AN INVESTIGATION OF CHEMICAL REACTION IN BIODIESEL UTILISATION BY REACTIVE MOLECULAR SIMULATION

Cheng CHEN[1], Xi JIANG [1*]

[1] School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London E1 4NS, UK

[*]Corresponding author. Email: xi.jiang@qmul.ac.uk

ABSTRACT

The chemical reaction of biodiesel in combustion is more complex than traditional hydrocarbon fuels because of the existence of saturated and unsaturated fatty acid methyl or ethyl esters. In this study, a series of molecular dynamics simulation with reactive force field is performed to investigate the combustion and pyrolysis of the extensively tested biodiesel surrogate fuel, i.e., methyl butanoate. By analyzing the time dependence and spatial distribution of intermediates and stable products, the chemical reaction mechanism is elucidated. The formation of nitrogen oxides during methyl butanoate combustion under fuel-air conditions is studied for the first time by reactive force field. In the pyrolysis simulation of pure methyl butanoate, the performance of CHO-2008 and CHO-2016 is tested in terms of the transferability and capability. The reactive molecular dynamics can be employed as an effective method for chemical reaction modelling of biodiesel combustion both qualitatively and quantitatively.

Keywords: biodiesel, ReaxFF, molecular dynamics, pyrolysis, combustion

1.   INTRODUCTION

In recent years, renewable fuels are becoming increasingly important and their utilisation drives the development of new technologies for energy conversion systems such as internal combustion (IC) engines, which also have to meet the steadily tightened regulations on emission. These cutting-edge technologies should include conventional fossil fuels as well as the alternative biofuels simultaneously. Biofuels such as biodiesel can be derived directly from plants, i.e., energy crops, or indirectly from agricultural, commercial, domestic and industrial wastes.

Biodiesel is a mixture of fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs). It is compatible with conventional diesel and can be blended in any proportion with fossil diesel to create a stable biodiesel blend or used in its pure form [1]. The properties of biodiesel have obvious advantages versus petrodiesel such as renewable and sulphur-free but with drawbacks like poorer low-temperature properties and less stable for long-term storage [2]. Therefore, detailed research on its chemical properties is of high necessity.

The chemical kinetics of hydrocarbons in combustion has been the subject of numerous studies. However, fewer kinetic studies related to the oxidation of biodiesel have been performed at the experimental and modelling level. The main reason for the lack of information is the complexity in molecular structure of actual biodiesel compounds, which involves large aliphatic chains of 14-20 carbon atoms with C=C double bonds and ester groups [2]. The major path in past research related to chemical reaction studies of biodiesel combustion is from simple surrogate fuel, i.e., methyl butanoate (MB, $C_5H_{10}O_2$), toward more suitable and real surrogates like methyl hexanoate ($C_7H_{14}O_2$), methyl octanoate ($C_9H_{18}O_2$), methyl decanoate ($C_{11}H_{22}O_2$) and methyl stearate ($C_{15}H_{30}O_2$). As a relatively small methyl ester, MB was chosen initially to produce a manageable chemical kinetic mechanism [3]. Therefore, the chemical reaction of MB during utilisation is modelled in this study.

2.   SIMULATION METHODS

Recently, advances have been made in molecular dynamics (MD) with the reactive force field (ReaxFF)

used as an efficient method to simulate chemical reactions at the atomic level. It becomes popular due to its feasibility for large scale reactive systems [4, 5]. ReaxFF bridges the gap between intense computation of quantum mechanics (QM) methods and the incapability of reactive events of classical empirical interatomic potential. ReaxFF force field takes the following function for energy calculation:

$$E_{system} = E_{bond} + E_{over} + E_{under} +$$

$$E_{lp} + E_{val} + E_{tor} + E_{vdWaals} + E_{coulomb}$$

where E_{bond}, E_{over}, E_{under}, E_{lp}, E_{val}, E_{tor}, $E_{vdWaals}$, $E_{coulomb}$ represent bond energy, over-coordination energy penalty, under-coordination stability, lone pair energy, valence angle energy, torsion angle energy, van der Waals energy, and Coulomb energy respectively.

