Self-catalyzed nanoscale ammonium perchlorate for advanced composite solid rocket propellant

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Abstract
Ammonium perchlorate (AP) is still one of the most important oxidizers used. Improving propellant output becomes an interesting source for many researchers. Due to its large surface area and high surface energy, nanomaterials have a wide range of applications in propellant formulations. High surface energy is responsible for the relatively low energy of activation and higher burning composition. This paper reports on a liquid-state method of synthesizing nanoscale AP. The resulting AP particles were characterized using electron scanning microscopy (SEM), energy dispersive x-ray spectrometer (EDX), x-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermal gravimetric analysis (TGA). Kissinger and KAS techniques were used to measure the activation energy of nanoscale AP and microscale AP. The results showed that nanoscale AP possessed stronger catalytic activity than microscale AP where the temperature of decomposition fell from 452.8 °C to 388.1 °C and the heat released increased from 835.3 J g⁻¹ to 3127 J g⁻¹. The findings of the kinetics study showed that the nanoscale of the synthesized AP has a direct effect on the activation energy of AP, where the activation energy of AP decreased from 226.0. kJ.mol⁻¹ to 52.0 kJ.mol⁻¹.

1. Introduction
Due to its large surface area, which provides high surface energy, nanomaterials are in high demand for use in propellant compositions [1]. This high surface energy is responsible for the nanomaterial’s low activation power, decreasing the temperature of the nanoparticle’s decomposition [2]. To exploit the advantages of nanomaterial properties, high-energy materials such as royal department explosives (RDX) and high melting explosives (HMX) were prepared and used in the nanoform in which the energy release is very rapid, which is responsible for the high burning rate [3] and high specific impulse [4] of propellant compositions. AP is one of the most effective oxidizing agents used in various propellants [5]. AP thermal decomposition significantly affects the propellant’s combustion behavior. AP thermal decomposition, which is a part of the solid propellant combustion process, has a direct effect on propellant burning behavior [6]. The influence of the catalytic activity of nanometer-sized metal oxides upon the thermal decomposition of AP was experimentally studied on a large scale [2]. This could be attributed to the sensitivity of these formulation’s burning actions towards AP decomposition [7]. Several studies have shown that the size of AP particles influences their thermal decomposition, which directly affects the burning behavior of propellant formulations [8]. Nanoscale AP particles have been prepared using the Kumari method (non-aqueous method) [9, 10]. Next, AP particles were dissolved in methanol. Hydroxyl-terminated polybutadiene (HTPB) was then applied to the mixture, accompanied by solvent vacuum distillation to prepare AP particles in a nanoscale [9]. Using this process, preparing nanoscale AP was more complicated and not easier to get nanoscale AP free from the binder. Guoping Li et al. prepared AP focused on Nano-Limit Growth Energy Materials (NLGEM) using SiO₂ gel as nano-Limit Growth Skeleton Materials and using sol-gel process mixing crystallization solution [10]. AP was then recycled to form AP/SiO₂ (NLGEM) in the nanopores of the SiO₂ gel skeleton. The preparation of nanoscale AP particles

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was found to have a particle size range of 69 nm to 108 nm, however, the AP/SiO\textsubscript{2} NLGEM decomposition temperature was higher than that of pure AP which harmed the burning behavior of the propellants \cite{10}.

In the present study, nanoscale AP particles were synthesized for the first time using the liquid-state method based on the combination of co-precipitation and sonication techniques. This synthesized technique successfully produced high-purity nanoscale AP particles. The resulting nanoscale AP particles were characterized; their effect on the packing density of conventional composite solid rocket propellant (CSRP) formulation was evaluated concerning the mechanical and ballistics properties.

