Initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 (exo-tetrahydrodicyclopentadiene) on functionalized graphene sheets: Insights from ReaxFF molecular dynamics simulations

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Abstract

Functionalized graphene sheets (FGS) have proven to be an effective nanoparticle additive for jet fuels. In this study, the reactive force field (ReaxFF) molecular dynamics (MD) simulation is employed to investigate the initiation mechanisms of JP-10 pyrolysis and oxidation with FGS in comparison with normal JP-10 reactions. ReaxFF-nudged elastic band (NEB) calculations are performed to study the transition state and energy barrier for key initiation reactions in order to reveal the catalytic effect of FGS on JP-10 pyrolysis and oxidation. The results show that both pyrolysis and oxidation of JP-10 are advanced and enhanced in the presence of FGS, leading to earlier decomposition of JP-10 at a lower temperature and a faster reaction rate. It is found that the OH functional group on the FGS not only advances the initiation of JP-10 but also participates in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10. Moreover, the

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dehydrogenation of JP-10 without FGS is only observed at high temperatures. A deeper insight into
the enhancement resulting from the FGS is provided through the analysis of the results of transition
state and energy barrier for key initiation reactions. It is found that JP-10 decomposition initiated by
OH or H on the FGS occurs at a lower energy barrier than unimolecular decomposition or through
reaction with O2 thereby changing and enhancing the JP-10 initiation. In summary, this research
provides the scientific insight as to the potential use of FGS as a promising catalyst for JP-10 fuel
systems.

**Keywords:** JP-10; Functionalized graphene sheet; Molecular dynamics; Reactive force field;
Nudged elastic band calculation; Catalysis.

1. Introduction

Jet Propellant-10 (JP-10, exo-tetrahydrodicyclopentadiene) is a single-component hydrocarbon
fuel, which is used in aviation applications such as missiles, detonation engines, ramjets and
scramjets due to its extraordinary properties including high energy density [1], high heat capacity [2],
high thermal stability [3] and low freezing point [4]. The operational conditions for use of JP-10 as a
fuel in pulse-detonation engines can reach up to 2500 K and 100 bar [5]. Because of its broad
applications and superior qualities, numerous experimental [2, 6-14] and theoretical [5, 15-21]
studies have been reported for the pyrolysis and oxidation of JP-10. However, one problem of JP-10
and many other liquid hydrocarbon fuels, is that the slow ignition and combustion kinetics could lead
to poor performance for applications like pulse-detonation engines or ramjets [1]. Therefore, research
into the catalytic reaction of JP-10 is of theoretical and practical importance. Moreover, the addition
of additives can further increase the energy density of the fuel system [22, 23]. Particularly for
aeropropulsion systems where the cooling requirements are demanding, the catalytic
dehydrogenation and cracking of endothermic hydrocarbons like JP-10 is able to offer a better
chemical heat sink [24]. To date, the majority of the catalysts used for JP-10 reactions are metal-
based materials [1, 24-28] but these suffer from some disadvantages that cannot be ignored. For
example, there are non-energetic oxide passivation layers on the particles and undesired solid oxide reaction byproducts produced during the combustion process.

In recent years, graphene-based materials, especially functionalized graphene sheets (FGS) have been considered as effective catalysts for fuel and propellant combustion [29-35]. They can not only catalyse fuel combustion reactions, but also be energetically involved in the combustion process, and finally be consumed without producing residual particles. A pioneering work was undertaken by Sabourin et al. [29], who studied the combustion of monopropellant nitromethane enhanced by FGS colloidal particles. They found that the ignition temperature was lowered with the addition of FGS and the burning rate increased up to 175% over neat nitromethane, outperforming more conventional additives such as aluminium oxyhydroxide and amorphous silica oxide nanoparticles. Flame speed enhancement of another monopropellant nitrocellulose by graphene microstructures was also observed in Jain et al.’s [30] experiments. EL-Seesy et al. [31] investigated the impact of adding graphene oxide (GO) nanoparticles to Jatropha Methyl Ester (JME) in a compression ignition (CI) engine and reported that the JME-GO increased the brake thermal efficiency, peak cylinder pressure, highest rate of pressure rise, and peak heat release rate while reducing the duration of combustion and exhaust emissions of CO, UHC and NOx. Similarly, Paramashivaiah et al. [32] examined the effects of graphene nanoparticles addition to a diesel and biodiesel blend in a CI engine and observed similar effects on engine performance and emission.

