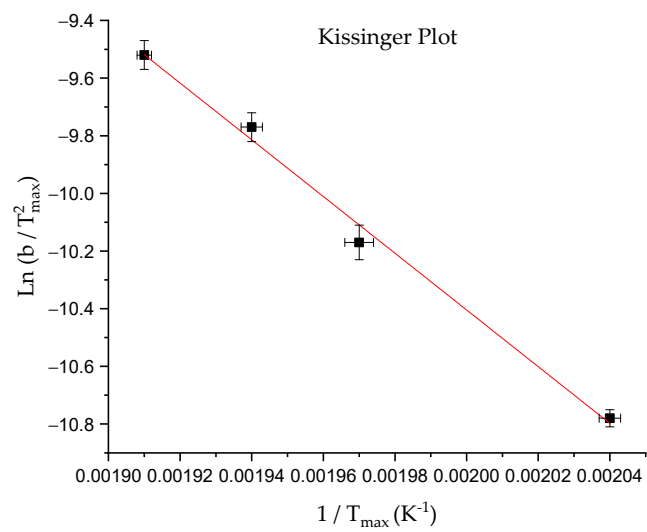


Figure 4. Kissinger plot of the AN-Mg-NC-AC composite.

Table 5. Detailed results of the activation energy (E_a) calculation for the AN-Mg-NC-AC-Bi₂O₃ composite using the Kissinger method.

T_{max}, K	$1/T_{max} (K^{-1})$	Heating Rate (β), K/min	$\ln (\beta/(T_{max})^2)$
490.76	0.002038	5	−10.78
511.59	0.001974	10	−10.17
513.82	0.001946	15	−9.77
518.33	0.001929	20	−9.59
From Kissinger Plot			
Slope:			−10,001.74
Intercept:			11.58
E_a :			91.45 kJ/mol

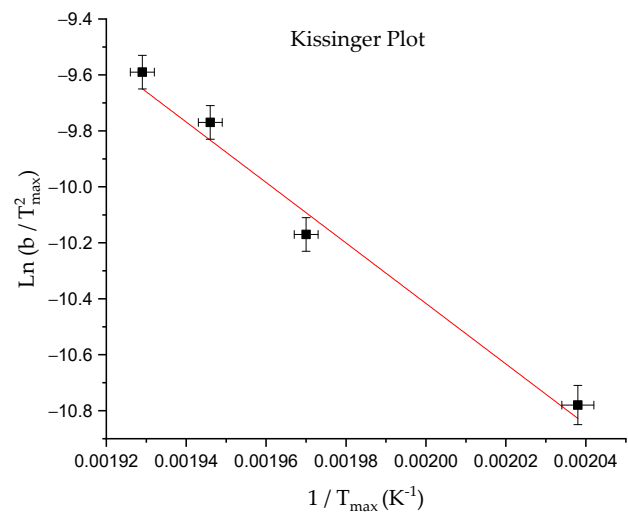


Figure 5. Kissinger plot of the AN-Mg-NC-AC-Bi₂O₃ composite.

For the AN–Mg–NC–AC–MoO₃ composite, the kinetic parameters of the thermal decomposition were calculated using the Kissinger method (Table 6).

Table 6. Detailed results of the activation energy (E_a) calculation for the AN–Mg–NC–AC–MoO₃ composite using the Kissinger method.

$T_{\max}$, K	$1/T_{\max}$	Heating Rate (β), K/min	$\ln (\beta/(T_{\max})^2)$
492.17	0.002032	5	−10.78
511.60	0.001967	10	−10.17
515.72	0.001939	15	−9.78
520.63	0.001921	20	−9.51
From Kissinger Plot			
Slope:			−10,023.35
Intercept:			11.55
E_a :			91.65 kJ/mol

Figure 6 demonstrates that the obtained data points exhibit a good linear relationship, which validates the use of the Kissinger method for calculating the activation energy (E_a). The negative slope obtained from the linear fit directly relates to E_a . The larger the absolute value of the slope, the higher the E_a . The consistency of the data points along the linear fit suggests reliable and reproducible measurements of $T_{\max}$ and heating rates.