2. Experimental work

2.1. Materials

Ammonium perchlorate with different average particle sizes of (400 μm, 200 μm, 150 μm, and (7–11 μm)) was procured from (Sigma Aldrich). Acetone (solvent), dichloromethane (anti-solvent), Dioctyl azelate (DOZ) (plasticizer), Hexamethylene diisocyanate (HMDI) (curing agent), Methyl aziridinyl phosphenoxyde (MAPO) (bonding agent), and Hydroxyl-terminated polybutadiene (HTPB), manufactured by free radical solution polymerization, with an average molecular weight of 2,500 and a hydroxyl value of 43 mg KOH/g were purchased from (Sigma Aldrich). Aluminum powder, with an average particle size of (40 μm – (8–22 μm)) was procured from (Morgan Company). All materials were used as received without further purification.

2.2. Synthesis of nanoscale AP by the liquid state method

Firstly, AP microparticles as received were crushed using a mortar and pestle. Then, 6 g of AP was dissolved in 100 ml of acetone using a magnetic stirrer at room temperature for 12 h. The AP-acetone mixture was then added drop by drop to 200 ml of dichloromethane under a high-amplitude sonication using a sonication probe for 30 min. Dichloromethane acts as an anti-solvent during the liquid state methodology. Gradually, small droplets of AP in the form of nanoparticles start to precipitate. The precipitated AP nanoparticles were then collected and subjected to a distillation process followed by drying before weighing the product. The yield of the obtained nanoscale AP particles was found to be 95% approximately. All electrical equipment used during the synthesis of nanoscale AP was flameproof and properly grounded. The complete experimental setup was installed in a fume hood to reduce exposure to hazardous solvent/chemicals. Personal safety facilities were utilized including masks, aprons, gloves to reduce the hazards levels. Figure 1 simply explains the steps of the liquid state process to obtain AP nanoparticles.

2.3. Characterization

A scanning electron microscope (CARL ZEISS EVO MA 10) was used to investigate the surface morphology, particle size, and purity of synthesized nanoscale AP particles with three detector types of secondary electrons (SE), back-scattered electron (BSE), and energy-dispersive x-ray spectrometer, (EDX, Bruker Quanta 200). The
purity and average particle size were investigated by (XRD, Thermo-Scientific XTRA Powder diffract-meter), over the angle range from 5 to 80 °C; Scherrer’s formula was used to estimate the crystallite size.

2.4. Catalytic analysis
The thermal decomposition analysis for AP and the synthesized nanoscale AP particles (self-catalyzed AP) was performed with (DSC, Q20 USA). The analysis required a 5 °C min⁻¹ heating rate, N₂ atmosphere, a temperature range of 20 °C to 500 °C, and a 1.0 mg sample weight. The weight loss change of AP particles (microscale, nanoscale) was investigated versus temperature using (TGA 55, USA). The measured sample was heated at a heating rate of 5 °C min⁻¹ from 50 to 500°C below the N₂ flow rate of 25 ml min⁻¹.

2.5. Kinetics analysis
The TGA experiments were performed at four temperatures 2, 4, 6, and 8 °C min⁻¹. It is very important to obtain the third kinetic parameters that are the pre-exponential variable (A), kinetic model (f(t)), and activation energy (Eₐ) for kinetic analysis, which should be calculated to obtain all kinetic definition points. There are many analytical methods available today that could be used to evaluate the kinetic parameters of solid-phase reactions. The two key methods for evaluating the kinetic parameters are iso–convensional (model-free) and model fitting methods, which could be used either isothermally or non-isothermally [11, 12].

2.5.1. Activation energy calculation
The sample decomposition reaction activation energy (Eₐ) could be measured using Kissinger’s method (equation (1))[13]

\[
\frac{-E_a}{R} = \frac{d \ln(\beta/T_p^3)}{d(1/T_p)}
\]

