Effects of dense concentrations of aluminum nanoparticles on the evaporation behavior of kerosene droplet at elevated temperatures: The phenomenon of microexplosion

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ABSTRACT

The evaporation behavior of kerosene droplets containing dense concentrations (2.5%, 5.0%, and 7.0% by weight) of aluminum (Al) nanoparticles (NPs) suspended on silicon carbide fiber was studied experimentally over a range of ambient temperatures (400–800 °C) under normal gravity. The evaporation characteristics of the pure and stabilized kerosene droplets were also examined to provide a comparison. The results show that at all of the tested temperatures, the evaporation behavior of suspended kerosene droplets containing dense concentrations of Al NPs was different from that of pure kerosene droplets and exhibited three stages of evaporation; an initial heating up stage, \(d^2\)-law evaporation and then the microexplosion stage. The phenomenon of microexplosion was not observed during the evaporation of pure or stabilized kerosene droplets at the same temperatures. The microexplosions occurred early in the droplet’s lifetime and with a much greater intensity, for either an increase in the ambient temperature or an increase in the NP loading rate. For all of the Al NP suspensions, regardless of the concentration, the evaporation rate remained higher than that of either pure or stabilized kerosene droplets at higher temperatures (700–800 °C). The intense microexplosions occurring at these temperatures led to a substantial enhancement in the evaporation rate. However, at lower temperatures (400–500 °C), the delayed onset with lower intensity of the microexplosions was not able to increase the evaporation rate significantly, and it remained similar to that of pure fuel droplets. The maximum increase in the evaporation rate (48.7%) was observed for the 2.5% Al NP suspension droplet at 800 °C.

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1. Introduction

The specifically tailored high-energy–density fuels are a compelling need of the next generation combustion and propulsion systems. The energy–density of available conventional fuels is a major limiting factor in the current liquid propulsion systems; therefore, there is an immense necessity of enhancing the energy content of both traditional and future synthetic fuels. One possible way to accomplish this is to load a liquid hydrocarbon fuel with high-energy–density solid NPs in form of a stable suspension, slurry or gel. A stable suspension of solid NPs in a liquid fuel is called nanofluid fuel which is a new class of nanofluids and is fundamentally different from slurry fuels. These suspensions with low concentrations (~10 wt.%) of NPs compared to slurry fuels which contain relatively high solid loadings (40–80 wt.%) of micron sized particles and were studied decades ago [1]. Low concentrations of NPs will not significantly change the physical properties such as the density, viscosity or boiling point of the base fuel so that current fuel delivery systems can still be used, with only slight modifications [2].

High loadings of NPs (~10 wt.%) would enable the production of high-energy–density fuels but they can also induce some potential side effects, as found in slurry fuels, which have limited their practical applications. The major problems associated with the use of slurry fuels are the stability of the micron-sized particles in the liquid fuels and particle agglomeration during evaporation and combustion which resulted in slow burning rates and incomplete combustion of the agglomerations and consequently reduced the combustion efficiencies [1]. However, reducing the particle size from micro to nano scale can provide a solution to such problems, for as metallic particles size approaches the nano scale, their thermal-physical properties often change significantly. Several studies have described lower melting temperatures [3,4] and a reduced melt heat of fusion for nano-sized metal particles [5,6]. Also, nano scale...
energetic materials have a much higher surface to volume ratio compared to micron-sized particles, which allows more fuel to be in contact with the oxidizer [7] and consequently results in a higher combustion efficiency. Furthermore, it is expected that due to the addition of nano scale particles, the size of the agglomerates should be reduced. The agglomerates may also be shattered by the microexplosions which occur due to the addition of NPs and are previously observed in kerosene based nanofluid fuels at elevated temperatures [8].

