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Full Length Article Combustion mechanism of nanobubbled dodecane: A reactive molecular study

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ABSTRACT

Keywords: Nanobubbles Dodecane Combustion ReaxFF Molecular dynamics simulation Blended fuels, created by adding methanol to ammonia or incorporating nanobubbles such as a hydrogen nanobubbles into existing fuels, offer significant opportunities for decarbonization of combustion devices. Nanobubbles (NBs), defined as gaseous cavities smaller than 1 µm in diameter, possess unique characteristics such as long-term stability, the capacity for free radical generation, and a high surface-to-volume ratio. These attributes make them potential candidates for various industrial applications, including water purification, medical engineering, and the energy and power sector. However, the fundamental understanding of the effects of NBs on chemical processes such as combustion cannot be easily captured through experimental techniques. Alternatively, reactive molecular approaches can provide a clear understanding of the impact of NBs on the combustion process. In this study, ReaxFF molecular dynamics simulations were utilized for a comparative study of the combustion of pure dodecane and hydrogen, nitrogen, and oxygen nanobubbled samples. The findings reveal that nitrogen NBs lower the activation energy to 52.89 kcal/mol for samples with a density of 0.17 g/mL by boosting the production of intermediates and radicals, which in turn increases dodecane consumption. In contrast, oxygen NBs increase the activation energy to 66.93 kcal/mol for samples with the same density, reducing dodecane consumption. At 2000 K, C₂H₄ is the primary product in pure, hydrogen, and oxygen nanobubbled samples, while water is the most prevalent in nitrogen nanobubbled sample at a density of 0.017 g/ mL. Moreover, a temperature increase significantly enhances the thermal decomposition of the fuel in pure sample compared to nanobubbled samples. Additionally, as the density of hydrogen nanobubbled samples increases, there is a corresponding rise in fuel consumption, and water emerges as the primary product in samples with a density of 0.25 g/mL at 2000 K.

1. Introduction

Fossil fuels, including diesel, petroleum, natural gas, and coal, serve as the primary energy sources globally. However, their finite, nonrenewable nature and their role in exacerbating global warming conflict with the objectives of the Paris Agreement [1–3]. This agreement seeks to achieve a decarbonized society by the latter half of this century, emphasizing the importance of finding sustainable energy solutions. Alternative fuels like ammonia and hydrogen offer significant potential for decarbonization [4,5]. Yet, they face notable challenges, such as hydrogen's high reactivity, posing safety risks during storage and combustion, and ammonia's slow chemical conversion rate. Additionally, ammonia's nitrogen content can also result in substantial NOx emissions upon combustion [6,7]. Blended fuels, formed by mixing components like methanol to ammonia and nanobubbles such as hydrogen nanobubbles into existing fuel, offer a significant opportunity for decarbonization [8–10].

Nanobubbles (NBs) are minute gas-filled cavities with a spherical cap shape, typically measuring below 1 μ m in diameter [11]. They can exist as surface NBs or within bulk solutions [12,13], generated through various methods like cavitation [14], electrolysis [15], ethanol–water exchange [16], and membrane techniques [17]. The distinctive characteristics of NBs, such as their long-term stability, capability for free radical generation, elevated surface-to-volume ratio, and expedited mass transfer efficiency, render them indispensable additions in numerous domains [18–21]. These include aquaculture [22], wastewater treatment [23], medical applications [24], as well as power and energy sectors [25,26]. In energy and power applications, NBs serve various roles. They contribute to enhancing the production of biofuels from renewable biomass energy sources by accelerating bacterial and

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metabolic activities [27]. NBs can act as nano-additives in host liquids for renewable energy applications, particularly when the thermophysical properties of the host liquids are critical, as they possess the capability to alter molecular interactions and thermophysical properties within the medium [28]. Moreover, blending NBs with fuels like diesel, biodiesel, gasoline, and alcohol has been explored as a practical approach to improving combustion properties, reducing emissions, and increasing fuel conversion efficiency [9,10,29].