In this study, all the simulations are performed using the ADF package [6]. The simulation systems are divided into two relevant serials, i.e., combustion of MB in fuel rich air conditions and pyrolysis of pure MB. For the combustion, 100 MB molecules, 300 O_2 and 1200 N_2 are placed randomly in a cubic box of 76.26 Å edge length. Similarly, 100 pure MB molecules are placed in a cubic box of 43.93 Å edge length for pyrolysis simulation. The density of both cases is equal to 0.2 g·cm^{-3}. The temperature is set up as 2000 K. In ReaxFF simulations, employing a high temperature and pressure to accelerate the reactions and facilitate the simulation process is a common strategy [4, 5, 7-9]. The total simulation time for each system is set up as 100 ps with 0.1 fs time step. Canonical ensemble (NVT) is used for all the simulations in conjunction with the Nosé-Hoover thermostat employing a damping of 10 fs.

3. RESULTS AND DISCUSSION

For the combustion simulation, the spatial distribution of reactants consumption, formation of hydrocarbons, oxygenated components and NxOy are shown in Fig 1. Time history of combustion and thermal decomposition are shown in Fig 2 and Fig 3 respectively. Clearly, the number of MB molecules decreases rapidly at the beginning of simulation and reaches almost zero at around 60 ps. The time evolutions of N_2 and O_2 molecules consumed in the combustion process show a similar tendency to MB. After 60 ps, the numbers of N_2 and O_2 reached stability at about 900 and 100 respectively. The dominate stable products are CH_3, CO_2, C_3H_6, C_3H_7, $etc.$ Methyl radical CH_3 has a minor decrease at 35 ps before the stable state while CO_2 and C_3H_6 grow steadily.

Basically, the oxidation of MB initially proceeds via thermal decomposition and yields radicals, $e.g.$ CH_3. Research on pyrolysis of MB can help understand the kinetic mechanisms and isolate some key reaction pathways in engine relevant conditions. In this study, two different versions of ReaxFF parameters for hydrocarbon and oxygen, i.e., CHO-2008 and CHO-2016 are employed and compared for the pyrolysis simulation of pure MB molecules. The time dependence of pyrolysis products is shown in Fig 3. Although CHO-2008 has been tested widely for large hydrocarbon combustion, it is unable to describe the chemistry of small hydrocarbon oxidation, especially the conversion of CO_2 from CO. In order to solve the deficiency on molecular size and structure, it was improved to CHO-2016 by Ashraf and van Duin [10]. Therefore, it is valuable to test the CHO-2016 for MB pyrolysis regarding its accuracy and transferability.

A series of pyrolysis species including small hydrocarbons (C1 to C4), oxygenated products like CO, CO_2, radicals and esters are detected and identified by both CHO-2008 and CHO-2016. These agree well with most of the experimental results as a whole. Comparing the consumption of MB in Fig 3, it decreases almost exponentially in CHO-2008 until the pyrolysis completed at 30 ps, whereas the corresponding reaction in CHO-2016 presents a different trend which can be divided into three stages. MB molecules decompose to 60 steeply at the beginning of the pyrolysis followed by a linear decrease until 70 ps and a relatively-slow step-like descent.

