



Ethanol oxidation with high water content: A reactive molecular dynamics simulation study



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ABSTRACT

Ethanol is a potential alternative to conventional fossil fuels. However, the required dewatering process to produce anhydrous ethanol is extremely energy-intensive and expensive. A promising solution is the direct use of hydrous ethanol for combustion applications, which can dramatically reduce the production cost. Many researchers have undertaken experiments demonstrating the feasibility and advantages of burning hydrous ethanol solely as a fuel. In this study, molecular dynamics (MD) simulation with the reactive force field (ReaxFF) is employed to investigate the fundamental reaction mechanisms of hydrous ethanol oxidation in comparison with the ethanol oxidation under fuel-air condition in order to understand the effects of water addition on ethanol oxidation. The results show that the reaction rate of ethanol oxidation is faster in water than in nitrogen environment and the presence of water advances the ionisation process and accelerates the radical production rate thereby enhancing the oxidation reaction. Additionally, it is suggested that the water content plays a vital role in reactions at low temperatures but that effect can be ignored at high temperatures. The detailed reaction pathways and time evolution of relevant key species indicate that H_2O promotes many reactions involving OH generation and these OH radicals also facilitate its reactions with C_1 & C_2 intermediates as well as the dehydrogenation of C_1 & C_2 intermediates. Similarly, CO production is reduced in hydrous ethanol oxidation as a result of CO reaction with OH converting the CO to CO_2 ultimately. Therefore, it is the addition of water that promotes the OH production due to the chemical effect of H_2O leading to the enhancement of ethanol oxidation and reduction of CO production. In summary, this research provides the scientific base for the direct use of hydrous ethanol as a fuel for combustion systems with a low cost.

1. Introduction

The finite resources of conventional fossil fuels and the severe problem of combustion emissions have prompted the development of environmentally-friendly alternative fuels. Ethanol, as a widely acknowledged renewable resource has numerous advantages. When ethanol is used as a fuel additive in internal combustion (IC) engines, it can suppress soot formation and reduce pollutant emissions [1]. Moreover, the high knock resistance of ethanol can increase the overall octane rating of blends of ethanol and fossil gasoline, potentially permitting spark ignition (SI) engine operation at higher compression ratios and thus thermal efficiencies [2]. However, ethanol derived from biomass has inherent high water content, and the distillation and dehydration processes needed to obtain anhydrous ethanol are both energy-intensive [3]. Data shows that the energy required for ethanol distillation grows exponentially as the fraction volume of ethanol increases and 37% of the total production cost is spent on dewatering

activities [4]. Therefore, it is of great interest to study oxidation of hydrous ethanol with high water concentration, as this could dramatically save energy and cost during production by enabling the direct use of hydrous ethanol.

Hydrous ethanol oxidation has been studied for a long time by both experiments and simulations. Rahman et al. [5] investigated the combustion characteristics of wet ethanol by laser ignition. They found that the combustion rate was accelerated with the addition of water in ethanol and the laser ignition delay was shorter compared to the anhydrous ethanol. Their simulation also demonstrated that the adiabatic flame temperature and laminar burning velocity were reduced as a result of the water blending. The phenomenon of laminar burning velocity decrease was also observed in Liang et al.'s experiment and numerical modelling [6]. Breaux and Acharya studied the effect of water addition on swirl-stabilized ethanol/air flames and concluded that the exhaust temperature was decreased leading to the reduction of nitrogen oxides emissions [7]. A homogeneous charge compression ignition

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(HCCI) engine retrofitted with an exhaust heat recovery system was developed by Saxena et al. and they explored the direct use of wet ethanol as the fuel [8]. The results showed that the best operating conditions for the engine could be achieved by burning hydrous ethanol. Similar outcomes for the usage of wet ethanol in an HCCI engine were obtained by Mack et al. [9]. Munsin et al. tested the performance and emissions of a SI engine fuelled with hydrous ethanol and reported that both regulated and unregulated emissions could be reduced if a catalytic converter is provided [10]. To sum up, it was suggested that direct oxidation of hydrous ethanol could be more efficient [11] and cost-effective [12] than dehydrated ethanol in many combustion applications, including IC engines. On the other hand, burning hydrous ethanol reduces the fuel calorific value, and the presence of water blended with ethanol has seen increased specific fuel consumption in engine experiments, and can result in higher NO_x emissions if ignition timing is advanced in order to take advantage of enhanced knock resistance and produce higher power output [13]. In tests of hydrous ethanol in a SI engine at constant load and speed, with an increase in water content from 20% to 40%, Munsin et al. [10] observed increases in engine-out emissions of formaldehyde and acetaldehyde in addition to CO and HC. Furthermore, the use of hydrous ethanol in blends with fossil gasoline can result in phase separation, compromising the stability and storage potential of the fuel blend [14].

