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# Water assisted liquefaction of lignocellulose biomass by ReaxFF based molecular dynamic simulations

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## ABSTRACT

ReaxFF based molecular dynamics (MD) simulation provides opportunities for fundamentally understanding pyrolysis of lignocellulose biomass through precisely controlled reaction conditions and monitoring of reaction evolution processes. Despite demonstration of simulating the pyrolysis process of dry lignocellulose, MD investigation of this process assisted by water is yet to be performed. This is important considering that hydrothermal liquefaction could be promising to concentrate the energy of biocrude yielded from lignocellulose biomass. In this paper, roles of water on the pyrolysis process of the lignocellulose were investigated by ReaxFF MD simulation. In the simulation, both dry cellulose and lignin systems as well as their systems containing 33% and 66% water by weight were studied at a temperature range of 1250–2000 K at a time scale of 6 ns. Products were characterized by studying their phases, H/C, O/C ratios, and their higher heating values (HHV) that are used to evaluate their value as fuels. Time evolutions of water and other chemical products were investigated to determine the role of water in the reactions and to reveal the reaction mechanism. Compared with dry systems, pyrolysis of the cellulose in presence of water shows several interesting trends, including enhanced breakdown of the cellulose polymer, increased oxygenation of the products, and shift of the final products from char to oil. In contrast, lignin remains largely unaffected by water, and simulation has reproduced experimental results of lignin char formation at elevated temperature in liquefaction. Moreover, it is found that the temperature plays an important role in the reactions. As temperature increases the water's oxygenating effects in the cellulose is decreased. These theoretical results provide solid evidence for unveiling the reaction mechanism of biomass pyrolysis, offering useful guidance for processing wet biomass to liquid fuels.

## 1. Introduction

Biomass is considered as a renewable, green, and carbon-neutral source to satisfy increasing needs for fuels and raw chemical materials [1]. Current main biomass sources for producing alcohol and diesel are based on food crops (such as maize, sugarcane, soybeans, rapeseed, and palm oil). Processing of these biomass requires long biological fermentation time and is criticized for threatening food security [2]. Alternative to food crops, biomass from grass, wood, and other nonfood components is being considered by biofuel industries. These components contain primarily cellulose, hemicellulose, and lignin and are called lignocellulosic biomass. Fast pyrolysis has been used to convert the lignocellulose biomass to useful products such as bio-oils. Nevertheless, so far the produced bio-oils by the fast pyrolysis have not been good enough to serve as transportation fuels due to their high oxygen content, low energy density, thermal instability, and high corrosiveness. Such properties lead to difficulty of ignition, coking upon heating, and degradation and clogging of engines and fuel filters [3,4]. The bio-oils also show increases of viscosity and phase separation during storage [5], posing difficulties for further application.

Hydrothermal liquefaction is a high temperature process, which is similar to the pyrolysis but is carried out in water. It produces a biocrude that is distinct from the bio-oil produced by fast pyrolysis. Generally, the products from the hydrothermal liquefaction are insoluble in water, more deoxygenated, and have higher energy densities [6], which are beneficial to their uses as the liquid fuels. The biocrude produced by the hydrothermal liquefaction has also shown high stability in accelerated aging tests [7], alleviating some problems associated with the bio-oil by the fast pyrolysis. Furthermore, the process is also favored for converting wet biomass, as much less energy is needed than that in the pyrolysis process in which more energy must be required to vaporize the inherent moisture [8]. Experimental work also shows that water enhances oil yields, showing a potential of the hydrothermal liquefaction of lignocellulosic biomass in producing liquid biofuels and value-added chemicals [9]. Nevertheless, the reaction path in the hydrothermal liquefaction is complicated and the products differ over a

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wide range of experimental conditions. Thus, questions on whether water merely serves as solvent or also acts as a reactant still remain. To answer these questions, fundamentally understanding the reaction process is needed, which can be investigated through computational simulation.

There is some simulation work on the pyrolysis process of dry lignocellulose at the atomic scale [10,11]. They found that in cellulose systems, glycoaldehyde ($C_2H_4O_2$) and levoglucosan ($C_6H_{10}O_5$) and their precursors evolve in significant quantities at low temperatures, while levoglucosan formation is suppressed at higher temperatures. Additionally, their results further validated the strategy of using elevated temperature to accelerate pyrolysis reactions. Simulations on lignin systems showed depolymerization of lignin polymer at 1100 K, and then near-complete fragmentation of the polymer by 1400 K, followed by formation of char at 1600–2000 K [10]. A molecular dynamic (MD) simulation based on the reactive force field (ReaxFF) potential has been employed to study effects of supercritical water in coal pyrolysis [12]. It is found that due to solvation mechanisms, the presence of supercritical water reduces the energy required to cleave the linear C—O bonds that connect aromatic rings, thus catalyzing the breakdown of the coal. Similarly, C—O bonds connect much of the cellulose and lignin polymers, indicating the potential of water to catalyze their breakdown as well. Despite these progress, MD investigation of lignocellulosic pyrolysis assisted by water is yet to be performed. Considering the potential of hydrothermal liquefaction, fundamentally understanding the reaction mechanism, especially disclosing roles of the water in the process, is very critical. In this work, to understand this reaction mechanism, dry and aqueous systems were simulated and compared using the ReaxFF MD potential by monitoring reaction evolution and analyzing final products.