In recent years, there has been a growing interest in research on blended fuel combustion due to the influence of added components on combustion characteristics. Oh et al. [9] conducted an experimental study on the effect of adding hydrogen NBs to gasoline engines' combustion performance. In their research, they adjusted the air-to-fuel equivalence ratio to stoichiometric levels for both gasoline and the hydrogen NB gasoline blend. The results revealed improvements in the power output and brake specific fuel consumption (BSFC) of gasoline engines with the hydrogen NB gasoline blend compared to conventional gasoline at a specific engine load. In another experimental study, Nakatake et al. [30] utilized a super miniature ejector-type mixer to continuously mix nano air-bubbles into the fuel line, aiming to explore the impact of air NBs on diesel engine performance. They noted an increase in charging efficiency and a slight decrease in the density of exhaust smoke. It is also reported that adding a small amount of hydrogen to the incoming fuel-air mixture enhances flame velocity and allows the engine to operate with leaner mixtures. Consequently, this leads to a more complete burn of the existing fuel, resulting in significant reductions in exhaust emissions, increased power, and improved mileage [31]. By blending gases in combustion engines, researched have found improved engine performance and lower emissions. It was noted that the injection of nitrogen has a considerable impact on combustion and exhaust emissions [32]. Yan et al. [33,34] explored the thermal and chemical effects of hydrogen addition on methane combustion. The findings indicated that increasing hydrogen concentration contributed to enhanced ignition and improved methane conversion rates. Sun et al. [35] conducted a hybrid experimental and macro-simulation study to investigate the combustion characteristics of ammonia/n-dodecane mixtures. They observed that the inclusion of ammonia in the gas mixture leads to an increase in the thickness of the laminar flame.

While experimental and macro-scale simulations offer insights into blended fuel combustion, including engine performance and exhaust gas emissions, they struggle to capture intricate molecular-level interactions and reaction mechanisms affecting combustion dynamics. ReaxFF molecular approaches enable detailed exploration of combustion processes at the atomic scale, providing precise information on chemical interactions at the atomic level during combustion. Liu et al. [36] explored the mechanisms of methane/hydrogen blended combustion through reactive molecular dynamics simulation. They noted that the initial reaction pathways of methane were altered in the presence of hydrogen. In another ReaxFF study, Song et al. [37] reported that active species exert a significant influence on the oxidation mechanism of ethanol during their investigation of the combustion mechanism of ethanol/nitromethane. Given the pivotal role of chemical interaction between blended components and hydrocarbon fuels in combustion processes and characteristics, as well as the potential of nanobubbled fuel to improve combustion properties, this study examines the impact of three types of NBs, namely hydrogen, nitrogen, and oxygen, on the combustion characteristics of dodecane using the ReaxFF molecular approach to understand the effect of the type of introduced NB, temperature, and density of samples on their combustion characteristics.

2. Theory and modelling

Nanoscience stands as one of the most captivating contemporary scientific fields, focusing on materials and systems with unique physical and chemical properties at the nanoscale. It offers profound insights into the behavior of matter at the level of individual atoms and molecules, representing a crucial stride towards practical applications [38]. Additionally, atomistic-scale computational techniques provide a potent avenue for exploring, developing, and optimizing the promising properties of novel materials. Molecular approaches encompass a range of methods, including quantum mechanics (QM) and molecular dynamics simulation (MD). Quantum dynamics in molecular and solid-state systems involve solving the time-dependent Schrödinger equation, describing the combined electron and nuclear dynamics. However, exact solutions for the multicomponent equations of motion, governing the total electron-nuclear wave function, are exceedingly challenging and feasible only for simplified model systems with few electrons and nuclei in low dimensions. Consequently, while methods grounded in quantum mechanics offer valuable theoretical insights at the electronic level, they often prove computationally demanding for simulations involving the full dynamic evolution of a system. In contrast, molecular dynamics, which applies Newton's second law and employs various potentials to replicate atom interactions, predicts the motion of atoms over time, enabling researchers to explore complex systems via molecular approaches [39-41].

