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Mechanism and Kinetics of the Diesel Combustion: A ReaxFF Molecular Dynamics of the multi-component fuel model

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Highlights

- Temperature and pressure would influence the product distribution and reaction rate.
- CO and H_2 were the main products in combustion simulations.
- Mechanisms of all compounds and reaction rate constants (*k*) were obtained.
- Important radicals and intermediates were captured and analyzed.

1. Introduction

Within a quite long period of time in future, the combustion of fuel would still be the main source of energy for human beings[1], that is to say, combustion would continuously play a vital role in aerospace, ships, vehicles, and power engineering, etc. Since 1970s century, complex mechanism researches of combustion have been widely carried out. However, human's understanding of the essence of combustion is still far behind human' application toward combustion. In this work, ReaxFF (reactive force field) molecular simulations were conducted to investigate the effect of temperature, pressure, O_2/fuel ratio. In particular, mechanism and pathways, reaction rate constant (*k*), and some important radicals were also concerned.

2. Methods

To give a better description of diesel, a multi-component fuel model was constructed, including 15 hexadecane molecules, 15 cyclopentane molecules, 10 benzene molecules, and 10 naphthalene molecules, which represent long-chain alkanes, cycloalkanes, monocyclic aromatics, and polycyclic aromatics (Shown in Figure 1). For temperature-dependent simulations, the system was minimized and equilibrated at 100 K for 10 ps and then heated to 2500 K, 2750 K, 3000 K, and 3250 K with a heating rate of 50 K/ps using NPT ensemble. For pressure-dependent simulations, pressures were set at 10 MPa, 50 MPa, and 90 MPa at the temperature of 3000 K. The C/H/O force field which utilized in this work was obtained from others' research.[2]

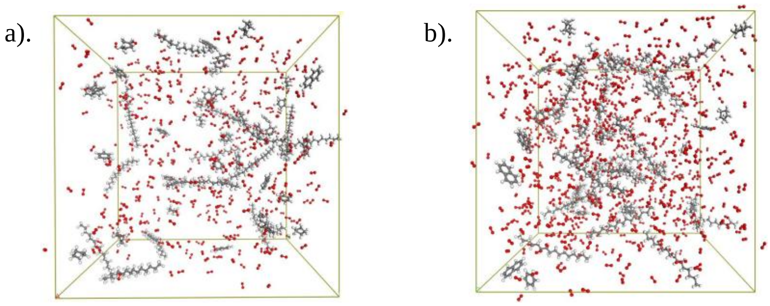
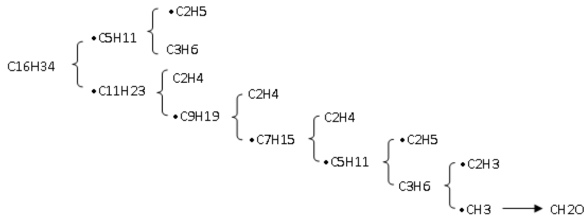
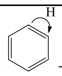
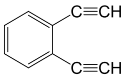


Figure 1. Multi-component diesel model with a). 400 O2 molecules and b). 700 O2 molecules.

3. Results and discussion

Through analyzing the trajectory files, reaction mechanism of each component in diesel model was obtained. Table 1 displays pathways with high probability of each reactant. For hexadecane, the long chain broke into small species through C_2 abstract reactions firstly, and the earliest-generated oxide was formaldehyde. Other ring compounds would open rings initially.

Table 1 Initial combustion mechanism of different reactant of multi-component diesel model.

Initial combustion mechanism	Initial reaction type	Final product
	Pyrolysis → oxidation	7 CO 1 CO2 2 CH2O 2 C3H4 (2) 2 •C2H3 (1) 1 C7H4 (2)
#C5H10 → 2 •H + •CH2-CH=CH2-CH=CH2 →2 •H + •C2H3 + C3H4	Dehydrogenation → ring opening	1 CH2O 1 •C2H3 (1) 1 CO 1 C3H6O (2)
C6H6 →  → •C2H3 + C4H3	Hydrogen transfer → ring opening	3 CO 2 C2H2 (1)
#C10H8 → 2•H + 	Dehydrogenation → ring opening	1 C2H2 (1) 2 C2H2O (2) 1 CO 2 •C2H3 (2) 2 C2HO (2) 2 C2H2O (2)

Hydrogen radical was captured by oxygen radical or another hydrogen radical, not existed as the form of radical.

Some radicals such as •CH_2, •HO_2, etc. are highly active and play a vital role in combustion process, however, they are difficult for experimental methods to detect. Figure 2 displays the time evolution of these radicals in the system of 3000 K, 50 MPa. •CH_2 and •CH radicals were mainly produced in the early stage and gradually decreased while the number of •HO_2 and •CH_2O_2 radicals approximately unchanged once generated.

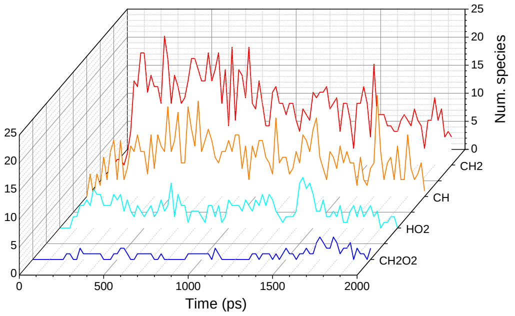


Figure 2. Time evolution of important radicals in combustion simulations at 3000 K, 50 MPa.

4. Conclusions

The product distribution and reaction rate was significantly affected by both temperature and pressure. CO and H_2 were the main product in all the simulations. In combustion process, long-chain alkanes would pyrolysis into small species firstly and then react with O_2, while dehydrogenation and ring opening reaction would initially take place on other ring compounds. The reaction rate constants (k) of main elementary reactions were calculated. •CH_2 and •CH radicals were mainly generated in the early stage and gradually decreased, while •HO_2 and •CH_2O_2 fluctuated within small ranges.

References

[1] C.K. Westbrook, F.L. Dryer, Progress in Energy & Combustion Science, 10 (1984) 1-57.
[2] C. Ashraf, A.C.T. van Duin, J. Phys. Chem. A, 121 (2017) 1051-1068.

Keywords
ReaxFF molecular dynamics, combustion, multi-component model