Autoignition and combustion characteristics of heptane droplets with the addition of aluminium nanoparticles at elevated temperatures

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A R T I C L E    I N F O

Article info

Article history:
Received 18 March 2014
Received in revised form 19 May 2014
Accepted 18 July 2014
Available online 4 August 2014

Keywords:
Droplet combustion
Autoignition
Nanofluid fuels
Nanoparticles
Aluminium
Heptane

A B S T R A C T

We investigate the effects of high ambient temperatures and various concentrations of nanoparticles (NPs) on the autoignition and combustion characteristics of heptane-based nanofluid droplets. A single, heptane (n-C7) droplet containing 0.5%, 2.5%, or 5.0% by mass of aluminium (Al) NPs mounted on a silicon carbide fibre was exposed to a rapid increase in temperature (from room temperature to temperatures in the range 600–850 °C) at atmospheric pressure and under normal gravity, and the autoignition and combustion characteristics were observed. The ignition delay, burn rate, and combustion characteristics of pure and stabilised heptane droplets were also examined for comparison. The results show that, as with the pure heptane droplets, the ignition delay of the NP-laden heptane droplets (n-Al/heptane) followed an Arrhenius temperature dependence. The reduction in the ignition delay time with increasing temperature depended on the loading of NPs in the droplet. The overall activation energy obtained for dilute NP concentrations (0.5% by mass) was smaller, and that for dense (2.5% and 5.0%) concentrations of NPs was larger, than that of the pure heptane droplets. Consequently, the addition of 0.5% Al NPs to heptane resulted in ignition at 600 °C, which is not observed with stabilised heptane or 2.5% and 5.0% n-Al/heptane droplets. At higher temperatures, the ignition delay of the n-Al/heptane droplets was comparable to that of pure heptane droplets. The combustion of the n-Al/heptane droplets did not follow the classical d2-law, in contrast to the combustion of the pure and stabilised heptane droplets. Regardless of the NP concentration, the n-Al/heptane droplets exhibited disruptive burning behaviour, which was characterised by multiple expansions and ruptures or ‘microexplosions’. During these microexplosions, the NPs were ejected from the droplets, and the intensity of the microexplosions increased with increasing temperature; consequently, the burning time and total combustion time of the droplet was reduced. Due to these intense and frequent microexplosions, almost no residue from the Al NPs remained on the fibre following combustion, and a separate Al flame was not observed. The average gasification (burns) rate of the n-Al/heptane droplets remained equal to that of pure heptane droplets at relatively low temperatures (600–700 °C); however, at higher temperatures (750–850 °C), it was significantly faster than that of the pure heptane droplets.

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1. Introduction

Energetic materials including aluminium (Al) and boron (B) have long been of interest to the propulsion and combustion community due to their large combustion energies. Recent advances in nanotechnology have enabled the large-scale production of nanoparticles (NPs), which have shown significant advantages over micron-sized particles for combustion applications. When the size of metallic particles is reduced from the micron- to nanometer-scale, the thermophysical properties often change substantially. Numerous studies have reported a decrease in the melting point and heat of fusion of nanometer-scale metal particles [1–3]. There have been a number of reports of the effects of addition of NPs to solid fuels and propellants [4–8], citing advantages over micron-sized particles, including improved energy density, a shorter ignition delay, and an increased burn rate [4].

The use of metallic nanopowders as fuel additives has received much recent attention. Here, we describe the addition of NPs to liquid fuels, forming so-called nanofluid fuels, which have received
considerable interest for applications in combustion and propulsion. Nanofluid fuels are a new class of nanofuels, and consist of stable suspensions of energetic NPs in conventional liquid fuels. Nanopowders of energetic materials, including Al, B, carbon (C), iron (Fe), and cerium oxide (CeO₂), have been used as additives suspended in conventional liquid fuels in such a way as to improve the ignition and combustion characteristics. Previous studies have shown significant advantages of such nanofuel fuels. Van Devener and Anderson [9] found enhanced catalytic effects for CeO₂/JP-10 nanofuel fuel, and reported a significant reduction in the ignition temperature of JP-10. Tyagi et al. [10] observed an increased hot-plate ignition probability of diesel fuel laden with Al and Al₂O₃ NPs. Sabourin et al. [11] obtained enhanced burn rates and reduced ignition temperatures by adding functionalised graphene sheets to monopropellant nitromethane. Allen et al. [12] found a 32% reduction in the ignition delay of Al/ethanol and a 50% reduction in the ignition delay of Al(JP-8) nanofuel fuels compared with their base fuels. Jones et al. [13] obtained an increased heat of combustion with high loadings of Al NPs in ethanol.

As with the evaporation [14] of NP-laden fuel droplets, the combustion of nanofuel fuel droplets is more complex than that of pure liquid fuel droplets due to the multi-component, multi-phase, and multi-scale nature. There have been a number of studies of the combustion of nanofuel fuel droplets. Gan and Qiao [15] observed disruptive combustion of droplets with micron- and nanometer-scale Al particles in suspension with ethanol and n-decane. The disruptive behaviour of the micron-scale suspensions occurred later and with a greater intensity compared with nanometer-scale suspensions with the same surfactant and particle concentrations. Gan et al. [16] observed simultaneous combustion of both the droplet and the NPs with dilute suspensions of B and Fe NPs in n-decane and ethanol. However, in dense suspensions, most particles were combusted as large agglomerates following the consumption of the liquid fuel.

These reports of the combustion of nanofuel fuels [15,16] describe the simple qualitative behaviour of the combustion of the nanofuel droplets, where the droplets are ignited by a heated wire. Therefore, the effects of NPs on the autoignition delay times and the droplet combustion behaviour at various elevated temperatures are not accurately described. In addition, they are not able to explain the effects of the NPs on combustion rate constants. To the best of our knowledge, there have been no studies reporting the effects of the addition of various concentrations of NPs on the autoignition and combustion characteristics of nanofuel fuel droplets at elevated temperatures.

