Research article

Reactive force field simulation studies on the combustion behavior of *n*-octanol

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ABSTRACT

n-Octanol is a new promising fuel which is considered as an alternative to conventional diesel. In order to understand the combustion characteristics of *n*-octanol, reactive molecular dynamics (ReaxFF MD) simulation of *n*-octanol has been carried out at temperatures from 2000 to 4000 K with equivalence ratios ranging from 0.5 to 2.0. Ethylene and formaldehyde have been found to be major intermediates in the oxidation of *n*-octanol which is in agreement with the available experimental data. Reaction mechanisms have been proposed for the formation of major intermediates (C_2H_4 and CH_2O) and final products (CO and CO_2) from where it is revealed that intermediates are mainly consumed by the build-up of hydroxyl and hydroperoxyl radicals. It was observed that the CO and CO_2 formation from formaldehyde and ethylene starts with the attack of molecular oxygen or hydroxyl radical or hemolytic O—H bond cleavage. Overall, a good qualitative agreement with the available experimental data in terms of product distribution has been found. The results indicate that ReaxFF MD simulations can give a detailed description of the reaction mechanism and product distribution for the combustion for oxygenated fuel such as octanol.

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1. Introduction

Petroleum-based liquid fuels such as gasoline and diesel have dominated the transportation sectors in the twentieth century. But the need to reduce the emission of greenhouse gases and the dependency on fossil fuels have motivated researchers across the globe to look for alternative and renewable sources of fuels. Fuels derived from various bio-based feedstocks have attracted great attention in recent decades [1–3]. Oxygen containing biofuels, such as alcohols, have shown considerable promise, because they are renewable and considered to be neutral with regard to net greenhouse gas emissions [4–15]. Octanol has generated a considerable amount of interest where recently new pathways were described to obtain *n*-octanol from biomass or bio-oil. Julis et al. [16] have discovered a new route for the production of *n*-octanol from carbohydrate feedstock. Starting with furfural and acetone, an overall 73% yield of *n*-octanol was obtained in a step-wise procedure and 54% overall in a one-pot procedure. Akhtar et al. [17] have engineered a synthetic pathway for the synthesis of *n*-octanol from glucose and fatty acids in *Escherichia coli BL21* (DE3) by overexpression of three enzymes (thioesterase, carboxylic acid reductase and aldehyde reductase)

and one maturation factor (phosphopantetheinyl transferase). The majority (73%) of the fatty alcohol was localised within the media without a requirement of detergent or solvent overlay.

n-Octanol is found to have better fuel properties as compared to ethanol and *n*-butanol. It has higher energy density (33.7 MJ/L) as compared to ethanol (19.6 MJ/L) and *n*-butanol (29.2 MJ/L). It also has a comparable energy density with petro-diesel (40.3 MJ/L). Another important terminology in compression-ignition (CI) engine is cetane number where a high cetane number indicates a high self-ignition tendency. *n*-Octanol has a cetane number (CN) of 39 which is much higher than *n*-butanol (CN ~ 17) and ethanol (CN ~ 11) but slightly less than petro-diesel (CN ~ 45–50). Solubility of fuel in water is another important aspect which has to be considered with regard to its pipeline compatibility. Solubility of *n*-octanol in water is very low ~0.59 g/L as compared with ethanol (miscible) and *n*-butanol (~77 g/L). *n*-Octanol having vapor pressure of 0.08 mmHg is also much less than ethanol (~55 mmHg) and *n*-butanol (~7 mmHg) but slightly less than petro-diesel (~0.4 mmHg). This makes them safe in terms of storage, handling and transportation. The viscosity of *n*-octanol (4.4 cST @ 40 °C) is again close to the upper limit of the diesel viscosity range (1.8–5.8 cST @ 40 °C), while the boiling point of *n*-octanol (195 °C) is at the low end of the diesel boiling curve (180–300 °C). Overall, based on properties, *n*-octanol is a suitable fuel for operation in compression ignition (CI) engines [17].

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Table 1
Equivalence ratio, number of molecules and temperature of the studied system.

Equivalence Ratio (Φ)	n-Octanol/oxygen	Temperature (K)	Box size (Å)	Ensemble
0.5	10/240	3000–3500–4000	$30 \times 30 \times 30$	NVT
1.0	10/120	2000–2500–3000–3500–4000	$30 \times 30 \times 30$	NVT
2.0	10/60	3000–3500–4000	$30 \times 30 \times 30$	NVT