There has also been increasing interest in using graphene-based materials as additives for jet fuels. Huang and Li [33] explored the ignition and combustion characteristics of jet fuel liquid film containing graphene powers and indicated that the mixture could be ignited with a shorter delay time and that the ignition of graphene occurs prior to that of the jet fuel. Ghamari and Ratner [34] tested the combustion characteristics of colloidal droplets of Jet-A fuel and various carbon-based nanoparticles. Graphene nanoplatelets were found to have an outstanding performance by yielding more than a 7% increase in burning rate at only a 0.1% particle loading. Li et al. [35] recently
reported that the application of GO nanosheets on Jet A-1 fuel improved its combustion performance in air in terms of acceleration of initial linear burning velocity, reduction in ignition delay and decrease in strength and speed of initial transmitted wave. Compared with those jet fuels consisting of extremely complex hydrocarbon mixtures, it is certainly of great interest to study the FGS as a promising catalyst for enhancing the reactions of the single-component hydrocarbon fuel JP-10 where ignition and combustion kinetics are crucial.

To sum up, graphene-based materials are effective catalysts for enhancing fuel and propellant combustion but the understanding of the underlying mechanisms is very limited. Following Sabourin et al.’s [29] pioneering work, Liu et al. [36] studied the enhanced thermal decomposition of nitromethane on FGS by ab initio molecular dynamics (MD) simulations and demonstrated that the catalytic activity originates from the lattice defect complex within the graphene sheet. A reactive force field (ReaxFF) MD simulation research on self-enhanced catalytic activity of FGS in the combustion of nitromethane was completed by Zhang et al. [37]. However, no computational research has been conducted to investigate the potential enhancement by FGS of the reactions of complex hydrocarbons like JP-10 comprising a tricyclic structure. The study of JP-10 as a single-component hydrocarbon fuel is much easier relative to other jet fuels that consist of many hundreds of dissimilar hydrocarbons. In this study, ReaxFF MD simulations are performed to investigate the initiation mechanisms of enhanced pyrolysis and oxidation of JP-10 on FGS and ReaxFF-nudged elastic band (NEB) calculations are conducted to study the transition state and energy barrier for key initiation reactions. Finally, the catalytic effects of FGS on JP-10 pyrolysis and oxidation are revealed.

2. Methodology

2.1. Reactive force field (ReaxFF) molecular dynamics (MD) simulation

The ReaxFF MD is a powerful method for modelling dissociation, transition and formation of chemical bonds within a reactive system. In contrast to quantum mechanics (QM)-based methods,
ReaxFF features the long-time large-scale reactive MD simulations, which are impractical or impossible to achieve with QM methods. It is computationally much cheaper than QM methods while maintaining a high level of accuracy. The concept of bond order is the kernel of ReaxFF and the force field parameters are obtained from QM calculations or/and experimental data. Bond orders are calculated directly from interatomic distances (Eq. (1)) and continually updated at every iteration thereby allowing for connectivity changes [38].

\[
\text{BO}_i = \text{BO}_i^\sigma + \text{BO}_i^\pi + \text{BO}_i^{\pi\pi}
\]

\[= \exp\left[p_{bo\sigma}\left(r_{ij} / r_{ij}^\sigma\right)^{p_{bo\sigma}}\right] + \exp\left[p_{bo\pi}\left(r_{ij} / r_{ij}^\pi\right)^{p_{bo\pi}}\right] + \exp\left[p_{bo^{\pi\pi}}\left(r_{ij} / r_{ij}^{\pi\pi}\right)^{p_{bo^{\pi\pi}}}\right]
\]  

where BO is the bond order between atoms \(i\) and \(j\), \(r_{ij}\) is interatomic distance, \(r_{ij}^o\) terms are equilibrium bond lengths, and \(p_{bo}\) terms are empirical parameters. Equation (1) is continuous for transitions between \(\sigma\), \(\pi\), and \(\pi\pi\) bond character, producing a differentiable potential energy surface as required for calculating the interatomic forces. Equation (2) describes the general energy contributions to the ReaxFF potential as shown below [39]:

\[
E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lp}} + E_{\text{val}} + E_{\text{tor}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}
\]

where \(E_{\text{system}}, E_{\text{bond}}, E_{\text{over}}, E_{\text{under}}, E_{\text{lp}}, E_{\text{val}}, E_{\text{tor}}, E_{\text{vdWaals}}\) and \(E_{\text{Coulomb}}\) represent total energy, bond energy, overcoordination energy penalty, undercoordination stability, long pair energy, valence angle energy, torsion angle energy, van der Waals energy, and Coulomb energy, respectively.

Further details of the ReaxFF formulation and development can be found in previous articles [38, 40-42]. Additionally, ReaxFF MD has proven to be an effective method for studying hydrocarbon/oxygenated hydrocarbon oxidation with [43-45] or without [39, 46, 47] catalysts.