Here, we experimentally investigate the autoignition and combustion behaviour of heptane-based nanofuel droplets. The effects of the NP loading and ambient temperature on the droplet autoignition and combustion characteristics were examined. We used n-heptane (n-C₇H₁₆) as the base fuel because it is a simple, highly pure, single-component liquid hydrocarbon with an abundance of available experimental data regarding the evaporation, autoignition, combustion, and reaction characteristics. It is therefore useful to investigate the effects of the addition of NPs to this liquid hydrocarbon fuel. Al NPs were used as energetic additives, and the ambient temperature was varied in the range 600–850 °C. These temperatures are higher than the autoignition temperature of heptane (220 °C), and also both below and above the melting point of Al NPs (660 °C). The ambient pressure was maintained at atmospheric pressure, i.e., 0.1 MPa.

### 2. Experimental method

The materials and instruments used in this work were the same as those used in the experimental investigation of the evaporation characteristics of heptane-based nanofuel droplets described in Ref. [17]. The size distribution of Al NPs is in the range of 30–250 nm with average diameter of most probable particles 70 nm [17]. All materials were used as received and without further treatment, except for the Al NPs, the surfaces of which were coated with oleic acid (OA). A planetary ball mill (Retsch PM100, GmbH, Germany) was used to modify the surface of the Al NPs.

#### 2.1. Preparation of stable nanofuel fuels

The heptane-based nanofuel fuels were prepared using a two-step method. In this method, the NPs were uniformly suspended in a base fluid by applying various physical and chemical homogenisation techniques. Because the metallic NPs were available at an industrial scale, it is economical to produce a number of nanofuels with various concentrations of NPs, either in the laboratory or at a larger scale. Surface modification was applied to the Al NPs in order to improve the dispersion stability in heptane. The surfaces of the NPs were coated with OA using a ball mill, and oxide-free, ligand-protected and fuel-soluble Al NPs were obtained [18]. The NP-to-OA ratio was optimised as 1:1 in order to obtain stable suspensions of NPs in heptane. The resulting NP/OA paste was dispersed in heptane via vigorous agitation. In this manner, a homogeneous suspension was obtained, which remained stable for 2 h with no obvious sedimentation of the NPs. Further details of this procedure can be found in Refs. [14,19].

#### 2.2. Experimental apparatus and procedure

The experimental setup used to investigate the autoignition and combustion characteristics of a single fibre-suspended nanofuel droplet at elevated temperatures was the same as that described in Refs. [20–23]. This experimental arrangement has been used to study the evaporation behaviour of heptane- and kerosene-based nanofuel droplets [14,17,19]. The experimental procedure, data reduction, and analysis are described in detail in Refs. [14,17,19]. Experiments were carried out with a single nanofuel fuel droplet suspended by a 100-µm-diameter SiC fibre. The initial average diameter of the droplets was 1.0 ± 0.10 mm. The ambient temperature was varied in the range 600–850 °C at intervals of 50 °C, and the ambient pressure was maintained at 0.1 MPa. A high-temperature ambience was provided using a free-falling electric furnace, and the oxidizing environment was dry air. The combustion process was recorded using a high-speed charge-coupled device (CCD) camera (X-Stream XS-3 with a maximum speed of 1390 fps at a resolution of 1280 × 1024). Due to low internal memory (4 GB), the images were recorded with a speed of 300 fps at a resolution of 512 × 512. A flexible image-processing method was developed using Matlab to obtain the diameter of the droplets from the images. The procedure for calculating the diameter of droplet from the captured images was described in our previous study [17]. Briefly, in this method, a threshold value for pixel gray level was carefully set to count the pixels in the droplet zone. Then area of a circle having the same number of pixel which droplet had is calculated, which in turns give the diameter of the droplet using the law of proportions with the reference diameter of SiC fibre (100 µm). In some cases, the droplet is being distorted during the combustion process. However, by using this code, the diameter of this irregular-shaped droplet was calculated within a reasonable accuracy. This method was executed iteratively for each image, allowing us to obtain the temporal variation of the droplet diameter d during combustion. If the combustion of the droplet follows a d²-law, the combustion rate constant may be expressed as the time derivative of the droplet diameter squared, i.e., \( K_c = -\frac{d(d^2)}{dt} \). In this manner, the droplet combustion rate con-
constant was obtained from the gradient of the temporal variation of the droplet diameter squared using linear regression.

3. Results and discussion

3.1. Droplet autoignition

Autoignition is the ignition of a combustible mixture without an external source. The autoignition characteristics may be described in terms of an ignition delay obtained as a function of the initial temperature of the gas, and the effects of other variables, including the pressure, equivalence ratio, droplet size, and fuel type, may be included via a parametric investigation [24]. The ignition delay is generally defined as the time between the creation of a combustible mixture and the appearance of a flame. The ignition delay may be considered as a physical delay plus a chemical delay. The time lag between the high-temperature exposure and the minimum amount of fuel vapours generated for ignition is the physical delay; the time between the availability of an ignitable amount of vapour and the overcoming of the activation energy is the chemical delay [25]. Note that, in the autoignition of homogeneous mixtures of fuel and oxidiser, there is almost no physical delay compared with that of an inhomogeneous mixture, as the time for mixing the fuel and air is not required [24]. Therefore, the ignition delay obtained from premixed gaseous mixtures (e.g., using a rapid compression machine or a shock tube) is significantly lower than a non-premixed configuration for the same fuel under the same operating conditions. In other words, the ignition delay of a premixed fuel and oxidiser is comprised almost entirely of the chemical delay. The experimental apparatus used here is based on a non-premixed configuration, and so the autoignition delay times described here should only be compared with data obtained using a similar experimental arrangement. Such data provide a fundamental understanding of the overall ignition characteristics of fuel droplets, which is important in the design and optimisation of practical liquid–fuel combustors. The experimental apparatus is relatively easy to use, and is appropriate for a comparative study to investigate the effects of the addition of NPs to a liquid hydrocarbon fuel on the overall autoignition and combustion characteristics, including the total ignition delay time, autoignition temperature, and the droplet autoignition and combustion behaviour.

In this section, we describe the effects of the addition of various concentrations of NPs to heptane droplets on the autoignition characteristics at a range of ambient temperatures. The autoignition delay time of pure heptane droplets was studied first as a baseline for comparison. This allowed us to distinguish the effects of the addition of NPs on the autoignition behaviour of the heptane-based nanofluid fuel droplets. The initial diameter of the pure heptane droplets was maintained in the range 0.945–1.059 mm in order to minimise the effects of variation in the droplet diameter on the autoignition delay time. The ignition delay time was defined as the time from the entry of the droplet into the furnace to the ignition radiation [26]. The occurrence of ignition was identified visually by the appearance of a flame through the use of high-speed colour photography [22].