Atomistic force-field methods rely on interatomic potentials to determine the energy of a system based on the positions of its atoms. Classical approaches are adept at capturing non-reactive interactions, including angle strain represented by harmonic potentials, dispersion described by van der Waals potentials, and Coulombic interactions depicted through various polarization schemes. However, these classical methods fall short when modeling reactive systems due to their treatment of molecular structures, such as constant bonds between atoms, charges, and dihedrals. On the other hand, ReaxFF method enables simulations that involve reactive events at the interfaces between solid, liquid, and gas phases by providing a transferable description of each element across phases. By utilizing a bond-order formalism alongside polarizable charge descriptions, ReaxFF accurately models both reactive and non-reactive interactions between atoms, enabling it to effectively capture covalent and electrostatic interactions across a wide range of materials [41,42]. The energy contributions to the ReaxFF potential can be delineated as follows [43,44]:

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{Specific}$$
(1)

where E_{bond} represents the energy associated with bond formation, which varies continuously with interatomic distance. E_{over} imposes an energy penalty to prevent atom overcoordination, based on atomic valence rules. E_{angle} and E_{tors} denote the energies linked to three-body valence angle strain and four-body torsional angle strain, respectively. $E_{Coulomb}$ and $E_{vdWaals}$ account for electrostatic and dispersive contributions across all atoms, independent of connectivity or bond order, whereas E_{Specific} integrates system-specific terms customized to capture unique properties. The ReaxFF potential, as described in Equation (1), encompasses both bond-order-dependent energy, $E_{bond} + E_{over} + E_{angle} +$ E_{tors} , and non-bonding interactions or bond-order-independent energy, $E_{vdWaals} + E_{Coulomb}$. The ReaxFF force field utilizes bond strength measurements based on the Tersoff method, employing bond order (BO) as a key parameter. This bond order reflects contributions from σ bonds, π bonds, and double- π bonds, and varies according to the distances between atoms and is expressed as [43,44]:

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi}$$

= $exp[p_{bo1}.(r_{ij}/r_o^{\sigma})^{p_{bo2}}] + exp[p_{bo3}.(r_{ij}/r_o^{\pi})^{p_{bo4}}] + exp[p_{bo5}.(r_{ij}/r_o^{\pi\pi})^{p_{bo6}}]$
(2)

where *BO* is the bond order between atoms *i* and *j*, r_{ij} is interatomic distance, and r_0^{σ} , r_0^{π} , and $r_0^{\pi\pi}$ correspond to the equilibrium bond lengths of the σ bond, π bond, and double- π bond, respectively. The terms from p_{bo1} to p_{bo6} are parameters used to model the bonds. In this study, the C/H/O/N-2019 ReaxFF potentials [45], incorporating parameters for carbon, hydrogen, and oxygen from the widely used C/H/O-2016



Fig. 1. Initial configuration of (a) a pure sample containing dodecane ($C_{12}H_{26}$) and oxygen molecules, featuring red carbon atoms, blue hydrogen atoms, and green oxygen atoms, and (b) a nanobubbled sample, orange NB atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Time evolution of (a) the number of dodecane molecules in pure and nanobubbled samples, and the number of chemical species, oxygen, and nanobubbles molecules within (b) nitrogen, (c) pure, (d) hydrogen, and (e) oxygen nanobubbled samples.

potential [46] for studying hydrocarbon combustion, alongside interactions for nitrogen atoms, were employed to investigate the combustion of nanobubbled dodecane fuel. All simulations were performed using the open-source LAMMPS package [47]. Visualization was performed with Ovito software [48], and the reaction network was generated using ReacNetGenerator [49].

All prepared samples underwent a relaxation process for 300 picoseconds (ps) in the NVT ensemble, followed by heating to the desired temperature. Subsequently, a combustion process was investigated over 2000 ps with a timestep of 0.1 fs (fs). Each prepared sample was studied



Fig. 3. The three most produced chemical species at 2000 K after 2000 ps within (a) pure, (b) oxygen, (c) hydrogen, and (d) nitrogen nanobubbled samples.

with three different initial structures. Nanobubbles, including oxygen, hydrogen, and oxygen, were incorporated into dodecane fuel to investigate the influence of NB type on the combustion characteristics of dodecane. Additionally, hydrogen nanobubble samples were examined at three different densities to elucidate the impact of the sample density on the combustion characteristics of nanobubbled dodecane fuel.

3. Results and discussion

3.1. Effects of nanobubble type

To prepare the sample for stoichiometric combustion, 100 dodecane molecules and 1850 oxygen molecules were randomly distributed within a cubic box with a side length of 90.64 Å in three dimensions, resulting in a sample density of 0.17 g/mL. NBs of three different types, each with a radius of 3 nm, were introduced into the pure sample. The dimensions of the box were adjusted to 95.05 Å, 93.80 Å, and 90.91 Å for oxygen, nitrogen, and hydrogen NBs, respectively. These NBs contained 365 oxygen molecules, 295 nitrogen molecules, and 345 hydrogen molecules. The initial configuration of the prepared samples has been illustrated in Fig. 1. The combustion process of the prepared samples was investigated for 2000 ps at 2000 K.