CHO-2008 and CHO-2016 employ the same QM results for the training of bond dissociation energies of C-O single bond, C=O double bond and C≡O triple bond. However, the valence angel parameters of CHO-2016 are re-optimized, $e.g.$ O-C-O, O=C-O and O=C=O, which affect the reaction in this study. From the comparison of initial pyrolysis pathway, it is observed that CHO-2016 can capture more pyrolysis pathways than CHO-2008. The unimolecular decomposition, R1: MB → CH_3OCO + C_3H_7 and α-cleavage reaction, R2: MB → CH_3 + $(CH_2)_2COOCH_3$ are observed simultaneously by CHO-2008 and CHO-2016 with R2 contributing the majority of the pyrolysis in CHO-2008. β-cleavage reaction, R3: MB → CH_2OCOCH_3 + C_2H_5 exists only in CHO-2008. Sensitivity analysis has shown that the time dependence of some important products like CO, CO_2 and C_2H_4 are sensitive to MB unimolecular decomposition reactions of R1-R3 [11]. Moreover, H-atom abstraction by OH and CH_3 are captured by CHO-2016 uniquely, i.e., R4: MB + OH →
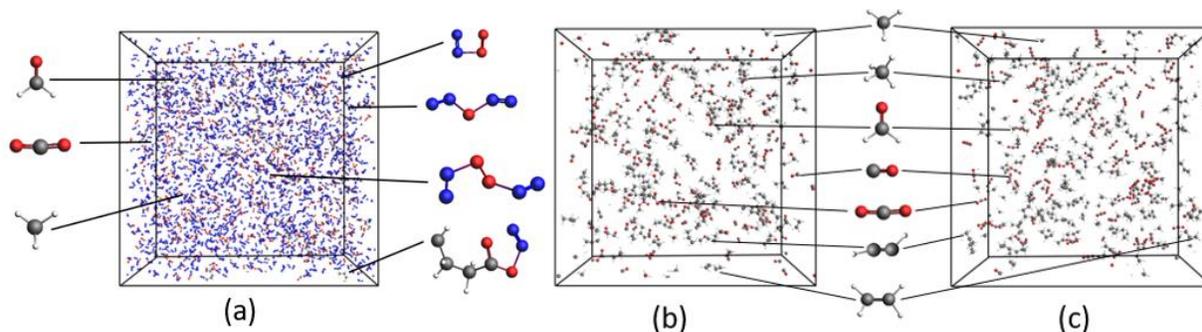
Fig 1. Snapshots of spatial distribution of the major combustion and thermal decompsition products of MB after 100 ps simulation. (a) combustion results by HCONSB force field, (b) pyrolysis results by CHO-2008 force field, (c) pyrolysi results by CHO-2016 force field. Grey spheres indicate the carbon atoms, white spheres indicate the hydrogen atoms, red spheres indicate the oxygen atoms and blue spheres indicate the nitrogen atoms.

$CH_2(CH_2)_2OCOCH_3 + H_2O$ and R5: MB + $CH_3 \rightarrow$ $CH_3CHCH_2OCOCH_3 + CH_4$. Apart from these pathways, another reaction related to the dissociation of C-O bond is observed in CHO-2016, i.e., R6: MB $\rightarrow$ CH_3O + $CH_3(CH_2)_2CO$. These pyrolysis pathways are in good accordance with the recent experimental results, performed mostly at 800-2000K with pressure range from 4 kPa to 4 MPa. In shock tube experiments by Farooq et al. [11], it was concluded that MB consumption was proceeded initially via unimolecular decomposition breaking of C-C or C-O. The C=O appears to be never broken and little initiation occurs via breaking C-H bonds due to its higher bond dissociation energy. In the premixed flame experiments on MB isomers by Yang et al. [12], it was found that the presence of the ester group modifies some of the C-H bond strengths in the alkyl groups. C-H bonds at the C adjacent to CO are weaker than in the corresponding alkane molecules resulting in modification to H-atom abstraction reaction rate.