3.1.1. Autoignition of a pure fuel droplet

Figure 1 shows a comparison of the ignition delay of the pure heptane droplets reported here and results reported previously [26–29]. For the purposes of comparison, the ignition delay data reported at atmospheric pressure (0.1 MPa) with the initial diameter of the droplets near to 1.0 mm was selected from Refs. [26–29] and included here in order to minimise the effects of variations in the droplet diameter on ignition delay time. The ranges of ambient temperatures and initial droplet diameters are listed in Table 1.

The ignition delay of the heptane droplets followed an Arrhenius functional form, with the logarithmic ignition delay times plotted on the ordinate and the inverse of the absolute ambient temperature shown on the abscissa. At atmospheric pressure, the ignition delay time decreased exponentially with increasing temperature, which conforms to pre-existing similar data [26–31]. As shown in the figure, despite the lack of data at low temperatures in Refs. [26–29], the ignition delays were in good overall agreement, with the exception of the data reported by Tanabe et al. [29], which was attributed to differences in the initial diameter of the droplets. At relatively high ambient temperatures (775–800 °C), however, all the data were in good agreement.

The data shown in Fig. 1 were fitted using linear regression, which indicates that they followed the functional form \( \tau = A \exp (D/T) \), where \( \tau \) is the ignition delay time, \( T \) is the ambient temperature, and \( A \) and \( D \) are constants. The values of the constants \( A \) and \( D \) for pure heptane were calculated from our experimental autoignition delay data, and found to be \( A = 0.02194 \) ms and \( D = 9824 \) K. The values of the constants \( A \) and \( D \) calculated from the experimental data reported in Refs. [26–29], along with the initial diameter of the droplets, are listed in Table 1. The constants for heptane reported here were approximately in the middle of the range of the previously reported data.

3.1.2. Autoignition of stabilised heptane droplets

To investigate the effects of addition of OA on autoignition characteristics of heptane droplet, the ignition delay times of stabilised heptane (OA added heptane) droplets were also measured. The ignition delay data of stabilised heptane (heptane/OA) droplets provide another baseline to differentiate the effect of NPs on droplet autoignition behaviour. Figure 2 compares the ignition delay data of stabilised heptane droplets containing 0.5%, 2.5% and 5.0% OA with the ignition delay times of pure heptane droplets at various ambient temperatures and a constant pressure of 0.1 MPa. Regardless of the concentration of OA, the stabilised heptane droplets exhibited almost same ignition delay times as pure heptane droplets in the temperature range of 650–850 °C. However, the addition of OA in heptane completely inhibited ignition at 600 °C. This is probably due to the phenomenon of evaporation suppression which is well-known and already reported in literature. The addition of surfactant usually creates a thin layer around the droplet’s surface and the diffusion of fuel component is...
To understand the effects of the ambient temperature, the autoignition delay times of Al NP-heptane droplets were measured using high-speed photography (300 frames per second). The droplets with diameters in the range 0.907–1.083 mm were formed and the ignition was detected using linear regression. It follows that the ignition delay times of Al NPs decreased the ignition delay at relatively low temperatures, whereas the NPs at higher concentrations of Al NPs increased the ignition delay. These results show that the addition of dilute concentrations of Al NPs to heptane droplets decreased the ignition delay at relatively low temperatures, whereas the addition of larger concentrations of Al NPs increased the ignition delay. At higher temperatures (750–850 °C), irrespective of the concentrations of the NPs, the ignition delay times of the n-Al/heptane droplets were comparable to those of pure heptane.

### 3.1.3. Autoignition of n-Al/heptane droplets

In this section, we discuss the effects of temperature and the concentration of Al NPs on the autoignition delay times of Al NP-laden heptane (n-Al/heptane) droplets. Droplets with diameters in the range 0.907–1.083 mm were formed and the ignition was detected using high-speed photography (300 frames per second).

#### 3.1.3.1. Effect of NP concentration on the autoignition delay time

Figure 3 shows the ignition delay times of heptane droplets and heptane-based nanofluid droplets containing 0.5%, 2.5%, and 5.0% Al NPs whose surfaces were coated with 0.5%, 2.5%, and 5.0% of OA, respectively, at various ambient temperatures and a pressure of 0.1 MPa. The addition of NPs significantly affected the ignition delay. At higher temperatures (750–850 °C), the ignition delay times were similar. The low (0.5%) and higher NP loadings (2.5% and 5.0%) exhibited opposite effects on the ignition delay times at lower temperatures. The most significant effect was the appearance of ignition at 600 °C for low NP loadings (0.5%). The addition of 0.5% NPs decreased the ignition delay at 600 °C, whereas the NPs at a concentration of 2.5% and 5.0% completely inhibited ignition at 600 °C. Similarly, at 650–700 °C with a NP loading of 0.5%, the ignition delay remained the same as that of pure heptane, whereas an increase in the NP loading (i.e., 2.5% and 5.0%) increased the ignition delay. These results show that the addition of dilute concentrations of Al NPs to heptane droplets decreased the ignition delay at relatively low temperatures, whereas the addition of larger concentrations of Al NPs increased the ignition delay. At higher temperatures (750–850 °C), irrespective of the concentrations of the NPs, the ignition delay times of the n-Al/heptane droplets were comparable to those of pure heptane.