Previous experiments and simulations have proved hydrous ethanol to be a promising alternative fuel, but the underlying mechanisms of hydrous ethanol oxidation are still poorly understood. Molecular Dynamics (MD) simulation with the Reactive Force Field (ReaxFF) is an efficient method to study oxidation reactions at the atomic level and it is becoming increasingly popular due to its feasibility for large scale reactive systems. Quantum Mechanics (QM) methods are able to produce extremely accurate results, but it is computationally very expensive or impossible to study the full dynamics of large reactive systems. Empirical Force Field methods are applicable for large scale simulations with acceptable computational resources but they usually cannot describe chemical reactions. The ReaxFF method is capable of modelling dissociation, transition and formation of bonds for chemical reactions based on the bond order concept, which helps to bridge the gap between QM and classical MD methods [15]. A high level of accuracy can be obtained even when conducting a large reactive simulation for a long time and it is much more computationally cost-efficient than QM methods. More details of the ReaxFF formulation and development can be found in [15–18]. On the other hand, MD or ReaxFF MD has its limitations. The principal limiting factor is the high computational cost of classical MD and especially ReaxFF MD, which sets a practical limitation on the size of the simulated system (to typically several millions of atoms at present [18]). This also sets a limit on the physical time that can be simulated up to microseconds. Therefore, classical/ReaxFF MD is best suited for fundamental studies of small and fast-changing systems, where the unknown mechanisms are dominated by molecular interactions. Such limitations have been significantly lifted in the past few decades, thanks to the rapid advancement in computing hardware and software. This trend is set to continue as the exascale computing era is fast approaching.

In this study, ReaxFF MD simulations are performed to investigate the fundamental reaction mechanisms of hydrous ethanol oxidation in comparison with ethanol oxidation under fuel-air conditions. By analysing the time evolution of the reaction and the atomic trajectory, the reaction rates and detailed reaction pathways are achieved. Finally, the effects of water addition on ethanol oxidation are revealed.

2. Computational methods

All the MD simulations are performed using the ReaxFF formulation implemented in LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) package [19,20], with a ReaxFF force field of C/H/O/N parameters [21]. Three 3-dimensional systems with different gas

Table 1
Construction details of the studied systems.

System	No. of Molecules				Size (Å)
	C ₂ H ₆ O	O ₂	H ₂ O	N ₂	
1	40	120	0	480	80.00
2	40	120	480	0	72.65
3	40	120	20	0	54.48

phase components and cubic simulation boxes are built at the same density of 0.062 g/cm³. The periodic boundary condition is applied in all three directions. The details of the reactive systems studied are shown in Table 1. The stoichiometric condition of ethanol and oxygen (1:3) is adopted in all the three systems. System 1 is chosen to represent the fuel-air oxidation environment. (In the air, the proportion of oxygen and nitrogen molecules is approximately 1:4, which is calculated based on their volume fractions and the total density.) It is worth noting that nitrogen reaction is not observed within the studied time scale of ReaxFF MD simulations. Hence, Systems 2 and 3 are simplified with no nitrogen molecules from the perspective of setting up and running the simulations. To study the effects of high water concentration, the 480 nitrogen molecules are simply replaced with 480 water molecules in System 2. For System 3, the number of water molecules is reduced to 20 in order to investigate the ethanol oxidation with different ethanol/water ratios. The size of the cubic simulation boxes is adjusted accordingly to keep the same density for all the three systems.

The canonical ensemble (NVT) is used for all the MD simulations in conjunction with the Nosé-Hoover thermostat employing a damping constant of 100 fs. Before the reactive simulation, every system undergoes energy minimization using the conjugate gradient algorithm to optimize the initial geometric configuration, followed by the NVT equilibration at 1000 K for 50 ps. After the equilibrium, a series of reactive NVT MD simulations for each system are performed for 1000 ps at temperatures ranging from 2000 K to 3000 K with an increment of 200 K. In previous ReaxFF MD simulations, particularly for combustion, employing a high temperature to accelerate the reactions is a common strategy to overcome the limitation of computing power [16,22–32]. More importantly, the present research is a comparative study of different cases, so the absolute temperature used is less important. A time step of 0.1 fs, which was found suitable for high-temperature (2500 K) ReaxFF MD simulations [16], is adopted for both the equilibrating and reactive simulations. The bonding information and dynamic trajectory are recorded every 100 fs. For species analysis, a 0.2 bond order cutoff is chosen to recognize the molecules forming during the simulation because a low cutoff value is helpful for capturing all the reactions involving those with very short-lived species [16]. Every case (one system at one temperature) has three parallel simulations set up to be averaged for further analysis and each of them has a unique starting configuration. Therefore, totally 54 simulations are carried out. The reaction pathways are analysed by Chemical Trajectory Analyzer (ChemTraYzer) scripts [27]. All the visualisations of simulation results are generated using Visual Molecular Dynamics (VMD) software [33].

3. Results and discussions

3.1. Time evolution of potential energy

Fig. 1 describes the time evolution of potential energy for ethanol oxidation in both O₂/N₂ and O₂/H₂O atmospheres at various temperatures from 2000 K to 3000 K. Overall, the potential energy firstly rises to a peak point and then drops down as the time passes. However, higher temperature leads to more rapid increasing and decreasing of the potential energy, which means that the heat absorption and release are accelerated so that the ethanol oxidation is promoted by the elevated temperature. The comparison of Fig. 1a and 1b clearly shows that the

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