Tracking the oxygen-containing molecules is important in MB decomposition as the fuel-bonded oxygen atoms are difficult to get free from their connected carbon atoms during the pyrolysis [11]. From Fig. 3, the time-history of CO and CO_2 show different trends in CHO-2008 and CHO-2016. In the results of CHO-2008, CO_2 reaches its maximum values about 100 sharply at 40 ps with almost the same rate of MB pyrolysis while only few CO is produced in the whole process. For the simulation result in CHO-2016, the number of CO molecules is always greater than CO_2 with CO reaching its plateau values faster than CO_2. Furthermore, the maximum number of CO_2 in CHO-2008 is more than twice greater than that in CHO-2016. It has been observed that CO is strongly sensitive to CH_3OCO produced by R1, as CH_3OCO has two possible reaction pathways, i.e., R7: $CH_3OCO \rightarrow CO_2 + CH_3$ and R8: $CH_3OCO \rightarrow CO + CH_3O$. In this research, CH_3OCO can exist shortly and pyrolysis into CO_2 directly by R7. Both CH_3O and $CH_3(CH_2)_2CO$ produced in R6 can further react into CO. Many other CO and CO_2 formation channels will be studied detailly in the future simulation regarding its temperature dependence. The relative or the ratio of production of CO and CO_2 is more important for the evaluation of soot prevention potential of biodiesel. In the experiment by Farooq et al. [11], a CO/CO_2 ratio of about 2/1 and a CO/MB ratio of 1/1 was found at the
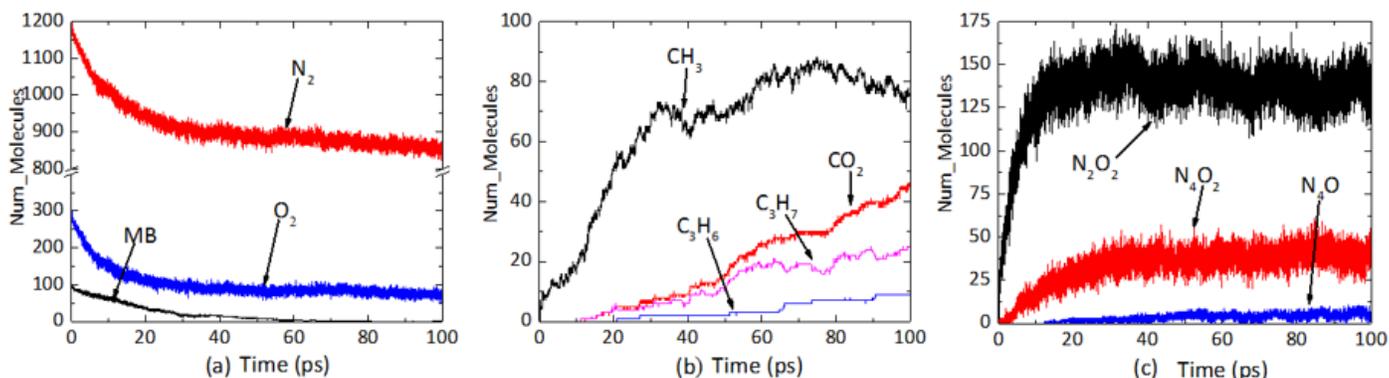
Fig 2. Time evaluation of main compounds during combustion of MB with O_2 and N_2 at 2000K and 0.2 g·cm^{-3}, (a) consumption of reactants, (b) stable products of hydrocarbons and oxygenic components, (c) products of NxOy.

temperature as high as 1545K. It is different from the CO/CO_2 ratio of 1/1 in the current CHO-2016 simulation result.
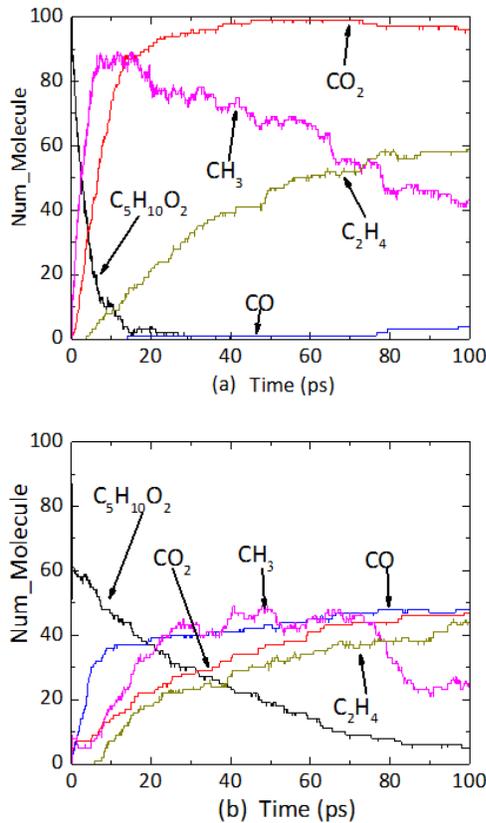
Fig 3. Time dependence of MB pyrolysis and stable products obtained at 2000K and 0.2 $g \cdot cm^{-3}$, (a) CHO-2008 force field, (b) CHO-2016 force field.