#### 3.1.3.2. Effect of ambient temperature on the autoignition delay time

To understand the effects of the ambient temperature, the logarithm of the ignition delay times of n-Al/heptane droplets containing 0.5%, 2.5% and 5.0% Al NPs, as well as of pure heptane droplets, were plotted as a function of the inverse ambient temperature, as shown in Figure 3. As with the pure heptane droplets, the autoignition delay times of the n-Al/heptane droplets were fitted using linear regression. It follows that the ignition delay times of the n-Al/heptane droplets also followed an Arrhenius functional form. However, the values of the constants strongly depend upon the Al NP loading in the droplet. With the dilute suspension (0.5%), a smaller value of D and larger value of A were obtained in comparison with pure heptane. However, with the 2.5% and 5.0% NP suspensions, larger values of D were obtained, as listed in Table 2. Irrespective of the concentration of the NPs, the lower (600–700 °C) and higher (750–850 °C) temperature ranges exhibited opposite effects on the ignition delay times of the n-Al/heptane droplets compared with pure heptane. For a given NP loading, if the ignition delay times were comparable to pure

### Table 1

<table>
<thead>
<tr>
<th>Source</th>
<th>Initial diameter range, $d_i$ (mm)</th>
<th>Temperature range, $T$ (K)</th>
<th>$A$ (msec)</th>
<th>$D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current study</td>
<td>0.925–1.058</td>
<td>873–1123</td>
<td>0.02194</td>
<td>9824</td>
</tr>
<tr>
<td>Faeth and Olson [27]</td>
<td>1.32</td>
<td>923–1031</td>
<td>0.00579</td>
<td>11,125</td>
</tr>
<tr>
<td>Saitoh et al. [28]</td>
<td>0.978–1.028</td>
<td>973–1023</td>
<td>0.29701</td>
<td>7375</td>
</tr>
<tr>
<td>Takei et al. [26]</td>
<td>0.933–1.057</td>
<td>950–1023</td>
<td>0.0039</td>
<td>11,388</td>
</tr>
<tr>
<td>Tanabe et al. [29]</td>
<td>0.700–0.750</td>
<td>900–1000</td>
<td>0.000469</td>
<td>13,383</td>
</tr>
</tbody>
</table>

#### Fig. 2

Comparison of ignition delay times of stabilised heptane droplets containing 0.5%, 2.5% and 5.0% OA with pure heptane droplets at various ambient temperatures.

#### Fig. 3

A Comparison of ignition delay data of n-Al/heptane droplets containing 0.5%, 2.5% and 5.0% Al NPs with pure heptane droplets under different ambient temperatures.
heptane droplets at 750–850 °C, then the delay times obtained at 600–700 °C were longer than those of pure heptane droplets. In contrast, if the ignition delay times were longer than that for a pure heptane droplet at 750–850 °C, then the delay times obtained at 600–700 °C were shorter than those of a pure heptane droplet.

To understand the underlying mechanism for this, it is necessary to investigate the vaporisation behaviour of the droplets before ignition. We obtained sequential images of the droplets and determined the normalised droplet diameter squared as a function of time, as shown along with a comprehensive discussion in Supplementary Material.

### 3.1.3.3. Droplet behaviour prior to autoignition

Figure 4 shows the time dependence of the normalised diameter squared of the heptane and n-Al/heptane droplets with Al NP loadings of 0.5%, 2.5%, and 5.0% up to ignition and at various ambient temperatures. Figure 4a shows these data at temperatures of 600, 650, and 700 °C on red, blue and black coloured x-axes, respectively. The initial heating period of the n-Al/heptane droplets was longer than that of the pure heptane droplets at temperatures in the range 600–650 °C. This initial heating time is defined as the time interval over which the droplet diameter decreased to 98% of its initial diameter. The successive vaporisation period of the n-Al/heptane droplets was reduced due to the increased evaporation rate. In addition, the NP-laden heptane droplets ruptured into smaller fragments. Such microexplosions have been observed in other multi-component fuel droplets [32]. Because of these ruptures, the droplets containing relatively high loadings (2.5% and 5.0%) of Al NPs lost a significant proportion of their mass, and were reduced to a diameter that could not be ignited at 600 °C. As the temperature increased from 600 °C to 700 °C, the diameter of the n-Al/heptane droplets increased, and they ruptured earlier. This behaviour was more prominent in the droplets containing higher concentrations of NPs.

Figure 4b shows the time dependence of the normalised diameter squared at 750, 800, and 850 °C on their corresponding coloured x-axes. At these elevated temperatures, the NP-laden heptane droplets expanded significantly. Depending upon the NP concentration, the droplet diameter increased by 8–37% from the initial diameter. Upon further generation of fuel vapours, the droplets ruptured into smaller droplets, ejecting fragments along with aggregates of NPs. Ignition occurred as they ruptured into smaller fragments. These microexplosions caused the n-Al/heptane droplets to produce sufficient vapour for ignition. For this reason, the droplets with Al NP loadings of 2.5% and 5.0% exhibited similar ignition delay times as the pure heptane droplets. At 850 °C, the droplets containing 5.0% Al NPs ignited slightly earlier than the pure heptane droplets.

Heptane is a highly volatile fuel and their droplets consist of a multi-component and multi-phase nature of the droplet affected the vapourisation rate and behaviour. Upon rupture of these bubbles, the droplets fragmented. Therefore, the diameter of the droplet decreased quickly before the time required to overcome the activation energy for combustion. This is why the n-Al/heptane droplets containing 2.5% and 5.0% Al NPs did not ignite at 600 °C. At 650 °C, the n-Al/heptane droplets loaded with Al NPs at 2.5% and 5.0% exhibited a reduction in diameter of approximately 80%; however, due to the increased temperature, they
overcame the activation energy and ignition was observed. For this reason, the ignition delay times were significantly longer than those of the pure heptane droplets. As the temperature increased further, the autoignition delay time of the NP-laden heptane droplets approached that of the pure heptane droplets. At 850 °C, the autoignition delay time of the 2.5% n-Al/heptane droplets was slightly shorter than that of the pure heptane droplets at the same temperature.

It follows that the addition of Al NPs to a liquid hydrocarbon fuel droplet can lead to early vapourisation or fragmentation, which can result in a decrease in the ignition delay time, especially at elevated temperatures. The lack of ignition at 600 °C and the delayed ignition at 650 °C with NP loadings of 2.5% and 5.0% can also be explained by the vapourisation and fragmentation of the droplets, and the chemical kinetics describing the ignition of heptane droplets. We may expect that the addition of Al NPs to a less volatile liquid hydrocarbon fuel, where ignition is diffusion limited, may lower the ignition delay time, and may also lower the ignition temperature.