All the ReaxFF MD simulations are performed using the REAXC package embedded in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software [48, 49], with the latest C/H/O ReaxFF force field parameters [39]. In total, four (pyrolysis and oxidation of JP-10 and
their mixture with FGS) three-dimensional and cubic systems with different sizes are established at the same density of 0.15 g/cm³. Periodic boundary conditions are applied in all the three directions. Each system contains 20 JP-10 molecules. For the two systems of JP-10 oxidation and its mixture with FGS, 10 oxygen molecules are introduced to focus on the comparison of initiation mechanisms rather than complete oxidation. The details of system construction as well as structure of JP-10 and FGS are shown in Fig. 1. Specifically, the FGS used in this study, which is modified based on a pristine graphene sheet, has 64 carbon, 12 oxygen and 30 hydrogen atoms, and it is placed in the centre of the simulation box. There are 2 identical functional groups on the graphene sheet and each functional group includes a divacancy decorated by 2 ethers with 4 additional OH groups attached to the C atoms nearby [36]. The edge C atoms of the graphene sheet are adjusted with H atoms. To keep the same density, the size of the cubic simulation boxes is accordingly changed for every system and the volume of the FGS is evaluated by creating a Conolly surface with a radius of 1.0 Å. As a result, the size of all the four systems (Fig. 1a, c, d and f) is 31.11 Å, 32.29 Å, 31.38 Å and 32.53 Å, respectively.
Fig. 1. System configurations for pyrolysis and oxidation of JP-10 and their mixture with FGS: (a) JP-10 pyrolysis, (b) JP-10 structure, (c) JP-10 oxidation, (d) JP-10 pyrolysis with FGS, (e) FGS structure and (f) JP-10 oxidation with FGS. C, H and O atoms are represented in grey, white and red, respectively.

The canonical ensemble (NVT) is employed for all the ReaxFF MD simulations and the system temperature is controlled by the Nosé-Hoover thermostat with a damping constant of 100 fs. The time step used in this study is 0.1 fs. To start with, energy minimization procedure by conjugate gradient algorithm is carried out for every system to eliminate the artificial effects on the initial geometric configuration. Then the system is equilibrated at the starting temperature 300 K for 50 ps. After the equilibrium, temperature is linearly raised to 2300 K during a time period of 1000 ps (heating rate: 2 K/ps), and finally kept constant at 2300 K for another 1000 ps (heating strategy shown in Fig. 3). Simulation results are outputted every 100 fs. A 0.2 bond order cutoff is adopted for species analysis to recognize the molecules/radicals forming during the simulation because a low cutoff value could benefit the capture of all the reactions including those with very short-lived species [40, 46]. All the visualizations of ReaxFF MD simulation results are produced using Visual Molecular Dynamics (VMD) software [50].

2.2. Nudged elastic band (NEB) calculation

Nudged elastic band (NEB) is a method for finding the transition state and calculating the energy barrier of a specific reaction between known reactants and products. A series of intermediate replicas are inserted and the spring force is applied between those replicas in order to find the minimum energy path. The NEB calculation is basically a simultaneous minimization procedure performed via damped dynamics. This method was developed by Henkelman and co-workers [51, 52], and has now been widely used in computational chemistry. All the NEB calculations are conducted by the NEB module in LAMMPS. The initial and final structures of all the studied
reactions are fully relaxed. Two or three intermediate replicas are generated depending on the
complexity of each reaction. The spring constant for connecting each replica is 1 kcal/(mol·Å).

3. Results and discussions

3.1. Detailed initiation reactions of pyrolysis and oxidation of JP-10 and their mixture with FGS

The time evolution of the number of JP-10 molecules for all the four systems is shown in Fig. 2. Both pyrolysis and oxidation of JP-10 are enhanced in the presence of FGS, resulting in the earlier decomposition of JP-10 at a lower temperature. Also, the average reaction rate of JP-10 is faster with the addition of FGS in both cases. The enhancement is further confirmed by the change in relative potential energy between JP-10 pyrolysis/oxidation with FGS and JP-10 pyrolysis/oxidation as shown in Fig. 3. These two lines have a similar trend, which increases to a peak firstly and then keeps decreasing. The increase in the difference of relative potential energy means that the heat absorption is accelerated in the systems with FGS. After about 1000 ps, the potential energy of the systems with FGS reaches their peak values and starts to drop down proceeding to the heat release stage but the potential energy of the systems without FGS is still climbing. As a result, the change in relative potential energy subsequently decreases. This also suggests that the reaction of both pyrolysis and oxidation are advanced and enhanced in the presence of FGS. In order to gain deeper insight into the enhancement, the detailed initial decomposition pathway of every single JP-10 molecule is tracked by analysing the evolution of species together with the visualization of trajectories. The results are summarized in Tables 1 and 2.
Fig. 2. Time evolution of JP-10 molecule number during NVT MD simulations of: (a) JP-10 pyrolysis and its mixture with FGS and (b) JP-10 oxidation and its mixture with FGS.