Tyagi et al. [9] found experimentally that with the addition of 0.1% and 0.5% (by volume) of Al and Al2O3 NPs, the hot plate ignition probability of nanoparticle laden diesel fuel was significantly higher than that of pure diesel fuel. Allen et al. [10] performed experiments using an aerosol shock tube and observed that the addition of 2% (by weight) of Al NPs to ethanol and JP-8 reduced their ignition delays by 32% and 50%, respectively. Jones et al. [11] determined experimentally the heat of combustion (HoC) of ethanol, containing various volume fractions of nano-aluminum (n-Al) and nano-aluminum oxide (n-Al2O3) particles. Their results indicated that 1% and 3% n-Al contents did not show enhancement, but that 5%, 7% and 10% n-Al contents increased the volumetric HoC by 5.82%, 8.65% and 15.31% respectively. Van Devenier and Anderson [12] observed that the ignition temperature of JP-10 was significantly reduced when using soluble CeO2 NPs as a catalyst. Later, their group produced oxide free, fuel soluble and air stable boron NPs that were also coated with the combustion catalyst ceria through a unique process [13,14]. Gan and Qiao [15] experimentally investigated the effects of nano and micro sized Al particles on the burning behavior of ethanol and n-decane fuel droplets. Their results indicated that for the same surfactant and particle concentrations, the disruption behavior of the micro sized suspensions occurred later and with a much greater intensity. Later, Gan et al. [16] investigated the combustion behavior of dilute and dense suspensions of boron and iron NPs in n-decane and ethanol. In dilute suspensions, simultaneous combustion of both the droplet and the NPs was observed, whereas in dense suspensions, most particles were combusted as large agglomerations after the consumption of the liquid fuel.

Isolated, single droplet combustion is considered a classical subject in combustion, which provides the opportunity to investigate the interactions of the physical and chemical processes, in a simplified geometrical configuration. The importance of the droplet vaporization/combustion phenomena in practical liquid fuel combustion systems has motivated a large number of researchers in the past. Droplet vaporization and combustion are similar in many aspects and the knowledge obtained from studying one of them provides insights to the other. Enhancement of vaporization leads to complete combustion with higher combustion efficiency. Furthermore, it is expected that the addition of Al NPs to heptane enhances its evaporation rate at high temperatures (above 400 °C). At lower temperatures (below 400 °C), the formation of large agglomerates results in a compact shell and suppresses the evaporation rate of heptane. More recently, experimental investigations on the effect of dilute concentrations (0.1%, 0.5% and 1.0%) of Al NPs on the evaporation characteristics of kerosene droplets at elevated temperatures (400–800 °C) have been conducted [8]. These nano-Al and kerosene (n-Al/kerosene) suspension droplets evaporate in the same way as pure kerosene droplets at temperatures in the range 400–600 °C and the added Al NPs enhanced the evaporation rate at all tested temperatures. Microexplosions were observed at high temperatures (700–800 °C) due to the addition of the Al NPs to kerosene droplets. The current study investigated the effects of high loadings of ligand-protected Al NPs on the vaporization behavior of kerosene droplets at elevated temperatures. Such an experimental study was necessary to verify the occurrence of microexplosions in the case of dense NP/kerosene suspension droplets and to develop an understanding of this phenomenon. The problem associated with this study is the stability of high loadings of metal NPs in liquid hydrocarbon fuels.

In the previous work [8], surface modified and ligand protected Al NPs were suspended in kerosene. Oleic acid (OA) was used for the surface coating of the Al NPs. The same surfactant, surface modification technique and procedure were adopted in the present study to prepare stable suspensions of dense concentrations of NPs in kerosene. The evaporation behavior of kerosene based nanofluid droplets at elevated temperatures with high loadings of Al NPs will provide valuable insights into the occurrence of microexplosions due to NPs and their effects on the evaporation rate of such multi-component hydrocarbon fuels. Therefore, in this study the effects of high loadings of NPs on the evaporation behavior of multi-component liquid hydrocarbon fuel (kerosene) droplets at elevated temperatures were experimentally investigated.

2. Experimental methods

The materials and instruments used in this study were the same as described in other recent research work [8]. All the materials, except for the Al NPs, were used in their original form as received without further treatment. Preparation of uniformly dispersed and stable NP suspensions in fuel is the key step before performing any experimental study with nanofluid fuels. The post synthesis surface modification concept was applied to the Al NPs purchased. The NPs were ground in a planetary ball mill (PM100) along with the OA and their surfaces
were coated with the ligand which improves their dispersion stability in liquid hydrocarbons. The amount of OA and the time of ball milling were optimized. The ligand protected Al NPs were dispersed in the kerosene fuel and 2.5%, 5.0% and 7.0% NP/kerosene suspensions were prepared. In this case and for the remainder of this paper mass percentage values are used. The surface modification technique used in the current study has been described elsewhere [14] and the procedure and amendments adopted here have been also explained in another recent study [8].