3.2. Droplet combustion

In this section, we discuss the effects of the addition of various concentrations of Al NPs on the droplet combustion at high ambient temperatures. The combustion rate constant and burning behaviour of pure heptane droplets was investigated as a baseline for comparison. This helped us to distinguish the effects of the addition of the Al NPs on the combustion behaviour of the heptane-based nanofluid fuel droplets. The temperature was varied in the range 550–850 °C, and the pressure was maintained at 0.1 MPa.

3.2.1. Combustion of pure fuel droplets

Figure 5 shows the normalised diameter squared of the pure heptane droplets as a function of time and at various ambient temperatures. At 550 °C, the 1-mm-diameter heptane droplet did not ignite; however ignition and subsequent combustion were observed at temperatures in the range 600–850 °C. Following ignition, the droplet expanded and then ruptured to form a smaller droplet; the diameter of the droplet was then reduced following the $d^2$-law. Shortly after ignition, bubble formation and subsequent rupture of the pure heptane droplet occurred via heterogeneous nucleation caused by the fibre. The combustion rates were calculated from the linear part of the combustion of the heptane droplets using a least-squares regression method as shown in the figure. For temperatures higher than 700 °C, there is a slight curvature in data in the end part of droplet lifetime where the droplet was significantly reduced and it gets an elliptical shape rather than spherical. Probably, the fibre effects (heat conducted from fibre) become significant in the end part of droplet lifetime, resulted in increased combustion rate which showed slight curvature in data at relatively higher temperatures.

A comparison between the combustion rates of the heptane droplets reported here and those reported in Ref. [33] is shown in Fig. 6 to show the consistency of the experimental apparatus. The combustion rates obtained here were higher at relatively low temperatures (600–700 °C), and were similar to the data in Ref. [33] at higher temperatures. This was attributed to differences in the droplet diameters and fibre diameters used in the two studies. Khan [33] suspended droplets with an initial diameter of 1.0–1.2 mm on quartz fibres with diameters of 0.125 mm and 0.2 mm, which were rounded at the tips with bead diameters of 0.25 mm and 0.35 mm, respectively. However, in this work, each droplet was suspended on a 0.1-mm-diameter SiC fibre with no bead at the tip, and droplets with similar initial diameters (in the range 0.945–1.059 mm) were used. There is a scatter in data reported in the figure. As mentioned that the fibre effects were observed during the combustion of heptane droplets therefore the presence of supporting fibre could be partially responsible for this scatter. In this sense, for highly volatile fuels, free fall droplet combustion would be much better for the measurement of combustion rate constant.

3.2.2. Combustion of stabilised heptane droplets

To investigate the combustion behaviour of NPs laden heptane droplet through a comparative analysis, it is important to examine the combustion characteristics of stabilised heptane (heptane/OA) droplet with the addition of various concentrations of OA at same elevated temperatures. The combustion behaviour of heptane/OA droplets serves as a better baseline than pure heptane droplets to identify the effects of the addition of NPs on droplet combustion behaviour.

![Fig. 5. Diameter squared histories of combusting pure heptane droplets at various ambient temperatures.](image-url)

![Fig. 6. Comparison of the combustion rates of heptane between present study and previous study by Khan [33] at various ambient temperatures and constant pressure of 0.1 MPa.](image-url)
Ignition was occurred and then droplet diameter was reduced by droplet combustion. After an initial transient heating up period, droplets exhibited three stages similar to binary-component fuel and the concentration of OA added to heptane, the heptane/OA corresponding coloured combusting heptane/OA droplets at 750, 800, and 850 shows the time dependence of the normalised diameter squared of figure 7.

Figure 7 shows the normalised temporal histories of diameter squared of combusting stabilised heptane droplets containing 0.5%, 2.5% and 5.0% OA at various ambient temperatures (a) at 600, 650 and 700 °C and (b) at 750, 800 and 850 °C.

3.2.3. Combustion of n-Al/heptane droplets
3.2.3.1. General combustion behaviour. The combustion of isolated n-Al/heptane droplets was investigated at temperatures in the range 600–850 °C and at atmospheric pressure. Prior to a comparative analysis and discussion regarding the combustion of the n-Al/heptane droplets, it is useful to review the literature related to the combustion characteristics of nanofluid droplets. Gan and Qiao [15] identified five distinct stages, i.e., preheating and ignition, classical combustion, microexplosions, surfactant flame, and aluminium droplet flame, in n-decane/nano-Al suspensions with a 10-wt. % loading of 80-nm-diameter Al NPs and a surfactant content of 2.5 wt. % (Sorbitan Oleate, better known as Span 80). During the combustion of droplets of nano-Al/ethanol suspension formulated with the same composition of surfactant and NPs, they observed similar stages; however, there were two differences. First, the droplets underwent swelling and subsequent contraction, with smaller droplets being ejected from the primary droplets, even prior to ignition. Second, fragmentation of the primary droplets was significantly more intense, which resulted in more particles undergoing combustion during the classical droplet burning and microexplosion stages for the nano-Al/ethanol droplets compared with the n-decane/Al droplets. Note that in that study, the droplets were ignited by a heated wire, whereas here, the droplets autoignited at various ambient temperatures.

Figures 8 and 9 show sequential images describing the combustion of pure heptane and n-Al/heptane droplets at 650 and 850 °C. These images of the burning droplets are shown to investigate the effects of elevated temperature on the combustion characteristics of nanofluid droplets. The subfigures a–d correspond to pure heptane and 0.5%, 2.5%, and 5.0% n-Al/heptane droplets, respectively. Figure 10 shows the temporal variation of the normalised diameter squared of the pure heptane droplets, as well as n-Al/heptane droplets containing 0.5%, 2.5%, and 5.0% Al NPs at various ambient temperatures on their corresponding coloured x-axes. A simultaneous, side-by-side visualisation of the data in these figures is shown in Supplementary Videos 2 and 3.

Figures 8a and 9a show the combustion behaviour of pure heptane droplets at 650 and 850 °C, respectively. Regardless of
the temperature, the pure heptane droplets exhibited three main stages: ignition, vapour accumulation, and $d^2$-law combustion (i.e., classical droplet combustion). As discussed in the previous section, the expansion of the droplet and subsequent rupture immediately following ignition (due to the effects of the fibre) were prominent in the data shown in Fig. 8a(ii–v), but were not detected at 850°C (see Fig. 9a). During the development of the flame, vapour accumulation (with a soot-shell appearance) occurred, which is a commonly observed characteristic of heptane droplet combustion [34]. Following this, an envelope flame was established, which was maintained for the majority of the lifetime of the droplet combustion.