Fig. 2a illustrates the time evolution of the number of dodecane molecules in pure and nanobubbled samples. It can be seen that the presence of nitrogen and hydrogen NBs accelerates the consumption of dodecane molecules, whereas the addition of oxygen NB leads to a decrease in dodecane consumption compared to the pure sample.

To delve deeper into the initial stages of the combustion process, an

examination was conducted regarding the number of chemical species and molecules at the combustion temperature for 60 ps. Fig. 2c illustrates the number of oxygen molecules and chemical species in the pure sample. Notably, no reaction was observed before reaching the desired temperature. However, despite the constant number of oxygen molecules, there was a noticeable increase in the number of chemical species at the combustion temperature over time. Further analysis of the formed species unveiled that the reaction commenced with the thermal decomposition of $C_{12}H_{26}$ to $C_{10}H_{21}$ and C_2H_5 . This decomposition process proceeded with the formed species decomposing into C8H17 and C₂H₄. In Fig. 2d, the number of chemical species and molecules in the hydrogen nanobubbled sample, inclusive of dodecane, oxygen, and hydrogen, is shown. Before reaching the desired combustion temperature, no reaction occurred. As the temperature reached the desired level, an increase in the number of chemical species was observed, while the number of hydrogen and oxygen molecules remained constant. The reaction initiation in this sample commenced with the thermal decomposition of C12H26. Likewise, the oxygen nanobubbled sample followed a similar trajectory to the pure and hydrogen nanobubbled samples, where the reaction commenced with the decomposition of the hydrocarbon fuel.

Conversely, within the nitrogen nanobubbled sample (Fig. 2b), reactions occurred near the desired temperature. Oxygen molecules reacted with nitrogen molecules, yielding the formation of N_2O_2 (dioxohydrazine). Additionally, interactions between nitrogen molecules and dodecane molecules resulted in the formation of $C_{12}H_{26}N_2$, at temperatures near 2000 K, which converted into $C_{12}H_{25}$ and HN₂. This unique behavior suggests that the reaction process in the nitrogen nanobubbled

Table 1

The most common reaction leading to water production within the pure, oxygen (ONB), hydrogen (HNB), and nitrogen (NNB) nanobubbled samples (the numbers on the arrows indicate the frequency of a reaction).

Pure	$O H \xrightarrow{4} H^{O}_{H}$	$\xrightarrow{3}$ H H	$H_{0}^{H} \rightarrow H^{0}_{H}$
ONB	$O H \xrightarrow{3} H^{O} H$	0^{-0} H $\xrightarrow{1}$ H $\xrightarrow{0}$ H	$H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H$
HNB	H H $\xrightarrow{11}$ H H $\xrightarrow{0}$ H	$O H \rightarrow H^{O} H$	$0^{-0}H \xrightarrow{2} H^{-0}H$
NNB	$O H \xrightarrow{82} H^{O} H$	$H_{0}^{0}H \xrightarrow{36} H^{0}H$	$H_{N} \xrightarrow{N}_{H} \xrightarrow{35}_{H} \xrightarrow{O_{H}}_{H}$



Fig. 4. Reaction network of intermediates and radicals originating from the introduced nitrogen nanobubbles that result in water production.

sample initiated through molecule reactions and formation of intermediates and radicals, rather than thermal decomposition, thereby accelerating the consumption of dodecane.

Fig. 3 displays the three most abundant chemical species at 2000 K at the conclusion of the simulation period. C_2H_4 , C_3H_6 , and CH_3 are the predominant species created in the pure, oxygen, and hydrogen nanobubbled samples. Conversely, water was the most produced species in the nitrogen nanobubbled sample. In addition to the species shown in Fig. 3, other chemical species such as CO and H_2O were detected in the pure, oxygen, and hydrogen nanobubbled samples. Moreover, compounds like CO, NO₂, and NO were also found in the nitrogen nanobubbled sample as well.