Where \( \beta \) is the heating rate and \( T_p \) is the derivative thermogravimetric (DTG) peak temperature at that rate. The activation energy could be calculated from the slope of the straight line of \( \ln(\beta/T_p^3) \) versus \( 1/T_p \). These rough integral temperatures approximation could cause \( E_a \) to be calculated inaccurately \[13, 14\]. According to Starink [15], a more precise formula was proposed for calculating \( E_a \), commonly known as the Kissinger—Akahira—Sunose equation (KAS) (equation (2))

\[
\ln \left( \frac{\beta_i}{T_p^{1.92}} \right) = \text{Const} - 1.0008 \frac{E_a}{R T_\alpha}
\]

2.6. Studying the effect of nanoscale AP particles addition on the packing density of conventional CSRP
The density of the packaging was determined by calculating the volume of the measured mass of the powder sample passed into the graduated cylinder. The packing density is expressed in grams per milliliter (g ml⁻¹) by the formula \( M/V_o \). AP, which is the main component in conventional CSRP formulations, was processed into coarse and fine fractions (400 μm, 200 μm) and (7–11 μm) respectively, where 400 μm, 200 μm and (7–11 μm) were percent in 55%, 23%, and 22% respectively from the percentage of AP in the conventional CSRP sample. In this study, addition of nanoscale AP particles occurred in different percentages; 3%, 6%, 9%, 12%, 15% and 18%, in three different case studies. The effect of the nanoscale AP particle addition on the conventional CSRP packing density was studied. The packing density was determined using graduated tubes and a shaker. A certain mass (5.0 gm) of AP powder, divided into coarse, fine, and ultrafine (nanoscale AP) fractions with different percentages into graduated tubes. At this stage, the shaking was introduced to enable filling the voids between AP microparticles by the AP nanoparticles. The packing density was determined in (mass (5 gm)/fixed volume) and the reading volume of the graduated tube was kept fixed.

2.7. Preparation of the propellant composition
Two propellant compositions, as shown in table 1, were prepared using a specific casting method which begins with the mixing of various ingredients using an 8 kg stainless steel mixer. The first sample represents a conventional CSRP composition while the second sample (X) represents the introduction of 9% nanoscale AP. The pre-polymer (HTPB), metallic fuel (Al), bonding agent (MAPO), and plasticizer (DOZ) were weighed as required and mixed well for 15 min at 50 °C. With a double cap, the temperature inside the stainless steel mixer was increased to 70 °C for 10 min. The dried oxidizer AP was divided into four equal portions and applied to continuous stirring within 10 min at 70 °C to the slurry in sequence. The slurry temperature was then reduced to 40 °C and the precisely measured curing agent (HMDI) weight has been applied. At this temperature, the stirring process under vacuum was continued for 15 min to ensure the homogeneity of the slurry. Stirring continued for another 5 min and the vacuum was released with nitrogen.
2.8. Characterization of the propellant composition

The hardness of the cured samples was determined using the hardness tester ZWICK (model 3102), apparatus that measures the needle penetration as a function of curing completion by the increase of the sample hardness.

Table 1. The chemical composition for composite propellant formulations.

| Ingredient (wt%) | Conventional | X  |
|-----------------|--------------|----|
| HTPB            | 10.45        | 10.45 |
| DOZ             | 2.625        | 2.625 |
| MAPO            | 0.30         | 0.30 |
| HMDI            | 0.625        | 0.625 |
| Al (40 μ)       | 11.00        | 11.00 |
| Al (8–22 μ)     | 6.00         | 6.00 |
| AP (400 μ)      | 38.00        | 33.80 |
| AP (200 μ)      | 16.00        | 13.80 |
| AP (7–11 μ)     | 15.00        | 15.10 |
| Nano AP         | 0            | 6.30 |
| Σ               | 100          | 100  |

Figure 2. SEM picture of (a) AP in microscale (b) nanoscale AP synthesized by liquid state method.