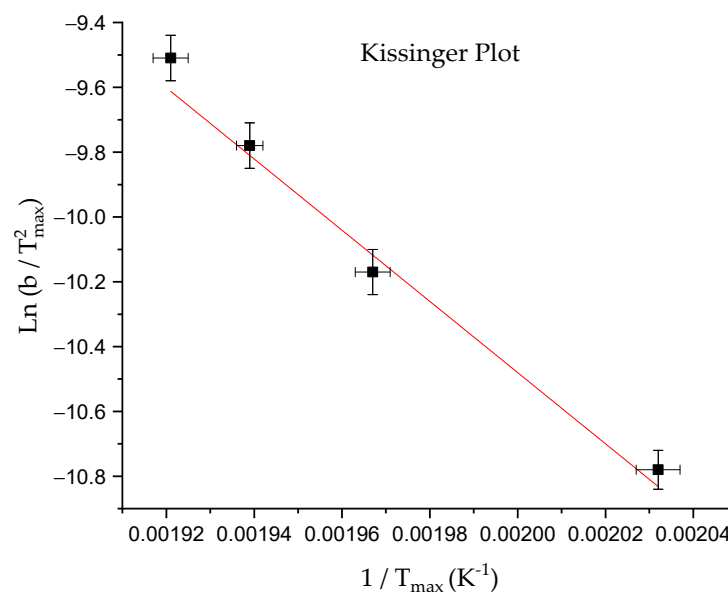


Figure 6. Kissinger plot of the AN–Mg–NC–AC–MoO₃ composite.

The Kissinger method provides a precise and efficient approach to calculating the E_a of the AN–Mg–NC–AC–MoO₃ composite. The E_a derived from this plot is 91.65 kJ/mol, signifying a lower energy barrier that must be surpassed for the reaction to advance compared to the basic AN–Mg–NC composite, which has an activation energy of 99.02 kJ/mol.

The kinetic parameters of the thermal decomposition for the AN–Mg–NC–AC–ZnO composite, as determined through the Kissinger method, are outlined in Table 7.

Table 7. Detailed results of the activation energy (E_a) calculation for the AN–Mg–NC–AC–ZnO composite using the Kissinger method.

$T_{\max}$, K	$1/T_{\max}$	Heating Rate (β), K/min	$\ln (\beta/(T_{\max})^2)$
492.38	0.002031	5	−10.77
510.99	0.001966	10	−10.11
516.23	0.001937	15	−9.78
521.11	0.001919	20	−9.51
From Kissinger Plot			
Slope:			−10,038.08
Intercept:			11.58
E_a :			91.76 kJ/mol

Figure 7 demonstrates that the data points exhibit a good linear relationship, which validates the use of the Kissinger method for calculating the activation energy (E_a). The negative slope obtained from the linear fit directly relates to the E_a . The larger the absolute value of the slope, the higher the E_a . The consistency of the data points along the linear fit suggests reliable and reproducible measurements of $T_{\max}$ and heating rates. The Kissinger plot provides a clear and effective way to determine the E_a of the AN–Mg–NC–AC–ZnO composite. Considering the total number of exothermic peaks identified through DSC analysis, the E_a for the AN–Mg–NC–AC–ZnO composite was determined to be 91.76 kJ/mol, indicating that the energy barrier that needs to be overcome for the reaction to proceed is lower than that of the basic AN–Mg–NC composite. The summary of the kinetic parameters of AN–Mg–NC and AN–Mg–NC–AC–Me_xO_y (Me = Bi, Mo, or Zn) and the comparison which was calculated using the Kissinger method are outlined in Table 8.