The design, fabrication and installation of the experimental apparatus is discussed in detail in previous studies [28–30]. The experimental procedure for the evaporation of the nanofluid fuel droplet along with the data reduction and analysis are described in the previous work [27]. An isolated n-Al/kerosene droplet was suspended by a fine SiC fiber (100 μm diameter). The initial average diameter of a droplet was 1.0 ± 0.10 mm. Nitrogen was used to provide an inert environment for evaporation. The ambient temperature was varied in the range 400–800 °C and the ambient pressure was kept constant at 0.1 MPa. High ambient temperatures were provided by an electric furnace. The evaporation process was recorded using a high speed charge coupled device (CCD) camera. The captured images were analyzed using a flexible image processing code to extract the droplet diameter. The temporal variation of the droplet diameter was obtained during the whole evaporation process. If the droplet evaporation follows the $d^2$-law then the evaporation rate can be expressed as the time derivative of the droplet diameter squared, $C = -d(d^2)/dt$ [31,32]. In that case, the droplet evaporation rate was obtained from the temporal history of the droplet diameter squared, by measuring the slope of its linear regression.

3. Results and discussion

3.1. Pure kerosene droplet evaporation

The evaporation rate of pure kerosene droplets was measured, compared with previous data and discussed in detail in recent research work [8]. The general evaporation behavior and measurements of the evaporation rates of pure kerosene droplets at elevated temperatures (400–800 °C) are essential for understanding the effects of the addition of high concentrations of OA and Al NPs on the droplet evaporation behavior. In pure kerosene droplets at elevated temperatures, the temporal variation in the droplet diameter squared becomes approximately linear while following the $d^2$-law in the last stage of evaporation. The evaporation rate increases consistently as the ambient temperature increases.

3.2. Evaporation of kerosene droplets with the addition of oleic acid

Before investigating the evaporation behavior of n-Al/kerosene droplets at elevated temperatures, the evaporation behavior of kerosene/OA droplets with high concentrations of OA (surfactant) were studied at the same temperatures. The evaporation behavior of the stabilized kerosene (kerosene/OA) droplets helps us distinguish the effect of NP addition on the droplet evaporation behavior.

Fig. 1 shows the normalized temporal histories of the diameter squared of kerosene droplets with 1.25% and 2.50% OA at various ambient temperatures; (a) at 400 and 500 °C, (b) at 600, 700 and 800 °C. The captured images were analyzed using a flexible image processing code to extract the droplet diameter. The temporal variation of the droplet diameter was obtained during the whole evaporation process. If the droplet evaporation follows the $d^2$-law then the evaporation rate can be expressed as the time derivative of the droplet diameter squared, $C = -d(d^2)/dt$ [31,32]. In that case, the droplet evaporation rate was obtained from the temporal history of the droplet diameter squared, by measuring the slope of its linear regression.

Fig. 2 shows that the evaporation behavior of kerosene/OA droplets with 5.0% of OA is similar to that of binary component fuel droplets. Likewise with binary component droplets [28], the stabilized kerosene droplets show a three stage evaporation process; a finite heating up period, $d^2$-law evaporation of the highly volatile component (kerosene) and $d^2$-law evaporation of the low volatility component (OA) as depicted in Fig. 2. The evaporation history at the above mentioned temperatures can be divided into two distinct stages, with an obvious difference in their diminishing rates, as shown in the figure. During the first stage of the evaporation time of the stabilized kerosene droplets was slightly longer than that for pure kerosene droplets as shown in the figure. OA is a low volatility component compared to kerosene while its addition to kerosene produces a monolayer at the surface of the droplet which inhibits the diffusion of kerosene so that slightly reduces the evaporation rate [33]. However, at high temperatures (700–800 °C), the total lifetime of the stabilized kerosene droplets was comparable to that of pure kerosene droplets and the effects of the addition of OA were diminished as shown in Fig. 1b.
3.2.1. Effect of temperature on the evaporation rate of stabilized kerosene droplets