The most significant distinction in the produced chemical species among the prepared samples lies in the production of water, within the nitrogen nanobubbled sample exhibiting the highest quantity. Further analysis of water production in the prepared samples shows that the hydrogen nanobubbled sample had the second highest water production, whereas the oxygen nanobubbled sample recorded the lowest amount of water production. To elucidate the mechanism underlying the influence of NBs on water formation, the reaction network was investigated [49]. Table 1 illustrates the most frequent reaction pathway resulting in the production of water within the prepared samples, with a notable emphasis on the reaction involving OH, which is particularly prominent in the nitrogen NB sample, primarily originating from H_2O_2 introduced by the nitrogen NB. Additionally, Fig. 4 provides further insight into the influence of blended nitrogen NB on the reaction path of the formation of intermediates and radicals.

Differences between the reaction pathways in the pure sample and the oxygen nanobubble (NB) sample are highlighted in Table 1. The pure

sample notably features the incorporation of hydrogen atoms from the dodecane structure into water molecules as the second most frequent reaction. Detailed tracking of hydrogen atoms in the fuel structure reveals this pathway: $C_{12}H_{26} \rightarrow C_{10}H_{21} \rightarrow C_7H_{15} \rightarrow C_4H_9 \rightarrow CH_3 \rightarrow CH_2O$ \rightarrow H₂O, demonstrating that hydrogen from dodecane thermal decomposition contributes to the formation of water. In contrast, this reaction pathway is absent in the oxygen nanobubbled sample. Furthermore, the comparison of dodecane consumption in Fig. 2a indicates higher dodecane consumption in the pure sample compared to the oxygen nanobubbled sample. The introduction of oxygen nanobubbles, which increase the availability of oxygen in the sample, can act as heat sinks by absorbing energy from the combustion process, thereby lowering reaction rates and decomposition of dodecane. Moreover, oxygen NB can quench radical species involved in combustion reactions, decreasing the frequency of chain reactions and reducing overall reaction rates. Additionally, the presence of excess oxygen molecules can dilute the concentration of fuel molecules in the combustion mixture, resulting in fewer fuel molecules available to participate in combustion reactions and consequently leading to slower reaction rates.

Fig. 3 highlights that water is the predominant product in the nitrogen nanobubbled sample, while the formation of C_2-C_3-C species prevails in the pure, hydrogen, and oxygen nanobubbled samples. It's crucial to note that a pivotal stage in the formation of soot during the oxidation of rich hydrocarbon fuels involves the recombination reactions of carbon-containing fragments, leading to the generation of species with two or more carbon atoms [50]. Within the neat dodecane sample and samples with hydrogen, and oxygen nanobubbles, C_2H_4 , C_3H_6 , and CH_3 exhibit the highest production levels. Interestingly, when comparing the production of C_2H_4 and CH_3 in these three samples as predominant products, it's observed that the addition of oxygen and hydrogen to the pure sample decreases the formation of C_2H_4 , with the lowest amount recorded for hydrogen nanobubbled samples. Conversely, the production of CH_3 increases, with the highest amount observed for the oxygen nanobubbled sample.

An examination of the reaction pathways and their frequencies leading to the production of C_2H_4 in pure and hydrogen nanobubbled samples, as shown in Fig. 5a and b, highlights the significant role of C_2H_5 in the formation of C_2H_4 . Notably, in the hydrogen nanobubbled sample (Fig. 5b), more C_2H_5 intermediates convert to HO₂ radicals compared to the pure sample. This increased conversion leads to the production of more water molecules and fewer C_2H_4 molecules in the hydrogen nanobubbled sample than in the pure sample. Furthermore, scrutinizing the reaction pathway for the formation of CH₃ in pure and oxygen nanobubbled samples (Fig. 6a and b) reveals the important role of CH₃O₂ as the most frequent reaction in CH₃ formation. Interestingly, in the oxygen nanobubbled sample, more CH₃O₂ converts to CH₃ compared to the pure sample. Consequently, blending NBs with the host



Fig. 5. Reaction paths of formation C₂H₄ within (a) pure and (b) hydrogen nanobubbled sample.

k



Fig. 6. Reaction paths of formation \mbox{CH}_3 within (a) pure and (b) oxygen nanobubbled sample.

fuel alters the production quantity by affecting the production and reaction of intermediates and radicals, thereby influencing the combustion process.