Figure 3. Elemental composition of nanoscale AP using EDX detector.
value. When shore A value for the propellant composition samples was constant for successive three days, curing was completed and samples are removed from the curing oven. The density of the cured samples was determined using Mettler Toledo XS205DU analytical balance. The density of the propellant composition samples was determined according to the standard ISO 1183-1:2004, method A. The density measurements were performed at 25 °C, where silicon oil was used as the immersion fluid. Mechanical properties such as tensile strength (TS) and strain of the cured propellant samples were evaluated using dumbbells on The Zwick Z050 universal test machine. All the ballistic properties of the prepared propellant formulations including the burning rate, operating pressure, specific impulse were measured using a standard two inches rocket motor. The tested formulations were cast successfully and the measurements were performed using a nozzle with throat diameters of 7.0, 7.3, and 7.6 mm. This secures certain operating pressures and burning rates for each examined formulation.

3. Results and discussion

3.1. SEM characterization
SEM micrographs represented in figure 2 showed that AP particles, raw material in liquid state method, and the synthesized nanoscale AP particles have an average particle size of 150 μm and 80 nm respectively. The surface of either AP microparticles or AP nanoparticles was smooth, the particles were almost round crystals and there were no sharp edges or cracks on the surface.

The elemental study of nanoscale AP particles was investigated using Bruker Quantax 200 with SEM-equipped energy dispersive x-ray spectrometer (EDX). Elemental analysis as shown in figure 3 indicated that there were no interfering elements identified in the chemical structure of nanoscale AP.
3.2. XRD characterization

The synthesized nanoscale AP particles were dried then introduced to the x-ray diffraction (XRD) to describe the crystal structure of the nanoscale AP particles. XRD diffractograms of synthesized nanoscale AP showed a pure crystalline structure for the synthesized nanoscale AP (figure 4). The XRD trends showed that all diffraction peaks comply with the International Center for Diffraction Data (ICDD) Joint Committee on Powder Diffraction Standards (JCPDS) [16]. The average crystal size of the nanoscale AP could be determined from the large diffraction peaks by the Debye-Scherer equation (equation (3)) [17].

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

Where \( k \) is a constant equal to 0.94, \( \lambda \) is the wavelength of Cu K\( \alpha \) radiation, \( \beta \) is the full width at half maximum height (FWHM) of the diffraction peak in radians, and \( \theta \) is the Bragg angles of the main planes. The Scherer formula was used to estimate the average crystal size of the nanoscale AP of 60 nm.

3.3. Catalytic activity measurements of nanoscale AP

DSC thermograms for the thermal decomposition of microscale and nanoscale AP particles are shown in figure 5. The analysis showed that the thermal decomposition of microscale AP particles occurs in three main stages: an endothermic stage of decomposition and two exothermic stages of decomposition [18–20]. The first stage is an endothermic decomposition at 242.1 °C, which could be due to the phase transition of AP from orthorhombic to cubic [21–23]. On the other hand, the second stage is the partial exothermic decomposition which occurs at 297.8 °C through the incomplete dissociation and sublimation with intermediate gaseous formation such as NH\(_3\) and HClO\(_4\) [20, 24, 25] as given in equation (4). The reaction of the evolved HClO\(_4\) and NH\(_3\) is incomplete at low temperatures; some of these species will be adsorbed to the surface of unreacted AP.
particles [21, 26, 27]. This partial AP decomposition stopped when HClO₄ and NH₃ completely covered the surface of the AP [21, 28]. This partial AP decomposition released a heat of 345.5 J g⁻¹.

\[
\text{NH}_4\text{ClO}_4 \leftrightarrow \text{NH}_4^+ + \text{ClO}_4^- \leftrightarrow \text{NH}_3(g) + \text{HClO}_4(g) \leftrightarrow \text{NH}_3(g) + \text{HClO}_4(g)
\]  

(4)

The third stage is the complete exothermic decomposition at 452.8 °C where reactions between the adsorbed HClO₄, NH₃, and other species lead to the complete decomposition of AP and the formation of several volatile terminal molecules such as HCl, H₂O, N₂O, Cl₂, NO, O₂ and NO₂ [19, 29, 30]. AP thermal decomposition was sensitive when nanoscale AP particles were present, where nanoscale AP showed high catalytic activity in AP particle thermal behavior. The effectiveness of nanoscale AP as a self-catalyzed oxidizer is that the high-temperature peak of decomposition has been reduced by 66 °C and overlapped with the low-temperature peak of decomposition with a total heat release of 3127 J g⁻¹. Nanoscale AP (self-catalyzed AP) provided a 375% increase in total AP heat release.