Fig. 3. Heating strategy and time evolution of relative potential energy between JP-10 pyrolysis/oxidation with FGS and JP-10 pyrolysis/oxidation. The noises of two sets of relative potential energy data are reduced by the Savitzky-Golay filter.
Table 1. Detailed initial decomposition pathways of every single JP-10 molecule in the systems of: (a) JP-10 pyrolysis and (b) JP-10 pyrolysis with FGS.

<table>
<thead>
<tr>
<th>No.</th>
<th>(a) Decomposition Reaction</th>
<th>Time (ps)</th>
<th>No.</th>
<th>(a) Decomposition Reaction</th>
<th>Time (ps)</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n+2} + \text{H}_{2} ]</td>
<td>934.3</td>
<td>11</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n} + \text{H}_{2} ]</td>
<td>1311.9</td>
</tr>
<tr>
<td>2</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n+2} + \text{H}_{2} ]</td>
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<td>12</td>
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<tr>
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<td>14</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n} ]</td>
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<td>15</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n} ]</td>
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<tr>
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<td>16</td>
<td>[ \text{C}<em>{n} \text{H}</em>{2n} ]</td>
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<td>19</td>
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<td>[ \text{C}<em>{n} \text{H}</em>{2n} ]</td>
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Table 2. Detailed initial decomposition pathways of every single JP-10 molecule in the systems of: (a) JP-10 oxidation and (b) JP-10 oxidation with FGS.

<table>
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<th>(a) Decomposition Reaction</th>
<th>Time (ps)</th>
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</tr>
<tr>
<td>7</td>
<td>+ HO₂ → <img src="image15.png" alt="image" /> + H₂O₂</td>
<td>848.2</td>
<td>17</td>
<td><img src="image16.png" alt="image" /> + H₂C=CH₂</td>
<td>1181.8</td>
</tr>
<tr>
<td>8</td>
<td><img src="image17.png" alt="image" /> + H₂C=CH₂</td>
<td>957.4</td>
<td>18</td>
<td><img src="image18.png" alt="image" /> + H₂</td>
<td>1190.1</td>
</tr>
<tr>
<td>9</td>
<td><img src="image19.png" alt="image" /> + H₂C=CH₂</td>
<td>957.6</td>
<td>19</td>
<td><img src="image20.png" alt="image" /> + H₂C=CH₂</td>
<td>1241.3</td>
</tr>
<tr>
<td>10</td>
<td><img src="image21.png" alt="image" /> + H</td>
<td>1012.1</td>
<td>20</td>
<td><img src="image22.png" alt="image" /> + H₂C=CH₂</td>
<td>1260.6</td>
</tr>
</tbody>
</table>
3.1.1. Validation of the ReaxFF method

In previous studies, the ReaxFF MD has proven to be an effective method for investigating the pyrolysis and oxidation of JP-10 [46, 53]. Especially, Chenoweth et al. [46] carried out a comprehensive comparison of the JP-10 decomposition products between various experimental [1, 7-9, 54, 55] and their ReaxFF MD results, where a high similarity was found. Among those many decomposition products discovered in experiments, only a couple of them such as C$_2$H$_6$ and C$_{10}$H$_8$ (napthalene) are not observed in the present research. Both Chenoweth et al.’s [46] and this study capture some decomposition products like C$_3$H$_5$ (allyl radical) and C$_5$H$_8$ (1,4-pentadiene), which were not found in those experiments, but were obtained in several recent experimental studies [6, 12, 14]. In addition to the comparison with experimental results, Chenoweth et al. [46] also validated the ReaxFF method by performing QM calculations and the results were in good agreement with each other. Moreover, the latest C/H/O ReaxFF force field parameters used in the present study have proven to be able to produce comparable results of decomposition pathways and Arrhenius parameters for JP-10 as in experiments [39]. Detailed uncertainty analysis including comprehensive and extensive comparison between QM/experimental and ReaxFF data included in the ReaxFF training set, and validation of the quality of the present ReaxFF force field for studying the JP-10 chemistry are provided in Ref. [39]. Therefore, it is appropriate to investigate the chemistry of JP-10 pyrolysis and oxidation using the ReaxFF MD method with the latest C/H/O parameters.