In contrast to the combustion of the pure heptane droplets, and regardless of the concentration of the Al NPs, the combustion of the n-Al/heptane droplets was mainly comprised of four distinct stages: ignition, microexplosion, vapour accumulation, and a surfactant flame. The first significant difference with combustion of the n-Al/heptane droplets was the appearance of microexplosions, rather than classical droplet combustion. Shortly following ignition, the heptane droplets containing NPs underwent severe expansion and contraction processes due to bubble nucleation inside the droplet and its subsequent rupture, as shown by the images labelled stage II in Figs. 8b and 9b–d. The formation of bubbles and growth in this stage caused oscillation of droplet which is clearly visible in Supplementary Videos. This process of bubble generation and rupture (i.e., microexplosion) commenced prior to ignition at relatively high temperatures (in the range 750–850°C), as shown in Fig. 10b. The droplet expanded by a factor of approximately 1.5–2 prior to rupture. During rupture, a few smaller droplets, along with NPs and/or aggregates of NPs, were ejected from the primary droplet. The emitted fragments were significantly smaller than the primary droplet, and burned along with the ejected NPs. Following ignition, the rupture of the primary droplet disturbed the development of an envelope flame, and enhanced the gasification of the liquid fuel significantly compared with the pure heptane droplets. This resulted in more vapour accumulation and soot-shell appearance than combustion of the pure heptane, as shown in the snapshots labelled stage III in Figs. 8b and 9b–d. At the end of stage III, an envelope flame was established around the droplet. The droplet exhibited disruption (i.e., swelling and contraction) behaviour again, and this process was repeated several times until the droplet diameter was reduced significantly. The disruptive burning behaviour can be identified by the distortions in the envelope flame surrounding the droplet. Most of NPs combusted during this process, and nearly all of the liquid fuel was consumed; the envelope flame became weaker and was almost extinguished. Shortly afterwards, a second flame appeared, which became brighter and, after a short duration (0.02–0.12 s), was extinguished, as shown in photographs labelled stage IV in Figs. 8b–d and 9b–d. This flame was similar to an envelope diffusion flame, also observed during the combustion of heptane/OA droplets and was identified as a “surfactant flame” in Ref. [15]. Following the extinction of this secondary flame (i.e., the surfactant flame), almost no agglomerates remained at the tip of the fibre.

These stages were more prominent at relatively high temperatures (700–850°C), as shown by the images in Fig. 9b–d. These
stages were observed at almost all temperatures, except for 650 °C. At this relatively low temperature, and with relatively high Al NP loadings of 2.5% and 5.0%, ignition occurred close to the end of the droplet lifetime; therefore, all the stages were omitted except for the first and last. The droplet expanded and contracted several times prior to ignition, which resulted in the ejection of multiple smaller droplets and NPs from the primary droplet, and consequently, a significant reduction in the diameter. Due to the very small diameter of the droplet at ignition, only one flame was observed, which may be considered as a surfactant flame. The other stages, which were observed in the case of the 0.5% n-Al/heptane droplets at the same temperature (see Fig. 8b), were not observed for Al NP loadings of 2.5% and 5%, as shown in Fig. 8c and d. In case of the 2.5% n-Al/heptane droplets, the diameter was reduced so much that an envelope flame was not established. However, with the 5.0% Al NP loading, a highly luminous envelope flame was observed. The brightness of the flame indicates that the NPs burned in the flame, as shown in Fig. 9d and snapshots (xxi, xxi).

Overall, during combustion of the n-Al/heptane droplets, some stages were similar to the observations of Gan and Qiao [15] during the combustion of other nanofluid droplets (i.e., microexplosion and a surfactant flame). However, other stages (classical combustion, and an Al droplet flame or Al agglomerate combustion) were absent, and instead, an additional stage (vapour accumulation or soot-shell formulation) was observed. Vapour accumulation or a sooty flame is characteristic of the combustion of heptane, which was observed during the combustion of pure heptane droplets,
Fig. 8 (continued)

(a) Ignition
(i) Stage I

(b) Development, propagation and establishment of flame
(ii-xi) Stage IV

(c) Toward the end
(d) Extinguish

(a) Ignition
(i) Stage I

(b) Development, propagation and establishment of flame in ii-iv
(c) Burning in iv-vi

(d) Bubble pops up
(ii-x) Stage IV
(e) Extinguish

\[
\frac{d_i^3}{d_i^2} = 0.048 \\
\tau = 1.125 \text{s}
\]

\[
\frac{d_i^3}{d_i^2} = 0.226 \\
\tau = 1.315 \text{s}
\]
and is in agreement with previous observations [35]. The absence of classical combustion is a significant and distinct feature. It has been reported [15] that most of the highly volatile liquid fuel is consumed during \( d^2 \)-law combustion. The remains of the droplet consisted mainly of NPs and surfactant, which accumulated to form a shell, and subsequently microexplosions occurred due to the trapped highly volatile fuel. These microexplosions occurred later in the droplet lifetime, similar to the behaviour observed in multi-component fuel droplets [32] or slurry fuel droplets [36]. Here, soon after ignition, instead of the \( d^2 \)-law dependence, the droplet expanded due to bubble formation inside it. This indicates that the liquid fuel was gasified not only at the droplet surface but also inside the droplet. Such early onset of bubble generation in the \( n \)-Al/heptane droplets was not possible due to homogeneous nucleation, because earlier in the droplets’ lifetime only the surface region was heated [32]. A comparison between the combustion behaviour of \( n \)-Al/heptane droplet (Fig. 10) and heptane/OA droplet (Fig. 7) proves that the microexplosions observed during the combustion of nanofluid droplet specifically in early lifetime of droplet (prior to autoignition) and during the major part of the droplet lifetime (in primary flame) were only due to the presence of NPs. The disruptions occurred during the secondary flame (surfactant flame) can be attributed a little to the addition of OA. The Al NPs may be heated more readily than the surrounding heptane, as well as by absorption of the heat radiating from the flame following ignition, leading to a temperature in excess of that of the surrounding liquid. Furthermore, the heterogeneous nature of the \( n \)-Al/heptane mixture is expected to provide nucleation sites for bubble generation, which is similar to the mechanism described for kerosene-based nanofluid droplets [14], where the Al NPs caused heterogeneous nucleation, which occurred early in the droplet lifetime and deep within the inner core of the droplet. The resulting microexplosions effectively transported the NPs to the outer regions of the droplet. This is the reason that the droplet fragmentation or microexplosions observed here occurred earlier in the droplet lifetime and became more intense with increasing temperature or NP concentration. The effects of an increase in temperature on the microexplosions were more significant compared with the effects of the increase in the concentration of the NPs. These intense microexplosions caused nearly all of the NPs to move out of the droplet, and to burn in a primary or secondary (surfactant) flame. Therefore, almost no agglomerates (i.e., residue) remained on the fibre and an ‘Al droplet flame’ was not observed. This indicates significantly improved combustion of the Al NPs here compared with previous reported observations.