TGA further investigated the thermal behavior of microscale AP; the wt.% was reported as a temperature feature as given in figure 6. The data showed that two major decomposition stages occurred for microscale AP, the first stage is partial exothermic decomposition which happens at 298 °C with a weight loss of 30% wt. This stage of decomposition may correspond to the initial DSC peak of exothermic decomposition at 297.8 °C. The second stage is the complete exothermic decomposition with a wt.% loss of 69.9% at 452 °C; this decomposition peak may lead to the second major exothermic decomposition peak at 452.8 °C in DSC.

Upon nanoscale AP (self-catalyzed AP) (figure 7), TGA data showed that nano AP undergoes two major exothermic decomposition peaks are overlapped with a 99.7% wt. percent loss. DSC and TGA data indicated
that nanoscale AP (self-catalyzed AP) have more activity when compared with the microscale AP thermal decomposition, which could have a direct effect on propellant formulations burning behavior.

3.4. Kinetic studies of nanoscale AP

3.4.1. Kinetic parameters obtained by Kissinger method

The thermal decomposition kinetics of nanoscale AP were studied using TGA non-isothermal technique with four heating rates 2, 4, 6, and 8 °C.min⁻¹ (figure 8) and the activation energy was calculated by Kissinger formula using the Kissinger method. The activation energy was obtained from the slope of the straight line from plotting ln (β/T²) versus 1/T at the selected four heating rates (figure 9), where T is the peak for the decomposition temperature obtained from the DTG thermogram (figure 8). From publications, the activation energy of microscale AP by the Kissinger method was 226 kJ.mol⁻¹ for a particle size of 150 μm [25]. The activation energy of the nanoscale AP was found to be 52 kJ.mol⁻¹. It is clear from these results that AP activation energy will significantly decrease from 226 kJ.mol⁻¹ to 52.0 kJ.mol⁻¹ due to decreasing the particle size to the nanoscale. The results confirm that nanoscale AP possesses excellent catalytic skills to increase the rate of AP decomposition.

Table 2. Nanoscale AP kinetic data obtained using the system (KAS).

| α reacted | Ea, (kJ.mol⁻¹) | Log A, s⁻¹ | r    |
|-----------|----------------|------------|------|
| 0.05      | 44.2           | 5.4        | 0.985|
| 0.10      | 58.9           | 6.9        | 0.989|
| 0.15      | 65.0           | 7.4        | 0.993|
| 0.20      | 66.0           | 7.4        | 0.996|
| 0.25      | 63.8           | 7.1        | 0.991|
| 0.30      | 61.2           | 6.2        | 0.991|
| 0.35      | 59.4           | 6.5        | 0.989|
| 0.40      | 58.0           | 6.3        | 0.987|
| 0.45      | 56.9           | 6.2        | 0.990|
| 0.50      | 56.1           | 6.1        | 0.989|
| 0.55      | 55.4           | 6.0        | 0.992|
| 0.60      | 55.0           | 5.9        | 0.994|
| 0.65      | 54.6           | 5.9        | 0.994|
| 0.70      | 54.2           | 5.8        | 0.994|
| 0.75      | 53.7           | 5.7        | 0.991|
| 0.80      | 53.8           | 5.7        | 0.992|
| 0.85      | 54.2           | 5.7        | 0.989|
| 0.90      | 55.4           | 5.8        | 0.988|
| Mean      | 57.7           | 6.2        |      |

Figure 10. SEM image of ammonium perchlorate particle size 400 μm.
Figure 11. SEM image of ammonium perchlorate particle size 200 μm.