3.1.2. Effects of FGS addition on JP-10 pyrolysis

The initial step of decomposition for every single JP-10 molecule in the systems of JP-10 pyrolysis and its mixture with FGS is presented in Table 1 and the corresponding time of occurrence is given. The JP-10 pyrolysis has been well studied by both experiment [12-14] and numerical modelling [17, 19, 20, 46] before, so this section focuses on the analysis of effects of FGS addition on the JP-10 pyrolysis. In consistency with Ashraf and van Duin’s [39] results, for normal pyrolysis, the JP-10 molecules mainly decompose into various smaller hydrocarbons by some dominant
pathways (i.e. C₈ & C₂, C₅ & C₅, C₇ & C₃ or C₁₀H₁₅ & H), whereas with FGS, the decomposition of
the first 4 JP-10 molecules begins with the dehydrogenation by the OH group on FGS forming H₂O
and the initiation of these 4 JP-10 molecules all occurs earlier than the first JP-10 decomposition
without FGS. After the initial dehydrogenation, it is also found that the secondary decomposition
into smaller hydrocarbons of these 4 C₁₀H₁₅ radicals happens at 883.8 ps, 893.4 ps, 959.6 ps and 995
ps, respectively, which is more efficient than those JP-10 molecules in normal pyrolysis reactions.
Additionally, the dehydrogenation of JP-10 without FGS (R13, R14 and R17 in Table 1a) is only
observed at a high temperature (2300 K), which also agrees well with the previous results [39].

There are in total 8 OH functional groups on the FGS. The results show that 6 of them are
consumed and the remaining 2 are retained at the end of the simulation. Hence, further to the first 4
OH groups, the complete reactions of the 5th and 6th OH group during the whole simulation time are
analysed as well and they are summarized in Table 3. As can be seen, the two series of reactions both
start from the separation of OH from the FGS. Then the OH quickly reacts with a hydrocarbon
radical forming an oxygenated hydrocarbon. Subsequently, the oxygenated hydrocarbon either reacts
with another hydrocarbon or directly decomposes to produce a smaller oxygenated hydrocarbon.
Next, this smaller oxygenated hydrocarbon goes through various reactions or decompositions
generating H₂O or CO eventually. It can be expected that the last 2 OH groups could also take part in
similar intermediate reactions to enhance the pyrolysis reaction, provided that the simulation time is
long enough.

Table 3. Complete reactions of the 5th and 6th OH group during the whole simulation time of JP-10
pyrolysis with FGS.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 5 OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1631.5</td>
<td>OH leaves the FGS</td>
</tr>
<tr>
<td>2</td>
<td>1637.9</td>
<td>OH + C₅H₅ → C₅H₆O</td>
</tr>
<tr>
<td>3</td>
<td>1771</td>
<td>C₅H₆O + C₇H₁₂ → C₁₀H₁₅ + C₂H₃O</td>
</tr>
<tr>
<td>4</td>
<td>1916.1</td>
<td>C₂H₅O → C₂H₂ + OH</td>
</tr>
</tbody>
</table>
Combining the above two paragraphs, the catalytic reaction steps for JP-10 pyrolysis on FGS can be summarized as follows (Fig. 4): (1) OHs leave the FGS; (2) OHs initiate the pyrolysis reaction by reacting with JP-10 forming C_{10}H_{15} and H_{2}O; (3) more OHs leave the FGS; (4) OHs take part in various intermediate reactions involving oxygenated hydrocarbons. It is indicated that the OH functional groups on the FGS can not only advance the initiation of JP-10 pyrolysis, but also participate in various intermediate reactions to further enhance the pyrolysis reaction.

### Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>OHs</th>
<th>Reaction</th>
<th>Product(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OH leaves the FGS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>OH + C_{6}H_{10}</td>
<td>\rightarrow</td>
<td>C_{6}H_{11}O</td>
</tr>
<tr>
<td>3</td>
<td>C_{6}H_{11}O</td>
<td>\rightarrow</td>
<td>C_{4}H_{7} + C_{2}H_{6}O</td>
</tr>
<tr>
<td>4</td>
<td>H + C_{2}H_{4}O</td>
<td>\rightarrow</td>
<td>H_{2} + C_{2}H_{3}O</td>
</tr>
<tr>
<td>5</td>
<td>C_{2}H_{3}O</td>
<td>\rightarrow</td>
<td>C_{2}H_{3} + CO</td>
</tr>
</tbody>
</table>

**Fig. 4.** Catalytic reaction steps for JP-10 pyrolysis on FGS: (1) OHs leave the FGS; (2) OHs initiate the pyrolysis reaction by reacting with JP-10 forming C_{10}H_{15} and H_{2}O; (3) more OHs leave the FGS; (4) OHs take part in various intermediate reactions involving oxygenated hydrocarbons.