4. CONCLUSIONS

Chemical kinetics of biodiesel surrogate fuel, i.e., methyl butanoate in combustion and pyrolysis are modelled by MD simulation with ReaxFF force field. The time history of reactants in fuel-air combustion condition is revealed. However, the primary nitrogen oxides founded are N_2O_2, N_4O_2 and N_4O, *etc.*, which are from the thermal formation mechanism relevant to the real engine combustion conditions. Predictabilities of CHO-2008 and CHO-2016 on pure methyl butanoate pyrolysis are evaluated in three aspects, i.e., time dependence, spatial distribution and chemical reaction pathways. Methyl butanoate decomposes exponentially in CHO-2008 while an abrupt decrease is shown at the beginning of CHO-2016 simulation. The general trend of main radicals, *e.g.* CH_3 and C_3H_7, is similar with discrepancy of their maximum numbers. CHO-2016 predicts a better CO/CO_2 ratio than CHO-2008 compared with the corresponding experimental results. Both unimolecular decomposition and H-atom abstraction reaction are

captured by CHO-2016. Overall, MD simulation with ReaxFF is a promising approach to illuminate the effect of molecular structure on biodiesel combustion.

REFERENCES
[1] Agarwal AK. Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in Energy and Combustion Science. 2007;33:233-271.
[2] Coniglio L, Bennadji H, Glaude PA, Herbinet O, Billaud F. Combustion chemical kinetics of biodiesel and related compounds (methyl and ethyl esters): experiments and modeling–advances and future refinements. Progress in Energy and Combustion Science. 2013;39:340-382.
[3] Lele AD, Vallabhuni SK, Moshammer K, Fernandes RX, Krishnasamy A, Narayanaswamy K. Experimental and chemical kinetic modeling investigation of methyl butanoate as a component of biodiesel surrogate. Combustion and Flame. 2018;197:49-64.
[4] Feng M, Jiang XZ, Zeng W, Luo KH, Hellier P. Ethanol oxidation with high water content: A reactive molecular dynamics simulation study. Fuel. 2019;235:515-521.
[5] Ashraf C, Shabnam S, Jain A, Xuan Y, van Duin AC. Pyrolysis of binary fuel mixtures at supercritical conditions: A ReaxFF molecular dynamics study. Fuel. 2019;235:194-207.
[6] G.te Velde FMB, Baerends EJ, Fonseca Guerra C, van Gisbergen SJA, Snijders JG and Ziegler T. SCM, Theoretical Chemistry. Vrije Universiteit, Amsterdam, The Netherlands. ADF2018; http://www.scm.com.
[7] Chen Z, Sun W, Zhao L. High-temperature and high-pressure pyrolysis of hexadecane: molecular dynamic simulation based on reactive force field (ReaxFF). The Journal of Physical Chemistry A. 2017;121:2069-2078.
[8] Chenoweth K, Van Duin AC, Dasgupta S, Goddard Iii WA. Initiation mechanisms and kinetics of pyrolysis and combustion of JP-10 hydrocarbon jet fuel. The Journal of Physical Chemistry A. 2009;113:1740-1746.
[9] Wang E, Ding J, Qu Z, Han K. Development of a Reactive Force Field for Hydrocarbons and Application to Iso-octane Thermal Decomposition. Energy & Fuels. 2017;32:901-907.
[10] Ashraf C, van Duin AC. Extension of the ReaxFF combustion force field toward syngas combustion and initial oxidation kinetics. The Journal of Physical Chemistry A. 2017;121:1051-1068.
[11] Farooq A, Ren W, Lam KY, Davidson DF, Hanson RK, Westbrook CK, *et al*. Shock tube studies of methyl butanoate pyrolysis with relevance to biodiesel. Combustion and Flame. 2012;159:3235-3241.
[12] Yang B, Westbrook CK, Cool TA, Hansen N, Kohse-Höinghaus K. Fuel-specific influences on the composition of reaction intermediates in premixed flames of three C5H10O2 ester isomers. Physical Chemistry Chemical Physics 2011;13:6901-6913.