3.2. Impacts of temperature

In order to explore the influence of temperature variations on the combustion process, an investigation was conducted within the temperature range of 1800 K to 2400 K, with 200 K intervals, under the samples density of 0.17 g/mL, with three different initial configurations for each temperature, totaling 48 simulations. The investigation entailed tracking the evolution of dodecane over a 200 ps timeframe to determine the reaction rate constant and activation energy. The reaction rate constant at each temperature is determined using the following integrated first-order rate law equation [51]:

$$t = \ln(N_0) - \ln(N_t) \tag{3}$$

where N_0 represents the initial number of dodecane molecules, N_t denotes the number of molecules at any given time t, and k stands for the rate constant. The rate constants obtained at various temperatures were utilized to construct the Arrhenius plot for the dodecane molecules. The activation energy and pre-exponential factor can be calculated using the Arrhenius equation, which is described as follow [51]:

$$k = A e^{\frac{-L_a}{RT}} \tag{4}$$

in which E_a signifies the activation energy, A represents the preexponential factor, and R is the universal gas constant. Therefore, the values of A and E_a can be determined by plotting the logarithm of the reaction rate constant against the inverse of temperature, as depicted in



Fig. 7. Arrhenius parameters extracted from fitted rate constants ln(k) versus temperature for (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen nanobubbled samples at a density of 0.17 g/mL.



Fig. 8. Number of total chemical and carbon species after 2 ps within (a) pure, (b) hydrogen, (c) nitrogen, and (d) oxygen samples.

Fig. 7. It is evident that the reaction rate increases with an increase in reaction temperature. The activation energy extracted from Fig. 7 for dodecane at 0.17 g/mL is 63.76 kcal/mol, aligning with the previous study's reported value of 63.68 kcal/mol [52]. Additionally, for the hydrogen nanobubbled sample, an activation energy of 62.73 kcal/mol was observed, whereas for the nitrogen nanobubbled sample, it was 52.89 kcal/mol, and for the oxygen nanobubbled sample, it was 66.93 kcal/mol. This comparison suggests that nitrogen and hydrogen NBs decrease the activation energy of fuel, while the incorporation of oxygen NB increases it.

To deepen the understanding of the effects of temperature and NBs on the initial stages of the combustion process, the total number of chemical and carbon species at 2 ps at temperatures of 1800 K and 2400 K was depicted in Fig. 8. It was observed that an increase in temperature was associated with a higher consumption of dodecane and the production of more carbon-based species in both the pure sample and the nanobubbled samples. At elevated temperatures, fuel molecules became more susceptible to thermal decomposition, resulting in their breakdown into smaller, more reactive fragments that readily participated in combustion reactions. However, an investigation into the rate of increase in the emergence of carbon-based species with rising

temperatures revealed that the rate of emergence of carbon-based species in the fuel within the pure sample, hydrogen, nitrogen, and oxygen nanobubbled samples was increased by 1033 %, 766 %, 283 %, and 221.08 %, respectively, when the temperature was raised from 1800 K to 2400 K. The comparison of the initial stages at 2 ps of the pure sample at lower and higher temperatures (Fig. 8) showed that in the pure sample, increasing the temperature accelerated carbon decomposition into smaller carbon-based species more than nanobubbled samples. Therefore, it can be concluded that the existence of NBs decreases the thermal decomposition of fuel at the initial stages. However, in nitrogen nanobubbled samples, increasing the temperature also led to an increase in the number of noncarbon-based intermediates and radicals, as the amount of HN2 and N2O2 at the higher temperature increased by 253.03 % and 175.18 %, respectively, compared to the lower temperature that accelerated the consumption of fuel molecules during the combustion process, as by the end of 200 ps, 93 % of the fuel had been consumed in the nitrogen nanobubbled sample at 2400 K, while 83.34 % of the fuel had been consumed in the neat dodecane sample. The hydrogen nanobubbled sample experiences an increase in both carbon-based and noncarbon-based intermediates and radicals as the temperature increases, similar to the nitrogen nanobubbled sample, resulting in a



Fig. 9. (a) Time evolution of the number of dodecane molecules, and (b) average pairwise energy within hydrogen nanobubbled samples across various densities.