3.1.3. Effects of FGS addition on JP-10 oxidation

Table 2 presents the initial decomposition step for every single JP-10 molecule and its corresponding time of occurrence in the systems of JP-10 oxidation and its mixture with FGS. The
analysis of effects of FGS addition rather than the simple JP-10 oxidation is emphasized in this section. The results show that the initiation of normal JP-10 oxidation includes two main stages, i.e. (1) decomposition of JP-10 and (2) reaction of JP-10 and other decomposed products with radicals like O₂, O, H, OH, HO₂ and H₂O₂, which is in accordance with previous experimental [6] and computational [5, 53] results. In contrast to JP-10 pyrolysis with FGS, the pathways are different although the decomposition of the first 4 JP-10 molecules in the system of JP-10 oxidation with FGS is still initiated by the reaction with OH. A new pathway is found, which involves the C-C bond cleavage followed by OH attachment to one of those two C atoms (R1 and R3 in Table 2b). The complete reactions that these two C₁₀H₁₆OH molecules undergo during the simulation time are listed in Table 4. They both firstly decompose into a smaller oxygenated hydrocarbon and then this oxygenated hydrocarbon goes through a series of reactions to finally form CO and H₂O, respectively. It is worth noting that a short exchange between intermediate products and FGS (R3 and R4 in Table 4 – No. 2 C₁₀H₁₆OH) is observed in the reactions of the second C₁₀H₁₆OH molecule. The same as JP-10 pyrolysis reactions, the initiation of the first 4 JP-10 molecules in the system of JP-10 oxidation with FGS all proceed earlier than the first JP-10 decomposition without FGS and the dehydrogenation of JP-10 without FGS (R12, R13, R15, R16 and R17 in Table 2a) only takes place at a high temperature (2300 K).

Table 4. Complete reactions of two C₁₀H₁₆OH molecules during the whole simulation time of JP-10 oxidation with FGS. The subscript of FGS represents the different forms of FGS containing different numbers of C, H and/or O atoms.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>674.2</td>
<td>C₁₀H₁₇O → C₂H₅O + C₈H₁₂</td>
</tr>
<tr>
<td>2</td>
<td>961</td>
<td>OH + C₂H₅O → C₂H₆O₂</td>
</tr>
<tr>
<td>3</td>
<td>1196.2</td>
<td>C₂H₆O₂ → CH₃ + CH₃O₂</td>
</tr>
<tr>
<td>4</td>
<td>1328.2</td>
<td>H + CH₃O₂ → H₂ + CH₂O₂</td>
</tr>
<tr>
<td>5</td>
<td>1594.9</td>
<td>H + CH₂O₂ → CH₃O₂</td>
</tr>
<tr>
<td>6</td>
<td>1595.2</td>
<td>CH₃O₂ → H₂O + CHO</td>
</tr>
</tbody>
</table>
7 1597.7  C₂H₃ + CHO → C₃H₄O
8 1598.4  C₃H₄O → H + C₂H₃O
9 1616.2  C₃H₅O → C₂H₃ + CO

No. 2 C₁₀H₁₆OH (3rd JP-10 molecule)

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1063.3</td>
<td>C₁₀H₁₇O → C₉H₁₄O + CH₃</td>
</tr>
<tr>
<td>2</td>
<td>1117.2</td>
<td>C₉H₁₄O → C₈H₁₆O + C₃H₄</td>
</tr>
<tr>
<td>3</td>
<td>1123.1</td>
<td>C₈H₁₀O + FGS₁ → FGS₂</td>
</tr>
<tr>
<td>4</td>
<td>1124.7</td>
<td>FGS₂ + C₁₀H₁₄ → FGS₁ + C₆H₁₀O + C₂H₄ + C₈H₁₀</td>
</tr>
<tr>
<td>5</td>
<td>1353</td>
<td>H + C₆H₁₀O → C₆H₁₁O</td>
</tr>
<tr>
<td>6</td>
<td>1353.1</td>
<td>C₆H₁₁O → C₆H₉ + H₂O</td>
</tr>
</tbody>
</table>

With respect to the 8 OH functional groups on the FGS, 6 of them are consumed, leaving 1 OH group and 1 attached O (lose the H) at the end of the simulation. The complete reactions of the 5th, 6th and 7th OH groups during the simulation time are shown in Table 5. Unlike those OHs in pyrolysis reactions which react with hydrocarbon intermediates, the 5th and 6th OH groups are attracted by an H radical directly generating H₂O and H₂, respectively, while the H is found to detach from the 7th OH and then dehydrogenize a hydrocarbon producing H₂. This difference results from the introduction of O₂ generating more OHs from HO₂ and H₂O₂ as well as some oxygenated hydrocarbons which both react with hydrocarbon radicals. Besides, the O₂ itself can also compete with OH’s reaction with hydrocarbons. Due to these reasons, O-H bond cleavage of the OH group on the FGS is only observed in the oxidation reactions. In addition, the H of OH can transfer between different O atoms on the FGS. For example, at 1228.4 ps, an H of OH moves to a nearby O of ether and transfers back to the original O of that OH later at 1512.6 ps. Similarly, in the two reactions of No. 6 OH in Table 5, after losing the H, the O of OH shifts to another edge C atom of FGS and finally leaves the FGS as CO. The remaining one OH group and one attached O could also be involved in the intermediate reactions to further accelerate the JP-10 oxidation if the simulation is continued.
Table 5. Complete reactions of the 5th, 6th and 7th OH groups during the whole simulation time of JP-10 oxidation with FGS. All reactions involving FGS relate to the OH group on it. The subscript of FGS represents the different forms of FGS containing different numbers of C, H and/or O atoms.