This lack of Al agglomerates is very important, and has not been observed previously. The formation of agglomerates during the combustion of slurry fuels (consisting of micron-sized particles) has been cited as a major problem restricting their application [36]. The intense microexplosions are the cause of this lack of formation of Al agglomerates; however, the effect of the surfactant (OA), as well as the method of using the surfactant, is expected to be significant in preventing the formation of Al agglomerates. Gan and Qiao [15] also found more intense and frequent microexplosions in ethanol/Al droplet combustion compared with the combustion of \( n \)-decane/Al droplets; however, those microexplosions did not lead to a complete lack of Al agglomerates. They observed ignition and combustion of Al agglomerates in the
$t - \tau = 0.000 \text{ s}$
$0.0033 \text{ s}$
$0.0133 \text{ s}$
$0.0300 \text{ s}$
$0.0467 \text{ s}$
$0.0533 \text{ s}$

(a) Ignition

(i) Stage I

$(b)$ Flame development

$(c)$ Microexplosion (Expansion in droplet

(iii-ix) Stage II

$0.0567 \text{ s}$
$0.0600 \text{ s}$
$0.0633 \text{ s}$
$0.0733 \text{ s}$
$0.1033 \text{ s}$
$0.1067 \text{ s}$

(d) Vapors accumulation

(xi-xiv) Stage III

$0.1233 \text{ s}$
$0.1833 \text{ s}$
$0.2667 \text{ s}$
$0.2733 \text{ s}$
$0.2767 \text{ s}$
$0.2833 \text{ s}$

and soot-shell establishment

(e) Disruptive burning (Distortion of envelope flame)

(xi-xviii) Stage IV

$0.3200 \text{ s}$
$0.3233 \text{ s}$
$0.3567 \text{ s}$
$0.3700 \text{ s}$
$0.3733 \text{ s}$
$0.3800 \text{ s}$

(f) Primary flame disappear

(g) Surfactant flame

(xx-xxiii) Stage IV

(h) Extinguish

Fig. 9 (continued)
ethanol/Al droplets, which comprised approximately 64% of the lifetime of the droplets (from 0.528 s to 1.464 s). Ethanol has a boiling point of 79 °C, which is significantly lower than that of heptane (98.4 °C) and the surfactant used in that study (Span 80) has a boiling point of 579 °C, which is higher than that of OA (360 °C). They reported that the intensity and frequency of microexplosions increased significantly when a base fuel with a lower boiling point was used, as well as a larger difference between the boiling points of the base fuel and the surfactant, and that the microexplosions observed in the ethanol/Al droplets were stronger than those observed during the combustion of the n-Al/heptane droplets reported here. However, in contrast to the observations reported in Ref. [15], Al agglomerates were not detected following the combustion of the n-Al/heptane droplets described here. Therefore, in contrast to the observations reported in Ref. [15], Al agglomerates were not detected following the combustion of the n-Al/heptane droplets described here. In addition to the intense microexplosions, the use of OA as surfactant, and that the microexplosions observed in the ethanol/Al droplets were stronger than those observed during the combustion of the n-Al/heptane droplets reported here. However, in contrast to the observations reported in Ref. [15], Al agglomerates were not detected following the combustion of the n-Al/heptane droplets described here. Therefore, in addition to the intense microexplosions, the use of OA as surfactant, and the surfactant coating of NPs with this ligand, is expected to be a significant factor explaining the absence of Al agglomerates. This may lead to the easy escape of the NPs because the surfactant is coated on the NP surfaces so that agglomeration of the Al NPs is suppressed, which in turn inhibits the formation of a compact shell that remains as one or more large Al agglomerates after the combustion of the liquid fuel. Distributed smaller bubbles were clearly visible during droplet expansion following ignition, as shown in Fig. 9c(iii,iv) and d(iii–v). The NPs presented separately or their smaller aggregates can cause the formation of such distributed smaller bubbles inside a droplet. Further experimental studies are required to explore the elimination of large agglomerates of NPs in nanofluid fuels droplet combustion and the underlying factors and mechanisms responsible for this phenomenon.

3.2.3.2. Average gasification rate of n-Al/heptane droplets. As discussed in the previous section, the combustion history of n-Al/heptane droplets did not obey the $d^2$-law; thus, the least squares method is not applicable to the calculation of the combustion rate constant. In heptane-based nanofluids, the droplets started to expand prior to ignition. For this reason, the combustion rate constant could not be calculated based on the droplet ignition diameter $d_i$ and burning time $t_b$. Instead, for the heptane-based nanofluid droplets, the average gasification rate (or burning rate) was defined as $K_b = \frac{d_i^2}{t_{tc}}$, where $K_b$ is average gasification rate, $d_i$ is the initial droplet diameter, and $t_{tc}$ is total combustion time of the droplet, which is the sum of the ignition delay time $t_i$ and burning time $t_b$. Although the droplet diameter squared did not vary linearly with time, the average gasification rate defined here is only a measure of the mass gasification rate, which provides the combined effect of NPs during the whole combustion process, i.e., the initial heating period, vaporisation, ignition, and disruptive burning.