Figure 12. SEM image of ammonium perchlorate particle size 7–11 μm.

Figure 13. Variation of calculated packing density with (nanoscale AP).
3.4.2. Kinetic parameters obtained by Kissinger—Akahira—Sunose (KAS) method

The activation energy was calculated by using the revised Kissinger—Akahira—Sunose (KAS) method. Nanoscale AP kinetic parameters are shown in Table 2. The mean value of the nanoscale AP activation energies was 57.7 kJ.mol\(^{-1}\). The activation energy of the measured microscale AP (KAS) system was 276 kJ.mol\(^{-1}\) for the particle size of 150 \(\mu\)m \[^{31}\]. The result of this information is that nanoscale AP decreases AP activation energy from 276 kJ.mol\(^{-1}\) to 57.7 kJ.mol\(^{-1}\), which means that the nanoscale AP particles have a great effect on the decomposition rate of AP.

3.5. Packing density results of adding nanoscale AP on the conventional CSRP

3.5.1. SEM inspection for solid ingredients

Previously we said that the main component in conventional CSRP is AP which is processed into coarse and fine fractions (400 \(\mu\)m, 200 \(\mu\)m) and (7–11 \(\mu\)m) respectively. Figures 10–12 show SEM images of the three different fractions of ammonium perchlorate particle sizes: 400 \(\mu\)m, 200 \(\mu\)m, and 7–11 \(\mu\)m respectively taken to insure the average of the particles size. For AP (coarse 400 \(\mu\)m) it is apparent from figure 9 that most of the particles are nearly spherical geometry with the size of 400 \(\pm\)15 \(\mu\)m in outer diameter.

It is apparent from figure 10 that AP (coarse 200 \(\mu\)m) particles are nearly spherical geometry as the same of (400 \(\mu\)m) with the average size of 200 \(\mu\)m in outer diameter.

The images of AP (fine 7–11 \(\mu\)m) shown in figure 11 clarified that the AP particles are agglomerates and have some irregular structures. The size is 10 \(\pm\)4 \(\mu\)m in outer diameter. AP crystals shapes are rounded (nearly spheres).

3.5.2. Effect of replacing coarse particles of AP by nanoscale AP

As shown in figure 13 and table 3, Partial substitution of coarse AP with ultrafine (nanoscale AP) particles showed a new trend in the packing density of AP particles, Thus the packing density was increased with the increase in the concentration of ultrafine (nanoscale AP) from 0% to 18%. Also, packing density was increased

| Set | Coarse 400 \(\mu\)m | Coarse 200 \(\mu\)m | Fine 7–11 \(\mu\)m | Ultrafine (nanoparticles) | Calculated Packing density (g ml\(^{-1}\)) |
|-----|---------------------|---------------------|-------------------|--------------------------|------------------------------------------|
| 1 A | 55                  | 23                  | 22                | 0                        | 1.02                                     |
| 2B  | 53                  | 22                  | 22                | 3                        | 1.19                                     |
| 3 C | 51                  | 21                  | 22                | 6                        | 1.21                                     |
| 4D  | 49                  | 20                  | 22                | 9                        | 1.25                                     |
| 5 E | 47                  | 19                  | 22                | 12                       | 1.28                                     |
| 6 F | 45                  | 18                  | 22                | 15                       | 1.31                                     |
| 7 G | 43                  | 17                  | 22                | 18                       | 1.35                                     |

Figure 14. Variation of the calculated packing density of replacing coarse and fine particles of AP by nanoscale AP.
by 32% when the concentration of ultrafine (nanoscale AP) reached 18%. Increasing the packing density with increasing concentration of nanoscale AP could be due to the presence of the nanoparticles which filled the voids between the coarse particles and fine particles. This filling made particles able to acquire smaller volumes, so the packing density increases. The conclusion from this study is that the maximum packing density of conventional CSRP could be achieved by replacing coarse particles of AP with 9% nanoscale AP with no bad effects on the mechanical properties of CSRP (where the accepted mechanical properties for CSRP should be as follows; strength >6.8 Kgf cm \(^{-2}\), elongation at maximum strength should be >32% and Hardness (Shore A) should be >45) [9]. The packing density increases by 22.5% when 9% of nanoscale AP replaced coarse particles of AP.