<table>
<thead>
<tr>
<th>Sequence</th>
<th>Time (ps)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 5 OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1018.7</td>
<td>$H + \text{FGS}_1 \rightarrow \text{FGS}_2$</td>
</tr>
<tr>
<td>2</td>
<td>1018.8</td>
<td>$\text{FGS}_2 \rightarrow \text{FGS}_3 + H_2O$</td>
</tr>
<tr>
<td>No. 6 OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1030.5</td>
<td>$H + \text{FGS}_3 \rightarrow \text{FGS}_4 + H_2$</td>
</tr>
<tr>
<td>2</td>
<td>1986.6</td>
<td>CO leaves the FGS</td>
</tr>
<tr>
<td>No. 7 OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1755.3</td>
<td>$\text{FGS}_5 \rightarrow \text{FGS}_6 + H$</td>
</tr>
<tr>
<td>2</td>
<td>1759</td>
<td>$H + C_8H_{10} \rightarrow C_8H_9 + H_2$</td>
</tr>
</tbody>
</table>

To summarize, the catalytic reaction steps for JP-10 oxidation on FGS follow the procedure (Fig. 5): (1) OHs leave the FGS; (2) OHs initiate the oxidation reaction by reacting with JP-10 via different pathways; (3) OH or H of OH is abstracted from or leaves the FGS; (4) OH or H take part in intermediate reactions involving the direct formation of H$_2$O and H$_2$. Again, it is the OH functional group that advances the initiation of JP-10 oxidation and further enhances the oxidation reaction by participating in various intermediate reactions.

Fig. 5. Catalytic reaction steps for JP-10 oxidation on FGS: (1) OHs leave the FGS; (2) OHs initiate the oxidation reaction by reacting with JP-10 via different pathways; (3) OH or H of OH is abstracted...
from or leaves the FGS; (4) OH or H take part in intermediate reactions involving the direct formation of H₂O and H₂.

### 3.2. Transition state and energy barrier for key initiation reactions

**Fig. 6.** Transition state and energy barrier for some frequently occurring and key JP-10 decomposition reactions from ReaxFF-NEB simulations. Figs. a–f are placed in the descending order.
of energy barrier and the calculated value of energy barrier is labelled in the bottom right corner in each figure. The C atoms of JP-10 molecule are numbered in the last figure.

Fig. 6 depicts the transition state and energy barrier for some frequently occurring and key JP-10 decomposition reactions extracted from Tables 1 & 2 by ReaxFF-NEB simulations. It is checked that all of the obtained transition states from NEB calculations accord with the dynamic trajectories of ReaxFF MD simulations. Among all these studied reactions, the decomposition of JP-10 to cyclopentene and 1,4-pentadiene (Fig. 6a) has the highest energy barrier of 156.81 kcal/mol. This decomposition procedure follows the sequential cleavage of C-C bonds: C₈-C₉ → C₁-C₂ → C₆-C₇, which is the same as Chenoweth et al.’s results [46]. The sequence of C-C bond dissociation for the reaction producing allyl in Fig. 6b is C₁-C₂ → C₇-C₁₀ → C₈-C₉ and the H attached to C₆ shifts to C₂ before the cleavage of C₇-C₁₀ bond. These reaction steps are also found in DFT calculations [20]. Fig. 6c demonstrates the formation of ethylene resulting from the successive breaking of C-C bonds between C₁ & C₉ and C₇ and C₈. The C₂-C₆ bond broken is seen at a later stage of the simulation leading to 1,5-cyclooctadiene structure. The JP-10 decomposition products of 1,5-cyclooctadiene and ethylene agree with the DFT [18] and ReaxFF MD [46] simulation results. These two reactions in Figs. 6b & c have very close energy barrier values. Figs. 6d & e illustrate the two scenarios of dehydrogenation of JP-10 at C₂ and C₄, respectively. Zhao et al. [14] computed the energy of C-H bond cleavage for every C position of JP-10 by DFT and found that the dehydrogenation at C₂, C₃, C₄ and C₉ are more preferable with the energy ranging from 92.73–97.04 kcal/mol. Three (C₂, C₃ and C₄) of these four dehydrogenations are observed in the present study and the calculated energy barrier for dehydrogenation at C₂ (89.31 kcal/mol) and C₄ (83.28 kcal/mol) is in good agreement with Zhao et al.’s DFT calculations. The conversion of JP-10 to two five-member ring structures were discovered in many studies [6, 7, 12, 14, 17]. The C₁-C₂ bond is broken first followed by further fragmentation via C₆-C₇ separation. In this study (Fig. 6f), before the C₆ is separated from C₇, one H attached to C₁₀ moves to C₁ producing two cyclopentenes eventually. Fig. 6g describes the formation
of 2-norbornene and propene from consecutive C5-C6 and C2-C3 bond scissions [6, 7, 17, 19], which also involves the H transfer from C4 to C5 prior to the cleavage of C2-C3 bond.