Before discussing the average gasification rate, first we provide a discussion of the burning time $t_b$ of the pure heptane and n-Al/heptane droplets. The aim is to aid the understanding of the effects of the NPs on the average gasification rate. Figure 11 shows a comparison of the burning time of the n-Al/heptane droplets containing 0.5%, 2.5% and 5.0% Al NPs with pure heptane droplets at
rupture in vii and viii (e) Vapors accumulation/ Soot-shell appearance (f) More (ix-xi) Stage III

microexplosions (g) Particle burning in flame (h) Near end of primary flame

(i) Surfactant flame (j) Propagation of surfactant flame and particle combustion by microexplosions (xviii-xxiii) Stage IV

Extinguish and particle combustion by microexplosions (k) (xviii-xxiii) Stage IV

(d)
various ambient temperatures. This figure shows that, as with the pure heptane droplets, the burning time of the heptane-based nanofluids droplets increased with increasing temperature. However, with the 0.5% and 2.5% Al NP loadings, the burning time obtained at relatively high temperatures (800–850 °C) was faster than that of the pure heptane droplets. This was due to the microexplosions, which were intensive at these temperatures. In contrast, the fast burning times at relatively low temperatures (650–700 °C) with the 2.5% and 5.0% NP loadings were due to delayed ignition that occurred almost at the end of droplet lifetime.

3.2.3.3. Effect of ambient temperature on the average gasification rate. Figure 12 shows the average gasification rate of n-Al/heptane droplets containing 0.5%, 2.5% and 5.0% Al NPs, as well as that of pure heptane droplets. The average gasification rate of the pure heptane droplets and the nanofluid droplets increased with the temperature. This trend was more pronounced with the n-Al/heptane droplets. At relatively low temperatures (650–700 °C), the gasification rate of the 2.5% and 5.0% n-Al/heptane droplets was equal to or slightly slower than that of the heptane droplets. However, at higher temperatures (750–850 °C), irrespective of the NP loading, the gasification rate of the nanofluid droplets was substantially faster than that of the pure heptane droplets.

The observed gasification rate of n-Al/heptane droplets was affected by the ignition (ignition delay time) and phenomenon of microexplosions occurring in nanofluid droplets. An early ignition (shortened ignition delay) enhances the gasification rate because after ignition, the appearance of flame around the droplet resulted in more and faster heat transfer to the droplet. On the other hand, microexplosions ruptured the droplet and a few smaller droplets, along with NPs and/or aggregates of NPs, were ejected from the primary droplet. This phenomenon also enhanced the gasification rate. At relatively low temperatures, due to high loadings (2.5%...
and 5.0%) of Al NPs, the ignition was obtained at the end of droplet lifetime. The microexplosions also occurred in the later part of the droplet lifetime. Therefore the observed gasification rate with NPs was equal or even slower than that of the pure fuel droplet. At relatively high temperatures, the ignition delay time of nanofluid droplets was comparable to that of the pure fuel droplets. The microexplosions occurred early in droplet lifetime and become more intense with increasing temperature or NP concentration. Consequently, the gasification rates with NPs become significantly higher. The driving mechanism controlling this behaviour is the mechanism of microexplosions in nanofluid droplets which was described in our previous study [14].

3.2.3.4. Effect of NP concentration on the average gasification rate. The data plotted in Fig. 12 also show that the average gasification rate of the nanofluid droplets varied significantly with the NP loading. An increase in the NP loading exhibited opposite effects on the gasification rates at relatively low (600–750 °C) and high (800–850 °C) temperatures. As the concentration of NPs increased from 0.5% to 5.0%, the gasification rate monotonically increased at higher temperatures, whereas at lower temperatures, as the NP loading increased from 0.5% to 2.5%, and the gasification rate decreased and became lower than that of the pure heptane droplets. At lower temperatures, a further increase in the concentration of NPs to 5.0% resulted in a slight increase in the gasification rate; however, it remained lower than that of the 0.5% NP suspension or of the pure heptane droplets.

4. Conclusions

We have experimentally investigated the effects of various concentrations of Al NPs on the autoignition and combustion behaviour of heptane-based nanofluid fuel droplets at various ambient temperatures. The aim of this work was to gain an improved understanding of the autoignition and combustion characteristics of these nanofluid fuels. The major results of this work may be summarised as follows.

(1) The ignition delay time of the pure heptane droplets and the n-Al/heptane droplets decreased exponentially with increasing ambient temperature, and can be described by the Arrhenius equation.

(2) At relatively low temperatures (600–700 °C), the addition of 0.5% Al NPs to heptane decreased the ignition delay time, whereas Al NP loadings of 2.5% and 5.0% increased the ignition delay time. At higher temperatures (750–850 °C), the ignition delay time of the n-Al/heptane droplets was comparable to that of the pure heptane droplets. At Al NP loadings of 2.5% and 5.0% NPs, the diameter of the droplets was reduced significantly due to bubble generation and rupture of the droplet; ignition did not occur at 600 °C at these NP loadings, although ignition was observed with pure heptane and 0.5% n-Al/heptane.

(3) In contrast to the pure heptane droplets, the n-Al/heptane droplets exhibited disruptive burning behaviour at all temperatures (600–800 °C), and did not obey the classical $d^2$-law. The NPs were ejected from the droplets via microexplosions that occurred early in droplet lifetime, and were more intense at higher temperatures and larger NP concentrations. Because of these intense and frequent microexplosions, almost no residue or agglomerated NPs remained on the fibre, and no separate Al flame was observed.

(4) The ambient temperature significantly affected the average gasification rate of the heptane-based nanofluid fuel droplets. At relatively low temperatures (650–700 °C), the gasification rate of the 2.5% and 5.0% n-Al/heptane droplets was equal to or slightly lower than that of the pure heptane droplets. At higher temperatures (750–850 °C), the gasification rate of the nanofluid droplets was substantially faster than that of the pure heptane droplets, irrespective of the NP concentration. This was attributed to the intense microexplosions, which reduced the burning time and the total combustion time of the n-Al/heptane droplets at these high temperatures.

Acknowledgment

This work was supported by the Midcareer Researcher Program through the NRF Grant funded by MEST (2010-000353).

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.combustflame.2014.07.015.

References