Fig. 3 shows a comparison of the evaporation rates of kerosene droplets containing 1.25%, 2.5% and 5.0% of OA and pure kerosene droplets for a range of ambient temperatures (400–800 °C). The evaporation rate of the kerosene/OA droplets is lower than or equal to that of the pure kerosene at all of the above mentioned temperatures as shown in the figure. The evaporation rate of the kerosene/OA droplets with relatively low concentrations of OA (1.25% and 2.5%) remained slightly lower than the evaporation rate of the pure kerosene droplets at all temperatures tested. The kerosene/OA droplets with 5.0% of OA have two evaporation rate curves; one for the kerosene component and the other for the OA component present in the stabilized kerosene droplets. The evaporation rate of the kerosene component in the 5.0% stabilized kerosene droplets is comparable to that of the pure kerosene droplets and remains the same in the range 400–700 °C and is slightly higher at 800 °C. However, the evaporation rate of the OA component in the 5.0% stabilized kerosene droplets is considerably lower than the evaporation rate of the pure kerosene droplets at all temperatures tested. These two curves are similar in that the evaporation rate of each component (kerosene and OA) of the stabilized kerosene droplets was increased by an increase in the temperature. The effect of the increase in the temperature has different impacts on the evaporation rate of the kerosene component and the OA component in stabilized kerosene droplets. A comparison of these two curves also shows that the evaporation rate of the kerosene component truly represents the evaporation rates of the 5.0% stabilized kerosene droplets.

These results indicate that similar to the addition of dilute concentrations of OA to kerosene [8], the addition of dense concentrations of OA to kerosene also has no considerable effect on the evaporation rate of kerosene droplets. The evaporation rate of the stabilized kerosene droplets, containing 1.25%, 2.5% and 5.0% of OA, is also nearly equal to the evaporation rate of pure kerosene droplets at all temperatures tested.

3.3. Evaporation of kerosene based nanofluid fuel droplets

In this section, the evaporation characteristics of n-Al/kerosene droplets are discussed.

Fig. 4 displays normalized temporal histories of the kerosene droplets’ diameter squared with the addition of 2.5%, 5.0% and 7.0% of Al NPs whose surfaces were coated with 1.25%, 2.50% and 3.50% of OA, respectively, at ambient temperatures ranging from 400 to 800 °C. To minimize the effect of the initial droplet size on the evaporation rate, droplets having similar initial diameters ranging from 0.977 to 1.074 mm were selected from the experimental data.

Unlike the dilute n-Al/kerosene suspension droplets [8], the general evaporation behavior of the dense n-Al/kerosene suspension droplets was not similar to that of pure kerosene droplets. The droplets with high loadings of Al NPs in kerosene showed three stages of evaporation; a finite heating up period, the kerosene component from the stabilized kerosene droplet evaporates. In the second stage the droplet becomes rich with OA and the OA near the droplet surface starts to evaporate. As the temperature increased from 400 to 800 °C, the difference between the evaporation of the high volatility and low volatility components in the third stage was decreased. Due to the reduced difference between the boiling points of kerosene and OA and the multi-component nature of the kerosene, the phenomena of bubble formation and microexplosion were not seen to take place even at high temperatures (700–800 °C). The evaporation rates of the stabilized kerosene droplets were calculated using the least squares regression method with the data corresponding to the linear part of the evaporation history except for the initial heat up period.

Fig. 3. A comparison of the evaporation rates of the stabilized kerosene droplets containing various concentrations of OA with pure kerosene droplets at different ambient temperatures and constant pressure of 0.1 MPa.

Fig. 2. Normalized temporal variations of the diameter squared of evaporating stabilized kerosene droplets containing 5.0% OA with each least-squares fit to the linear kerosene evaporation part (first stage) and to the linear OA evaporation part (second stage) at various ambient temperatures (400–800 °C) and constant pressure of 0.1 MPa.

Fig. 4a shows normalized evaporation histories for kerosene based nanofluid droplets with 2.5%, 5.0% and 7.0% of Al NPs at 400 and 500 °C. The kerosene droplets with 2.5% of Al NPs suspension show no bubble formation or microexplosions at the above mentioned temperatures. However, at these temperatures, the droplets containing 5.0% and 7.0% of Al NPs suspension exhibit bubble formation and they rupture at the end of the droplet’s lifetime. Due to the high loadings of NPs (5.0% and 7.0%), enough NPs
were accumulated at the droplet’s surface during evaporation that they produce a shell there in the last phase of the evaporation period. The shell temperature can exceed the boiling point of the liquid fuel causing nucleation sites to form inside the droplet and further fragmentation of the droplet. As the temperature increased from 400 to 500 °C or the NP concentration increased from 5.0% to 7.0%, the microexplosions started earlier in the droplet’s lifetime.