## 2. Simulation details

### 2.1. Methods

ReaxFF MD was used to model the hydrothermal reactions of the lignocellulose. Chemical reactions were simulated involving all energy contributions such as bond energy, lone pairs, valence geometry, over/under-coordination, torsion, and bond conjugation [13]. The use of shielded Van der Waals and Coulomb potentials with dynamic charge equilibration via the electronegativity equilibration method (EEM) allows for description of nonbonding interactions and coordination changes associated with the chemical reactions [14]. ReaxFF generates results consistent with quantum-mechanical calculations and experiments for numerous hydrocarbon reactions with far less computational load, indicating the potential for simulation of large reactive systems [13,15].

Simulation was conducted using the ReaxFF module implemented in the LAMMPS package [16], which was used by us to study the polymer conversion to graphene under laser irradiation conditions [17]. Cellulose chains with 10 glucose monomers were generated using Cellulose Builder [18] for building cellulose systems, each of which consists of 8 β phase cellulose chains. An individual chain is shown in Fig. 1a. Lignin polymer molecules were constructed using the Adler lignin model as shown in Fig. 1b [19], and each lignin system consists of 6 lignin molecules. Partial charges for the molecules were calibrated using the VASP package integrated in Materials Studio. Water molecules were then added around the biomass molecules. The water occupies 33 wt% and 66 wt% by weight while mass of the dry biomass was maintained the same. The cellulose system with 33 wt% water is shown in Fig. 1c. Exact amounts of added water molecules are shown in Table S1. Each system was constructed in a cubic box with periodic boundary conditions to eliminate surface effects. During construction initial low density is ensured to prevent overlapping of atoms. It was found that the ReaxFF parameters result in excessive water densities at low temperature, which would lead to unphysical system properties during equilibration (Fig. S1). To solve this problem, the lignocellulose systems were compressed using the Optimized Potentials for Liquid Simulations (OPLS) force field [20]. Water was simulated using the extended simple point charge model (SPC/E) [21]. They were compressed under NPT conditions at 1 atm pressure and 300 K to reach an appropriate density. Herein, these two potentials were combined for system equilibration in order to produce more realistic physical density and structure before simulation by ReaxFF. The compression produced dry cellulose systems with a density of 1.35 g/cm$^3$, 33 wt% wet systems with a density of 1.20 g/cm$^3$, and 66 wt% wet systems with a density of 1.09 g/cm$^3$. Dry lignin systems reached a density of 1.14 g/cm$^3$, and 33 wt% wet systems had a density of 1.17 g/cm$^3$, and 66 wt% wet systems had a density of 1.08 g/cm$^3$. The increased density of the 33 wt% wet lignin system may be due to adsorption of water into the lignin structure. It is possible because the dry lignin systems below experimental densities of 1.33 g/cm$^3$ may have voids for water to fill into [22]. Densities of our systems are closer to experimental values compared to previous simulation works, which simulated cellulose systems with a density of 1.08 g/cm$^3$ and lignin systems with a density of 1 g/cm$^3$ [10,11]. After compression, the systems were equilibrated for 1 ns by the OPLS potential under the NPT conditions. Then the potential was switched to the ReaxFF for simulation under NVT conditions. During the NVT simulation, volumes of the systems were maintained the same as the ones obtained from the NPT equilibrium. Systems were found to be reach stable pressures during annealing, with values depending on temperature and water content (Fig. S2).

In order to investigate the roles of water under various temperatures, systems with no water, 33 wt% and 66 wt% water were heated to 1250 K, 1500 K, and 2000 K. Experimental pyrolysis conditions range from 473 K to 1073 K [10,23,24]. Because the timespan of simulation is heavily restricted by computational power, elevated temperatures are usually used to accelerate reaction dynamics [11,25]. This allows for reactions to take place in nanoseconds, compared to the spans in the range of seconds to minutes employed in experiment [10,23–25]. Heating and cooling stages were performed in 500 ps (0.5 ns). The systems were held at their respective temperatures for additional 5 ns to capture their time-evolution processes at a time step of 0.25 fs. Compared with previous simulation time scales of 250 ps [11,12], this unprecedented long simulation time would allow for detailed analysis of time-evolved reactions.

### 2.2. Characterization

Characterization of the final products was conducted primarily with respect to their uses as fuels. Phases of the products were determined to be gas, liquid, or solid depending on their chemical makeup and weight. Zheng et al. characterized gases as compounds containing one to four carbons ($C_1$-$C_4$), compounds containing more than forty carbons ($C_{40+}$) as the solid, and the remaining as the liquid [11]. However presence of oxygen atoms in forms of hydroxyl or aldehyde groups makes $C_1$-$C_4$ compounds liquid or readily soluble in liquids at room temperature. $C_4$ hydrocarbons (not containing oxygen) are also easily liquefied under absolute pressures of up to 3 atm, and so they are considered as liquid in application. Herein CO, $CO_2$, and oxygen-free hydrocarbons of $C_1$-$C_3$ are characterized as gases. Solids and char are composed of $C_{40+}$ compounds, and liquid includes all remaining molecules. The products were then characterized by calculating their O/C and H/C ratios, and higher heating value (HHV) [26] for liquid products which are of primary interest as fuels. Water was excluded from O/C, H/C, and HHV calculations as a noncombustible component. To probe detailed insight into the chemical makeup of the liquid products, the distribution of molecular sizes was also calculated according to number of carbon atoms per molecule. Time evolution of systems and evolution of chemicals of interest were also recorded so that intermediate phases and products of the reaction can be tracked.