### 3.5.3. Effect of replacing coarse and fine particles of AP by nanoscale AP

As shown in figure 14 and table 4, Partial substitution of coarse and fine particles AP with ultrafine (nanoscale AP) particles showed a trend in the packing density of AP particles, Thus the packing density increased with the

### Table 4. Composition details of the second study set of trials for replacing coarse and fine particles of AP by nanoscale AP.

| Set   | Coarse | Fine 7–11 μm | Ultrafine (nanoparticles) | Calculated Packing density (g ml\(^{-1}\)) |
|-------|--------|--------------|---------------------------|------------------------------------------|
| 1A    | 55     | 23           | 22                        | 0                                        | 1.02                                     |
| 2B    | 54     | 22           | 21                        | 3                                        | 1.11                                     |
| 3C    | 53     | 21           | 20                        | 6                                        | 1.13                                     |
| 4D    | 52     | 20           | 19                        | 9                                        | 1.18                                     |
| 5E    | 51     | 19           | 18                        | 12                                       | 1.19                                     |
| 6F    | 50     | 18           | 17                        | 15                                       | 1.13                                     |
| 7G    | 49     | 17           | 16                        | 18                                       | 1.11                                     |

### Table 5. Composition details of the third study set of trials for replacing fine particles of AP by ultrafine (nanoscale AP).

| Set   | Coarse | Fine 7–11 μm | Ultrafine (nanoparticles) | Calculated Packing density (g ml\(^{-1}\)) |
|-------|--------|--------------|---------------------------|------------------------------------------|
| 1A    | 55     | 23           | 22                        | 0                                        | 1.02                                     |
| 2B    | 55     | 23           | 19                        | 3                                        | 1.08                                     |
| 3C    | 55     | 23           | 16                        | 6                                        | 1.11                                     |
| 4D    | 55     | 23           | 13                        | 9                                        | 1.13                                     |
| 5E    | 55     | 23           | 10                        | 12                                       | 1.12                                     |
| 6F    | 55     | 23           | 7                         | 15                                       | 1.11                                     |
| 7G    | 55     | 23           | 4                         | 18                                       | 1.08                                     |
increase in the concentration of ultrafine (nanoscale AP) from 0% to 12% and then decreased again. Increasing the packing density with the increase in the concentration of nanoscale AP from 0% to 12% could be due to the presence of the nanoparticles which filled the voids between the coarse particles and fine particles. Packing density increased by 17% when the concentration of ultrafine (nanoscale AP) reached 12%. Decreasing the packing density with increasing the concentration of nanoscale AP from 12% to 18% could be due to that all voids between particles already have been filled by nanoscale AP, so any increase in the concentration of nanoscale AP will have no impact on the packing density.

### 3.5.4. Effect of replacing fine particles of AP by nanoscale AP

As shown in figure 15 and table 5, Partial substitution of fine particles AP with ultrafine (nanoscale AP) showed a tendency in the packing density of AP particles. Thus the packing density increased with increasing the concentration of ultrafine (nanoscale AP) from 0% to 9% and then decreased again. Increasing the packing density when increasing the concentration of nanoscale AP from 0% to 9% could be due to the introduction of the nanoparticles which filled the voids between the coarse particles and fine particles. Packing density increased.
by 11% when the concentration of ultrafine (nanoscale AP) reached 9%. Decreasing the packing density when increasing the concentration of nanoscale AP from 9% to 18% because that all voids between particles already have been filled by nanoscale AP, so any more addition of nanoscale AP will be no longer effective on the packing density of the formulation.