Fig. 4b shows normalized evaporation histories for stabilized kerosene droplets with 2.5%, 5.0%, and 7.0% of Al NPs at 600, 700 and 800 °C. The most prominent characteristic of the evaporating n-Al/kerosene droplets at these ambient temperatures was the onset of bubble formation and microexplosions irrespective of the Al NP concentration. Between 600 and 700 °C, with 2.5% of Al NPs, the droplets were suddenly shrunk to smaller droplets by the release of accumulated vapors without any prior expansion. At 600 and 800 °C with relatively high concentrations (5.0% and 7.0%) of Al NPs, the evaporating droplets first expanded to a larger size and then ruptured. This expansion and contraction process was repeated several times. For 5.0% and 7.0% n-Al/kerosene droplets at 700 °C, the phenomenon of droplet fragmentation and microexplosion was observed in two stages; primary fragmentation and secondary microexplosion (see Supplementary video). The primary fragmentation includes the droplet’s diameter reduction without any prior expansion whereas the secondary microexplosion comprises a droplet diameter expansion and then reduction several times. These two microexplosion stages are separated by a small linear evaporation period. The 2.5% n-Al/kerosene droplets also exhibited the same two microexplosion stages at 800 °C. It is noteworthy to mention that microexplosions would be most effective if nucleation occurs early in the droplet lifetime and deep within the droplet’s inner core [17]. Fortunately, the heterogeneous nucleation sites (HNSs) produced at 800 °C, with the addition of 5.0% and 7.0% of Al NPs to kerosene, satisfied these two requirements simultaneously. These HNSs were produced early in the droplet lifetime (after 20–25% of the time span) and deep inside the droplet, consequently multiple intense microexplosions occurred in the remaining evaporating time. At a high temperature (800 °C), due to the strong particle dynamics (collisions, diffusion and Brownian motion) inside the droplet or due to the enhanced thermal diffusivity, the NPs present inside the droplet acquired a temperature higher than the liquid’s local boiling point, which converted to HNSs. Whereas at 700 °C, the early HNSs were produced at or near the droplet surface after 50% of the time span. Later, HNSs were created inside the droplet, however by that time much of the liquid droplet had already been gasified. At low temperatures (400–600 °C), the onset of microexplosion was further delayed (starting after 70–80% of the time span) so that most of the liquid fuel had already evaporated and the intensity was reduced. It is important to note that the microexplosions started a little earlier with an increase in the concentration of NPs at the same temperature. However, an increase in the temperature significantly affects the onset of microexplosions and they started quite early in the droplet’s lifetime with a much greater intensity.

3.3.1. Phenomenon of microexplosion

The phenomenon of microexplosion is very important to the evaporation and combustion of nanofluid fuels because it has the potential to enhance their evaporation/combustion performance by shattering the droplets into smaller particles, which yields faster and complete burning of the added Al NPs. For a better understanding of the nature and types of microexplosions, sequential photographs of evaporating n-Al/kerosene droplets are presented in the next figure.

Fig. 5a–c presents some sequential images of the evaporation behavior of stabilized kerosene droplets with 2.5%, 5.0%, and 7.0% of Al NPs at 800 °C, respectively. The phenomena of bubble formation and microexplosion are clearly observed here. In Fig. 5a–c, the second snapshot shows the end of the linear evaporation period (second stage). The third snapshot of Fig. 5a (at t = 0.695 s) shows the vapor formation at the droplet surface, due to this a slight increase in the droplet diameter was observed for the 2.5% n-Al/ kerosene. Due to the escape of these vapors, the droplet diameter is suddenly reduced in the subsequent pictures (at t = 0.700 and 0.705 s). After this the droplet vaporized linearly up to 1.065 s and then the droplet starts to expand due to internal bubble formation which is completed by 1.210 s, the droplet then ruptures at 1.215 s.