decrease in activation energy. A comparison of Fig. 8a and 8d reveals that the total number of species and carbon-based species in the oxygen nanobubbled sample at higher temperatures is less than that in the neat dodecane sample. As discussed and illustrated in Fig. 8, the presence of NBs decreases the rate of carbon decomposition at higher temperatures compared to the pure sample. In contrast to the pure sample, where increasing temperature provide more heat for fuel thermal decomposition, in the nanobubbled samples, part of this heat is absorbed by the NB atoms. In the case of nitrogen and hydrogen nanobubbled samples, this results in an increase in noncarbon-based intermediates and radicals, a phenomenon that is not observed in the oxygen nanobubbled samples. This indicates that oxygen atoms from the introduced NB into the fuel acts as a heat sink, thereby increasing the activation energy.

3.3. Influences of sample density

Molecular collisions and bonding reactions play crucial roles in pyrolysis and combustion processes. The change in sample density can serve as an approximation for different chemical species concentrations in macro studies [53]. Additionally, due to the importance of hydrogen engines fueled with a mixture of hydrogen and other fuels, three samples containing hydrogen NBs with various densities were prepared. Each sample consisted of 100 dodecane molecules and 1850 oxygen molecules, along with hydrogen NBs with a radius of 3 nm. These components were randomly distributed within cubic boxes with side lengths of 116.88 Å, 90.91 Å, and 79.95 Å to achieve hydrogen nanobubbled samples densities with 0.08 g/mL, 0.17 g/mL, and 0.25 g/mL, respectively to investigate the combustion process over a duration of 2000 ps.

Fig. 9a displays the time evolution of the number of dodecane molecules, illustrating that as density increases, more dodecane is consumed over time. This phenomenon can be attributed to the closer proximity of atoms as density rises, resulting in stronger interactions between them. As depicted in Fig. 9b, this in turn results in elevated pairwise energy, leading to more frequent and energetic collisions among atoms. Consequently, during combustion processes, the increased energy facilitates more efficient reactions, thereby driving increased fuel consumption rates over time.

As noted, an increase in density leads to higher fuel consumption over time. However, a detailed analysis of Fig. 9a indicates that in the initial stages of combustion, the density of the sample does not significantly affect the combustion process. But as time progresses, for example, after 1000 ps as shown in Fig. 9a, the density of the samples starts to significantly influence the rate of fuel consumption. In chemical reactions, molecules must surmount specific energy barriers to initiate reactions. The activation energy for a hydrogen nanobubbled sample at a density of 0.17 g/mL was previously calculated to be 62.73 kcal/mol. Using the same method, the activation energies for hydrogen nanobubbled samples at densities of 0.08 g/mL and 0.25 g/mL were determined to be 60.84 kcal/mol and 66.72 kcal/mol, respectively, as illustrated in Fig. 10. It can be observed that as the density of the sample increases, the activation energy also rises. Therefore, in denser systems, molecular interactions can generate additional or higher energy



Fig. 10. Arrhenius parameters derived from fitted rate constants ln(k) versus temperature for hydrogen nanobubbled samples at (a) 0.085 g/mL and (b) 0.25 g/mL densities.



Fig. 11. The total number of chemical species and the top five products in hydrogen nanobubbled samples at densities of (a) 0.08 g/mL and (b) 0.25 g/mL, measured at 2000 K after 2000 ps.





barriers. These barriers arise because molecules must find more precise orientations for reactions, given the increased number of neighboring molecules and the resulting interaction forces. The close proximity of many molecules requiring them to overcome additional rotational or translational energy barriers. Once these barriers are overcome, the more energetic collisions among atoms in denser samples lead to increased fuel consumption over time.

Fig. 11a and 11b depict the total number of chemical species and the five dominant products for hydrogen nanobubbled samples with densities of 0.08 g/mL and 0.25 g/mL, respectively. These figures confirm



Fig. 12. The reaction pathways and the frequency of the conversions in the formation of CH₂O within samples with densities of (a) 0.08 g/mL and (b) 0.25 g/mL, and H₂O within samples with densities of (d) 0.08 g/mL and (e) 0.25 g/mL within hydrogen nanobubbled sample (the numbers in the circles indicate the frequency of a reaction).