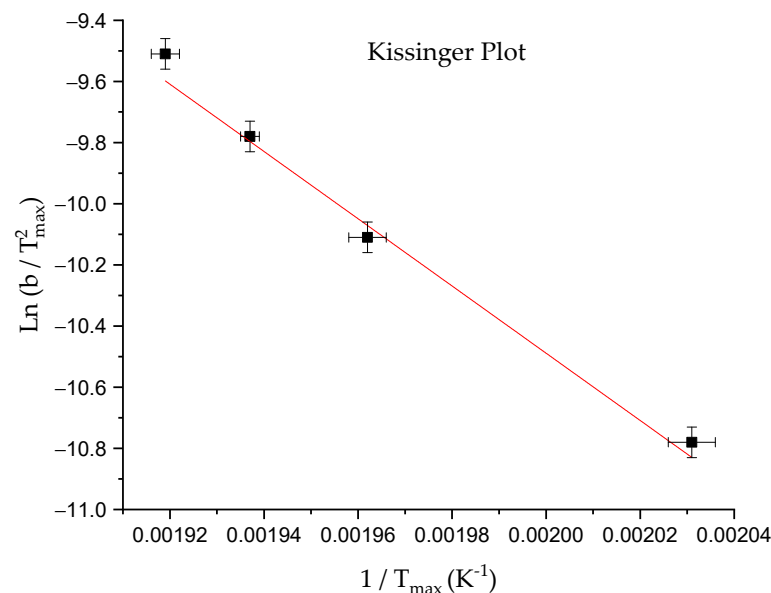
**Figure 7.** Kissinger plot of the AN–Mg–NC–AC–ZnO composite.

Table 8 presents a comparative analysis of the kinetic parameters related to the thermal decomposition of various ammonium nitrate (AN) and AN-based composites, as determined via the Kissinger method. The pure AN sample exhibits a range of $T_{\max}$ values, indicating diversity in their respective thermal decomposition temperatures. The activation energy (E_a) demonstrates notable variation among the pure AN samples, implying discrepancies in their thermal stability, potentially influenced by impurities or distinct experimental conditions. The $\ln(\beta/(T_{\max})^2)$ values for pure AN are predominantly

negative, a characteristic feature of substances with a high E_a , suggesting a pronounced temperature dependency of the reaction rate. In contrast, the $T_{\max}$ value for the AN–Pyrite composite is notably higher (648.15 K) than that of pure AN, signifying that the presence of pyrite enhances the stability of AN, necessitating a higher temperature for decomposition. The E_a value for AN–Pyrite is comparable to that of pure AN, indicating that while pyrite enhances thermal stability, it does not significantly alter the energy barrier for the decomposition reaction.

Table 8. Data summary of the kinetic parameters estimated using the Kissinger method at a heating rate of 5 K/min.

Composite	$T_{\max}$, K ($\beta = 5$ K/min)	$\ln (\beta/(T_{\max})^2)$	E_a , kJ/mol	Reference
Pure AN	543.00	−10.98	155.80	[33]
AN–Pyrite	648.15	−12.25	101.80	[34]
AN–Mg–NC	534.58	−12.37	99.02	Current study
AN–Mg–NC–AC–Bi ₂ O ₃	490.76	−10.78	91.45	Current study
AN–Mg–NC–AC–MoO ₃	492.17	−10.76	91.65	Current study
AN–Mg–NC–AC–ZnO	492.38	−10.77	91.76	Current study

In the current study, the thermal decomposition behavior of AN–Mg–NC and AN–Mg–NC–AC–Me_xO_y (Me = Bi, Mo, or Zn) composites was investigated. The results show that the $T_{\max}$ values of these composites are typically lower than those of pure AN and AN–Pyrite. This suggests that the obtained composites decompose at lower temperatures, which could be advantageous for applications that require lower decomposition temperatures. Furthermore, the E_a values for these composites are generally lower than those for pure AN, indicating that the AC–Me_xO_y additives aid in the decomposition process by reducing the energy barrier. Additionally, the values of $\ln(\beta/(T_{\max})^2)$ are less negative compared to pure AN, suggesting a decreased temperature dependency of the reaction rate and potentially a more controlled decomposition process.

4. Discussion

This study aimed to investigate the impact of activated carbon (AC) in conjunction with different metal oxides (Bi₂O₃, MoO₃, and ZnO) on the thermal decomposition kinetics of the basic AN–Mg–NC composite via the Kissinger method. The results offer convincing proof of the catalytic effectiveness of these additives in altering the thermal properties of the composite, thereby holding substantial implications for the advancement of sophisticated energetic materials.