For the 5.0% n-Al/kerosene droplet (Fig. 5b), after linear evaporation up to 0.850 s, internal bubble formation started and this appears at 0.920 s and the droplet ruptures at 0.925 s as shown in the captured frames. The second, third, fourth, fifth and sixth times bubbles appeared at 0.980, 1.120, 1.210, 1.240 and 1.270 s and the droplets rupture in the subsequent photos at 0.985, 1.125,
Fig. 5. Sequential photographs of vaporization of kerosene droplets containing various dense concentrations of Al NPs at same elevated temperature (a) 2.5% Al NPs (coated with 1.25% OA) at 800 °C, (b) 5.0% Al NPs (coated with 2.5% OA) at 800 °C, and (c) 7.0% Al NPs (coated with 3.5% OA) at 800 °C; camera speed: 200 fps.
1.215, 1.245 and 1.275 s, respectively. It is important to note that after the generation of the first bubble, the time taken to produce every subsequent bubble was lower than the time previously spent in bubble generation. Initially, it took a long time to produce HNSs inside the droplet, but once the NPs had a temperature higher than the liquid’s local boiling point they continuously gasified the surrounding liquid. Due to the accumulation of NPs, the heat transfer inside the droplet was increased so that more inner NPs were providing HNSs. It is also noteworthy that this irregular behavior was not observed in the evaporation process of pure or stabilized kerosene droplets.

In the case of the 7.0% n-Al/kerosene droplet (Fig. 5c), the internal bubble formation started after the second stage \((t = 0.715 \text{ s})\) but the bubble appeared at \(0.750 \text{ s}\) and continuously grows up to \(0.845 \text{ s}\). In the subsequent two pictures the droplet fragmented intensively. After that the remaining droplet expanded several times (at \(0.990, 1.080, 1.105, 1.215, 1.245\) and \(1.260 \text{ s}\)) due to bubble formation inside the droplet and then shrank as a result of its subsequent ruptures, which took place at \(0.995, 1.085, 1.110, 1.220, 1.250\) and \(1.265 \text{ s}\) as shown in the pictures. A comparison of the re-expansion of the droplets and their rupturing behavior between the 5.0% and 7.0% Al NP suspension droplets reveals that more intense microexplosions occurred with high Al NP concentrations at high ambient temperatures. A fast internal pressure build up caused by more HNSs provided by a high Al NP concentration at high temperatures, results in more aggressive microexplosion behavior such as a large expansion, severe bubble formation and more disruptive fragmentation. The microexplosion phenomenon started earlier with an increase in the concentration of the Al NPs at the same temperature.

There are two types of microexplosions which were observed here. One is droplet fragmentation without any prior droplet expansion. The other is the repeated expansion and subsequent rupture of the droplet. The first kind of droplet reduction was due to the sudden escape of vapors from the droplet surface. These gaseous liquids were produced at or near to the droplet surface by

![Images of droplet behavior](image-url)
the HNSs provided by the NPs. The second kind of microexplosion which was observed with high concentration of Al NPs during the latter part of the droplet lifetime at 400–700°C was due to the accumulation of NPs at the droplet surface. These NPs may gather to form a shell at the droplet surface and simultaneously raise the droplet surface temperature to close to the liquid local boiling point. The NPs present inside the droplet may also be heated beyond the liquid local boiling point, providing multiple HNSs and converting the surrounding liquid into vapor. This vapor expanded the droplet while increasing its diameter. By receiving further heat from the NPs these vapors became superheated, an intense pressure buildup was caused, which resulted in the catastrophic fragmentation of the droplet. An increase in the NPs concentration or an increase in the temperature resulted in an early accumulation or shell formation of the NPs at the droplet surface, which resulted in early onset of microexplosions. This is why microexplosions were observed during the major portion of the droplet’s lifetime with a greater intensity at 800°C in droplets containing a relatively high concentration of Al NPs. In the case of the 2.5% Al NPs, the added Al NPs were not enough to form a shell at the droplet surface which could raise its surface temperature. They only provided HNSs at or near to the droplet surface.

The residues obtained at the end of evaporation were collected to investigate the effects of microexplosions on shell formation of nanofluid fuel droplets as well as to confirm the physical state of the Al NPs present at the droplets’ surface. Residues of the 2.5% and 5.0% Al NP suspension droplets were obtained at two different temperatures (600 and 800°C) and studied using field-emission scanning electron microscope (FESEM) and energy-dispersive X-ray spectroscopy (EDX). The selected temperature values were below and above the melting temperature of the Al NPs (660°C), respectively. The residues were collected very carefully using the collection procedure as described in a recent study [8].