Very few studies have been carried out to understand the combustion behavior of n-octanol. Heuser et al. [18] have investigated the effect of n-octanol combustion on engine emissions. With n-octanol the particulate matter (PM) emissions were found to reduce by a factor of 20 as compared to diesel fuel. However, the slightly lower cetane number with respect to diesel fuel causes minor overleaning effects in particular at its lowest load. Thus, the hydrocarbon, CO and combustion noise emissions exceed than those of diesel combustion at low load operation. Kerschgens et al. [19] also investigated the combustion behavior of n-octanol in diesel engine. While on one side lower soot emissions and nitrogen oxide emissions were obtained, on the other hand the emissions of unburned hydrocarbons and CO were found to be rather high due to the longer ignition delay. To understand the phenomena further Cai et al. [20] carried out the chemical kinetic investigation on the oxidation of n-octanol. Ignition delay times and stable species concentration profiles were experimentally obtained for n-octanol oxidation in a shock tube and a jet stirred reactor, respectively. The oxidation of n-octanol was found to be initiated via hydrogen atom abstraction from the fuel by molecular oxygen. n-Octanol was mainly consumed by the build-up of OH radicals. The fuel's combustion characteristics were then compared to those of n-alkanes and short chain alcohols. The major differences between linear alcohols and alkanes with the same carbon chain length are the presence of the hydroxyl group in alcohols. Thus the hydrogen abstractions by OH and HO_2 radicals were found to play a dominant role in determining ignition delay times.

For a better understanding of n-octanol oxidation behavior, knowing its fundamental combustion characteristics is necessary. A detailed investigation on combustion reaction mechanisms can provide important information with respect to the intermediates. However, it becomes a challenge to disentangle the various fundamental combustion steps by experiments and compare the same with kinetic modeling methods. This necessitates the requirement of computational approach to help us widen our sight and provide an efficient way to understand the true nature of the complex combustion reactions. In theory, quantum mechanical (QM) methods can provide accurate reaction pathways and rate constants for individual elementary reaction. However, these methods are computationally expensive in providing the detailed description of complex reactions. Therefore, a number of empirical methods (molecular dynamics) have been developed in order to reduce the computational cost. Classical molecular dynamics simulations are able to describe systems with thousands of atoms but they fail to describe the processes of bond breaking and bond formation in the chemical reactions. In order to overcome the deficiencies of conventional MD simulations, bond order based reactive force field (ReaxFF) has been developed by Duin et al. [21] as an efficient method for describing chemical reactions. ReaxFF is a first principle based bond-order dependent reactive force field that provides an accurate description of bond breaking and bond formation. Parameters of this force field are derived from QM. Hence, the potential can nearly reproduce the accuracy of the ab initio calculation at much lower computational cost. ReaxFF has seen extensive use over the past 10 years modeling several different types of reactive systems including combustion, catalysis, fuel cells, and nanotubes [21–26]. In the present work, MD simulations for n-octanol has been carried out by employing the reactive force field (ReaxFF) as implemented in ADF software [27]. The ReaxFF force field for C/H/O systems as developed by van Duin et al. [21] has been used to simulate the oxidation of n-octanol. This will further elucidate the oxidation pathways of n-octanol under representative conditions such as temperatures (3000–4000 K) and equivalence ratios (0.5, 1.0, 2.0).

2. Computational details

ReaxFF is a reactive force field method that uses the concept of bond order to model the interactions in a chemical system. The bond order concept was first implemented by Tersoff [28] for silicon. Later on, Brenner [29] extended the Tersoff potential for carbon and hydrocarbons. Based on bond order concept, ReaxFF ensures smooth transition of bond formation and bond dissociation during chemical reactions. In ReaxFF force field, the general expression for the energy function is:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}. \tag{1}$$

Where, E_{bond} denotes the bond energy, E_{over} and E_{under} represent the over- and under-coordinated atom in the energy contribution, respectively. Other terms, including E_{val}, E_{pen}, E_{tors}, E_{conj}, E_{vdWaals}, and
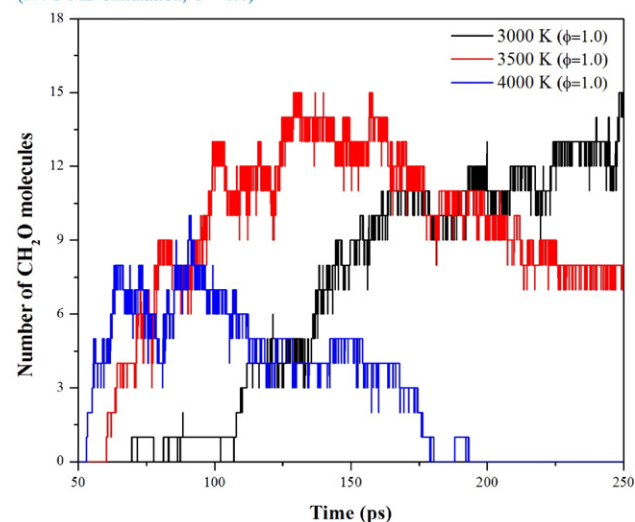

Fig. 1. a. Time evolution of potential energies at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). b. Time evolution of total number of molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). c. Time evolution of n-octanol molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). d. Time evolution of O_2 and H_2O molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). e. Time evolution of CO and CO_2 molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). f. Time evolution of C_2H_4 molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$). g. Time evolution of CH_2O molecules at temperatures 3000–4000 K (NVT-MD simulation, $\Phi = 1.0$).