Other species, i.e. O2, OH, H and HO2 are introduced in the JP-10 initiation reactions in Figs. 6h–n and the energy barriers of these reactions are all lower than the above unimolecular JP-10 decompositions as expected. Except for the two reactions in Figs. 6i & j, the remaining five all relate to the dehydrogenation of JP-10 at various C positions. It can be seen that the dehydrogenation of JP-10 by O2 has the highest energy barrier of 44.38 kcal/mol among these reactions, followed by the formation of two C10H16OHs with OH attaching to C4 and C3, respectively. The OH is more likely to attach to C3 compared to C4 because the energy barrier is much lower. Figs. 6k & l show the dehydrogenation of JP-10 by the OH functional group on FGS at C1 and C8 producing H2O and the energy barriers for these two reactions are almost the same. It is indicated that JP-10 decomposition initiated by OH is easier than by O2. The H2 formation via dehydrogenation of JP-10 by the H radical in Fig. 6m has a similar energy barrier as those decompositions initiated by OH. As presented in Table 5, the FGS can release the H of OH to participate in intermediate reactions, which could also be helpful for JP-10 initiation. It can be expected to see the JP-10 reaction with H of OH on FGS if the size of FGS is increased with more OH functional groups. The energy barrier of the dehydrogenation of JP-10 by HO2 generating H2O2 is slightly lower than those reactions in Figs. 6k–m. However, it needs HO2 as a precursor and the formation of HO2 is not that straightforward and easy as the release of OH or H from FGS. Based on the above analysis, it can be concluded that the energy barrier for JP-10 decomposition reactions initiated by the OH or potential H of OH on FGS is much lower than the unimolecular decomposition of JP-10 by the C-C or C-H bond scission. This considerable reduction in the energy barrier makes the reactions of JP-10 with OH or H on FGS more preferable than those cleavages of C-C or C-H bonds thereby changing and enhancing the JP-10 initiation.

4. Conclusions
The ReaxFF MD simulations are performed to investigate the initiation mechanisms of JP-10 pyrolysis and oxidation with FGS in comparison with normal JP-10 reactions. Moreover, the ReaxFF-NEB calculations are conducted to study the transition state and energy barrier for some key initiation reactions. The results show that both pyrolysis and oxidation of JP-10 are advanced and enhanced in the presence of FGS, leading to earlier decomposition of JP-10 at a lower temperature and a faster reaction rate. The detailed initiation reactions of pyrolysis and oxidation of JP-10 and their mixture with FGS are obtained to scrutinize the effect of FGS addition. Compared with pyrolysis of pure JP-10 mainly decomposing to various smaller hydrocarbons, the decomposition of JP-10 with FGS starts with the dehydrogenation by the OH functional groups on the FGS forming H2O. Similarly, in the system of JP-10 oxidation with FGS, the decomposition of JP-10 is initiated by its reaction with OH. In addition to the H2O formation, another pathway that involves the C-C bond cleavage followed by OH attachment to one of those two C atoms is observed. For both JP-10 pyrolysis and oxidation, as the reaction proceeds, more OH groups of FGS take part in various intermediate reactions involving oxygenated hydrocarbons or direct production of H2O and H2 as well. Moreover, the dehydrogenation of JP-10 without FGS only occurs at high temperatures. Therefore, it is the OH functional group on the FGS that not only advances the initiation of JP-10 but also participates in various intermediate reactions to further enhance the pyrolysis and oxidation of JP-10. A deeper insight into the enhancement resulting from the FGS is provided by the results of transition state and energy barrier for key initiation reactions. It is found that the JP-10 decomposition initiated by OH or H occurs at a lower energy barrier than unimolecular decomposition or through reaction with O2. This makes the reactions of JP-10 with OH or H on the FGS preferable thereby changing and enhancing the JP-10 initiation. This research lays the scientific foundation for the potential use of FGS as a promising catalyst for JP-10 fuel systems.

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**Declarations of interest:** none

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