Figs. 6 and 7 show the FESEM images of the residues after evaporation at 600 and 800°C for a 2.5% Al NP suspension. An overall view of the residue (Fig. 6a) shows that it was soft, powdery and
had been broken during the SEM sample preparation. The magnified view (Fig. 6b) of the residue shows that most of the NPs preserved their original spherical shapes at 600 °C. When the temperature increased to 800 °C, a large and compact residue was formed as shown in Fig. 7a. A closer view (Fig. 7b) shows that the residue was soft, crumbly and porous in nature. A further detailed view of the residue’s surface (Fig. 7c) revealed that it has been punctured by the NPs coming out of the surface through microexplosion. Fig. 7d shows a magnified view of the residue, which clearly shows that most of the NPs loosen their shapes, while being fused and stuck each other to form larger lumps.

Figs. 8 and 9 show the FESEM characterization micrographs of the 5.0% Al NP suspension residue collected at 600 and 800 °C. The droplet shrank and formed an elliptical shaped agglomerate on the SiC fiber as shown in Fig. 8a. This agglomeration seemed compact and porous because during the preparation of the SEM sample the whole lump was detached from the SiC fiber and was not broken into pieces as happened to the 2.5% suspension residue at the same temperature (Fig. 6a). Fig. 8b shows a magnified view of the residue, which disclosed that most of the NPs preserved their original shapes, whereas a few NPs fused, stuck together and loosened their original shapes. The agglomeration obtained at 800 °C (Fig. 9a) was squeezed, sticky and remained on the SiC fiber with holes at its surface. The effects of microexplosion on the evaporation residue were clearly noticeable here. A closer view of the residue (Fig. 9b) shows that its surface contained many small pores. A close up of the inside of a hole (Fig. 9c) shows the presence of well separated NPs. These NPs provided HNSs and produced enough vapors which on rupturing resulted in holes in the droplet surface. Magnified views (Fig. 9d) of the residue show that the Al NPs were densely packed; some of them fused a little and loosened their original spherical shapes but they did not form larger agglomerations. Due to maintaining their smaller size, pores were also present. With high loadings of NPs to kerosene, large and compact residue was formed with more perforations at the droplet’s surface due to microexplosions. However, evaporation rates for the 2.5% NP sus-
pension droplets were higher when compared to those of the 5.0% NP suspension droplets due to melting of the Al NPs present at the droplet's surface. In both cases the overall evaporation rate was substantially higher than the pure kerosene droplets' evaporation rate at 800 °C.

EDX was conducted to analyze the composition of these residues. The evaporative residues were mostly composed of Al and O, with small amounts of C. The O content was due to the oxidation of the Al NPs exposed to air after the vaporization and during the preparation of the samples for FESEM. The O contents were 5.38% and 20.7% (by weight) in the residues of the 2.5% NP suspension, evaporated at 600 and 800 °C, respectively as shown in Fig. 10. Similarly, Fig. 11 shows the O contents obtained from the 5.0% NP suspension were 4.51% and 16.6% (by weight) in the residues evaporated at 600 and 800 °C, respectively. This indicates high oxidation of the Al NPs to Al₂O₃. All of the residues were cooled down to room temperature in the presence of nitrogen before being taken out into air; therefore, the high oxygen content was due to the presence of elemental Al at their surfaces, which was oxidized. The EDX results imply that the residue obtained at 800 °C contained high amounts of elemental Al at its surface, which was thought to be the melted Al NPs or the Al NPs exposed through perforations in the droplet's surface.

3.3.2. Evaporation rate of n-Al/kerosene droplets

The evaporation rates of the n-Al/kerosene droplets containing dense concentrations of Al NPs were calculated from their evaporation history curves through a least squares fitting in the linear evaporation stage and by a two point fit in the microexplosion part. For the microexplosion stage, the use of the least squares method is not justified due to the droplet expansion and contraction. Therefore the rate of diminishment was simply estimated by measuring the slope between the two end points [34,35]. Fig. 12 shows a sample least squares fit and a two point estimation for n-Al/kerosene droplets containing 5.0% Al NPs.

The evaporation rates of these two stages were obtained using the above methodology and are plotted in Fig. 13a and b for comparison with the evaporation rates of pure kerosene droplets. Fig. 13a shows that at low temperatures (400–600 °C), the linear evaporation stage is dominant in the droplet evaporation lifetime, therefore their evaporation rates are close to the evaporation rates of pure kerosene droplets at these temperatures. Whereas at high temperatures, this stage comprises a small portion of the droplet lifetime and shows lower evaporation rates than the evaporation rates of pure kerosene droplets.