that the number of chemical species increases with density. This rise can be attributed to the enhanced rate of molecular collisions; as density increases, molecules are forced closer together, boosting the frequency of collisions. Additionally, higher densities modify thermodynamic conditions like pressure, potentially shifting reaction equilibria and facilitating the formation of a more diverse array of chemical species. In both samples, the primary products include C_3H_6 , C_2H_4 , and C_4H_8 . However, the sample with a density of 0.08 g/mL predominantly features CH₃ and C_2H_5 , whereas H₂O and CH₂O are more prevalent in the sample with a higher density. Table 2 illustrates the three most unique consumption path of CH₃ and C₂H₅, which are among the top five chemical species observed at lower densities, for hydrogen nanobubbled samples at a density of 0.08 g/mL and 0.25 g/mL. As it can be seen in the higher density sample, more CH₃ is converted to CH₄O (methanol), CH₃O (methoxy groups), and C₂H₆O (ethanol), which can be attributed to pressure-related effect on reaction dynamics and thermodynamics. High pressure, compressing molecules within a smaller volume, significantly boosts the frequency of molecular collisions, thereby enhancing the reactivity of CH₃ groups with other molecules. Furthermore, from the data presented in the table,

it is also observed that the conversion of C_2H_5 to C_2H_4 (ethylene) is more frequent under high pressure. Additionally, the formation of HO₂ (hydroperoxide) is accelerated under these high-pressure conditions. Likewise, the likelihood of producing C_2H_6O (ethanol) increases in environments where reactants are densely packed, resulting in more CH_3 and C_2H_5 being consumed over time in higher density samples compared to lower density one.

Fig. 12 illustrates the reaction pathways leading to the formation of CH₂O and H₂O, ranking among the top five products in higher density conditions in both lower and higher density hydrogen nanobubbled samples. Observations highlight the crucial roles of CH₃O and OH radicals in forming CH₂O and H₂O, respectively. In the higher density hydrogen nanobubbled sample, a notable increase in the conversion of CH₃O to CH₂O is observed. This enhancement is attributed to the elevated pressure, which not only increases the collision frequency among molecules but also boosts the overall reaction rate and the likelihood of engaging specific pathways that lead to CH₂O formation. Additionally, an increased production of OH radicals was observed under these high-pressure conditions, thereby increasing their probability of reacting to form water. This highlights the acute sensitivity of radical-driven reactions to changes in pressure and concentration in combustion environments, which serves to accelerate and refine pathways to product formation, such as the efficient conversion of hydroxyl radicals into water within the higher hydrogen nanobubbled sample.

4. Conclusion

In this study, the effects of the type of nanobubbles incorporated into dodecane fuel, temperature, and the density of the prepared samples on the combustion process were investigated using a ReaxFF reactive force field. The main conclusions drawn are as follows:

- (1) The incorporation of nanobubbles and their specific types influence the initiation of the combustion process and its products. In pure, hydrogen, and oxygen nanobubbled samples, combustion begins with the thermal decomposition of the fuel. Conversely, in the nitrogen nanobubbled samples, the emergence of intermediates and radicals interacting with the fuel initiates combustion. The higher production of OH radicals, stemming from H₂O₂ introduced by the nitrogen nanobubbles, results in water becoming the dominant product in nitrogen nanobubbled samples. Meanwhile, C₂H₄ emerges as the predominant species in pure, oxygen, and hydrogen nanobubbled samples at a density of 0.17 g/mL and a temperature of 2000 K.
- (2) In nitrogen nanobubbled samples, the elevated production of intermediates and radicals notably decreases the activation energy and boosts fuel consumption. Observations also show that raising the temperature leads to more extensive thermal decomposition of fuel in pure samples than in nanobubbled ones. Additionally, in both hydrogen and nitrogen nanobubbled samples, higher temperatures result in increased production of intermediates and radicals. On the other hand, oxygen nanobubbles in the oxygen nanobubbled samples function as a heat sink, significantly raising the activation energy and reducing fuel consumption.
- (3) In the hydrogen nanobubbled sample, increasing the density leads to a rise in activation energy, as denser systems facilitate molecular interactions that can create additional or higher energy barriers. However, once these activation energy barriers are overcome, the increased density results in more energetic and frequent reactions, subsequently enhancing the consumption of fuel energy over time.

CRediT authorship contribution statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data of this paper can be accessed from the Brunel University London data archive, figshare at https://brunel.figshare.com

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