3.6. Evaluation of the composite propellant formulations
3.6.1. Effect of nanoscale AP on mechanical and ballistic properties

The densities of the prepared composite solid rocket propellant formulations were carried out at 20 °C and reported in table 6.

Conventional CSRP samples have a measured density close to the theoretical density which is 1.75 g cm$^{-3}$, and formulation X which is composed of 9% nanoscale AP has a measured density far from the theoretical which is 1.85 g cm$^{-3}$. Figure 16 shows that replacing coarse particles of AP by 9% nanoscale AP causes an increase in the density of the whole formulation by 5.8%.

Table 8. Results of CSRP formulations mechanical properties at 25 °C.

| Formulation | Tensile strength $\sigma$ (kgf cm$^{-2}$) | Strain $\epsilon$ (%) |
|-------------|----------------------------------------|-----------------------|
| Conventional| 8.42                                   | 47.1                  |
| X           | 11.3                                   | 35                    |

Figure 17. Effect of replacing coarse AP by 9% nano AP on the hardness.

Figure 18. Propellant formulations tensile strength result.
Shore (A) was measured for all samples by using the hardness tester ZWICK (model 3102) as described. This study aimed to ensure the development of curing measured by increasing the sample hardness value and the hardening measurements were recorded in Table 7.

Conventional CSRP samples have been cured after 12 days and gave a hardness of 65, while the formulation X (9% nanoscale AP) remained the same with a hardness of 75. To explain this phenomenon, Figure 16 shows the effect of replacing coarse particles of AP by 9% nanoscale AP on the hardness of the investigated samples using experimental results, which illustrated that the introduction of 9% nanoscale AP particles caused a 15% increase in the hardness.

The determination of the mechanical properties of the prepared propellant formulations was an essential step to ensure that these propellant families were able to withstand the required thermal and mechanical loading through the processing and combustion process. At 25 °C, the mechanical properties of the propellant samples were performed. Table 8 displays the key parameters of the mechanical properties calculated.

According to the results tabulated in Table 8, the variations of the propellant maximum tensile stress and maximum strain versus different propellant formulations are shown in Figures 17–19 respectively. Results showed that the formulation (X) has a higher tensile strength than that of the conventional formulation by 34%. On the other hand, the formulation (X) was found to have a lower strain value than that of the conventional formulation by 25% due to replacing coarse particles of AP with 9% nanoscale AP.

The ballistic characteristics were measured experimentally with the same 2 inches testing motor with a nozzle throat diameter of 7, 7.3, and 7.6 mm. Operating pressure, burning rate, pressure exponent, and specific impulse were measured and listed together in Table 9.

By comparing the values of the burning rate, operating pressure, pressure exponent, and specific impulse of the formulation X versus the conventional formulation, it was clear that the formulation X has a higher burning rate of 9.5%, a lower pressure-exponent of 0.28 while the pressure exponent of the conventional formulation was 0.32. These results ensured that replacing coarse AP particles with 9% nanoscale particles enhanced the ballistic characteristics of the conventional propellant.

### 4. Conclusions

The synthesis of nanoscale AP particles was carried out successfully using a liquid-state method based on the combination of the co-precipitation technique and sonication. The average particle size of the synthesized nanoscale AP using a liquid-state method was 60–80 nm. Nanoscale AP particles possess better catalytic activity than microscale AP in which the temperature of decomposition decreased, the heat released increased and the...
activation energy decreased. The maximum packing density of conventional CSRP can be achieved by replacing coarse particles of AP with 9% nanoscale AP without any negative impact on the mechanical properties of CSRP (coarse to fine ratio 3:1). The synthesized nanoscale AP was evaluated in conventional CSRP formulation up to 9% with 86% solid loading by replacing coarse AP with nanoscale AP. The data revealed that an increase in the density (5.8%), the burning rate increased (9.5%) and the pressure exponent (n) decreased from (0.32 to 0.28) (stable combustion regime).

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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