In contrast to the second stage, the third stage (the microexplosion stage) comprises less of the evaporating droplets' lifetime at low temperatures due to the low intensity and tendency for microexplosions at these temperatures. Even for the 2.5% Al NP suspension, no microexplosion was observed at these temperatures. However at high temperatures, most of the droplet evaporation lifetime consists of microexplosions with a greater intensity so that the diminishment rate of this stage at these temperatures was considerably higher than with the evaporation rates of pure kerosene droplets as shown in Fig. 13b.

As discussed above, at low temperatures (400–500 °C) the second stage evaporation rates represented the evaporation rates of n-Al/kerosene droplets whereas at high temperatures (600–800 °C) it was the third stage evaporation rates. Therefore, these were plot-
3.3.3. Effect of Al NP concentration on the evaporation rate

Fig. 13c indicates that the evaporation rates of the n-Al/kerosene droplets containing dense concentrations of Al NPs were also affected by the concentration of NPs. As the NP concentration increased from 2.5% to 7.0%, the evaporation rates obtained at low ambient temperatures (400–500 °C) went from being slightly higher to being slightly lower than the evaporation rates of pure kerosene droplets. This is because an increase in the concentration of NPs in a droplet also increased their agglomeration in the final portion of its lifetime.

At relatively high ambient temperatures (700 and 800 °C), the evaporation rates were substantially increased with the NP concentration. The maximum increase was obtained with the 2.5% Al NP suspension. A further increase in the NP concentration decreased the enhancement in the evaporation rates but kept them higher than the evaporation rates of pure kerosene droplets at these temperatures. The enhancement in the evaporation rates was due to microexplosions observed in the n-Al/kerosene droplets at these temperatures and it is believed that these microexplosions occurred due to the presence of NPs in the droplets. In relatively higher NP suspension density (5.0% and 7.0%), the NPs accumulated at the droplet surface and formed a shell which controls the droplet’s surface temperature. Due to this shell, microexplosions started earlier in the droplet lifetime and occurred several times with an expansion and subsequent contraction each time. In addition, due to the presence of this shell, the droplet takes a longer time to shatter into smaller droplets and particles. Consequently, a low enhancement in the droplet diminishment rates was obtained for high NP suspension droplets. Whereas, for low (2.5%) NP loading rates, such a shell was not formed and the droplet easily ruptured into smaller sized droplets which resulted in higher evaporation rates.

4. Conclusions

The evaporation characteristics of kerosene based nano-fluid droplets with dense concentrations of Al NPs (2.5%, 5.0%, and 7.0%) were studied at various elevated temperatures (400–800 °C) under normal gravity. The main conclusions of this experimental study are summarized as follows.

1. With high loadings of Al NPs, the kerosene based nano-fluid droplet vaporized in a different way as compared to the pure kerosene droplet and exhibited an additional stage known as ‘microexplosion’. The classical $d^2$-law was not valid during this stage for kerosene based nano-fluid droplets.
The phenomenon of microexplosion was observed at all tested temperatures (400–800 °C) in kerosene based nanofluid fuel droplets containing dense concentrations of Al NPs. The absence of microexplosions in the pure and stabilized kerosene droplets indicates that this phenomenon was based solely on the presence of the Al NPs.

3. The microexplosions occurred earlier in the droplet’s lifetime and with a much greater intensity with either an increase in the ambient temperature or an increase in the NP loading rate at the same temperature. However, the effect of an increase in the ambient temperature on the intensity and onset of microexplosions was substantially higher than the NP loading rate.

4. The ambient temperature significantly affected the evaporation rates of the kerosene based nanofluid fuel droplets. Regardless of the Al NPs concentration, the intense microexplosions at 700 and 800 °C led to a substantial enhancement in the evaporation rate of kerosene droplets. However, at low temperatures (400–500 °C), due to the delayed onset and lower intensity of the microexplosions, the evaporation rate of the nanofluid droplets was not significantly affected and remained similar to that of pure kerosene droplets.

5. The evaporation rate of nanofluid fuel droplets was also affected by the concentration of the NPs. The evaporation rate enhancement increased with the NP concentration up to 2.5%, after which it decreased. The maximum increase was obtained at 800 °C with the 2.5% NP suspension, where the evaporation rate was increased by 48.7%.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.expthermflusci.2013.11.006.

References