The thermal properties of the AN–Mg–NC composite with and without the AC–Me_xO_y (Me = Bi, Mo, Zn) additives were evaluated using differential scanning calorimetry (DSC) analysis. The incorporation of AC–Me_xO_y additives led to a notable reduction in the decomposition peak temperature, as revealed by the DSC data. This significant decline in decomposition temperature highlights the catalytic function of these additives in improving the thermal reactivity of the basic composite.

The activation energies (E_a) for the decomposition reactions, determined via the Kissinger method, indicate a decrease in E_a for the composites incorporating the AC–Me_xO_y additives. This decline in E_a suggests a more efficient decomposition process, facilitated by the catalytic influence of the additives. The observed thermal behavior can be explained by the catalytic mechanism resulting from the synergistic effects between AC and Me_xO_y. The high surface area of AC facilitates the dispersion of metal oxides, which serve as catalytic sites. The metal oxide (Me_xO_y) promotes electron transfer processes, reducing the energy barriers for bond dissociation in the AN–Mg–NC composite.

The improved thermal characteristics of the AN–Mg–NC–AC–Me_xO_y composites have important implications for the advancement of energetic materials. The reduced

decomposition temperatures and activation energies indicate that these composites may attain increased burning rates and enhanced performance, which are crucial for their application in solid propellants. The results indicate that AC–Me_xO_y additives have the potential to customize the thermal properties of energetic materials, thereby boosting their effectiveness and dependability.

While this study has offered valuable insights into the catalytic effects of AC–Me_xO_y additives, additional research is required to comprehend the underlying mechanisms and to optimize the additive compositions for specific applications. Future studies could explore the impacts of varying ratios of activated carbon to metal oxides, along with exploring the potential advantages of using alternative metal oxides. Furthermore, it is imperative to examine the long-term stability and compatibility of these additives with other constituents in energetic formulations.

5. Conclusions

This study presents a conclusive demonstration of the substantial catalytic impact achieved by the incorporation of activated carbon (AC) in conjunction with metal oxides (Bi₂O₃, MoO₃, or ZnO) on the thermal decomposition kinetics of the basic AN–Mg–NC composite. Through a comprehensive analysis involving the DSC technique and the application of the Kissinger method, it was observed that the introduction of AC–Me_xO_y (Me = Bi, Mo, Zn) significantly reduces the decomposition peak temperature ($T_{\max}$) and lowers the activation energy (E_a) of the composites. The DSC results revealed a decrease in the peak decomposition temperature from 534.58 K (for AN–Mg–NC) to 490.15 K (with AC), 490.76 K (with AC–Bi₂O₃), 492.17 K (with AC–MoO₃), and 492.38 K (with AC–ZnO), underscoring the catalytic efficacy of the additives. Furthermore, the E_a values decreased from 99.02 kJ/mol for the basic composite to approximately 93.63, 91.45, 91.65, and 91.76 kJ/mol with the inclusion of AC, AC–Bi₂O₃, AC–MoO₃, and AC–ZnO, respectively.

From a scientific standpoint, these catalytic effects can be attributed to the ability of AC–Me_xO_y (Me = Bi, Mo, Zn) additives to facilitate the more efficient breakdown of chemical bonds in the basic AN–Mg–NC composite. Activated carbon provides a substantial surface area for interactions, while metal oxides serve as active sites for catalysis. These sites likely enhance electron transfer processes and lower the energy barriers for the decomposition reactions, resulting in decreased decomposition temperatures and reduced activation energies. The synergistic interaction between activated carbon and metal oxides accelerates the thermal decomposition process, making the energetic material more reactive and efficient.

The obtained results highlight the potential of AC–Me_xO_y additives to significantly improve the performance, efficiency, and reliability of AN-based energetic materials, making them highly suitable for advanced solid propellant applications. The enhanced thermal properties and reduced activation energies suggest that these composites can achieve higher burning rates and superior overall performance, which are essential factors in the development of effective and reliable solid propellants.

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