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# Molecular dynamic investigation on hydrogen production by furfural gasification in supercritical water

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## ABSTRACT

Supercritical water gasification is an efficient and clean way to convert biomass to hydrogen-rich gas. Furfural is an important intermediate determining the product distribution so the conversion mechanism of furfural in supercritical water is important. The reactive force field method (ReaxFF) combined with the density functional theory (DFT) method were utilized to investigate the furfural conversion mechanism in supercritical water. The first ring-opening bond position was predicted and the cracking energy was calculated as 266.49 kJ/mol. The decomposition pathways of furfural in supercritical water at the atomic level were revealed and product distribution was obtained. Moreover, the supercritical water gasification process was also compared with steam gasification and pyrolysis to investigate the superiority of supercritical water gasification.

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## Introduction

Global warming and energy crisis are hot topics worldwide [1,2]. The long term traditional utilization of fossil fuel, such as oil, coal and natural gas, has caused environmental pollutant and greenhouse effect, and also makes climate change of the whole world and the resource exhaust [3,4]. Scientists have been looking for renewable energy and sustainable energy to take the place of fossil energy gradually [5–8].

Biomass has been declared as an energy source for half of the world's population [9,10] and has become an important energy carrier in recent years [11,12]. In some industrialized

countries, biomass has offset the drop in use of fossil energy and became truly indispensable and biomass is a kind of renewable energy with great potential. Recent studies have shown that biomass can be used for preparation of transportation fuel [13,14]. Furfural is the main intermediate product in the process of biomass depolymerization. Due to its high reactivity, furfural needs to be hydrogenated to improve the stability, melting point and calorific value for further storage and utilization [15]. Meanwhile, biomass gasification has been identified as a possible method for the production of H<sub>2</sub> [16]. Therefore, part of the furfural was converted to produce hydrogen, which would directly be consumed during the hydrogenation of the rest of furfural to make the whole system independent.

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Hydrogen production from furfural has attracted researchers' attentions. Wang [17] conducted thermodynamic analysis to study the pyrolysis characteristics of furfural residues and concluded that three order-model can be utilized to describe the pyrolysis process. Resasco [18] investigated three kinds of metal catalysts for the hydrodeoxygenation process of furfural. Jand [19] proposed a new configuration involving a dual action fluidized-bed reactor. The gas yield reached 2 m<sup>3</sup> hydrogen-rich gas per kg of biomass. The above results were helpful for the pyrolysis process and gasification process of furfural residues. In recent decades, supercritical water (SCW) gasification method has become researchers' focus due to the high solubility, high diffusivity and high reactivity for organic matters [20–24], and supercritical water gasification of biomass is declared to be clean and effective especially for feedstocks with high water content [25–29]. The conversion of the furfural is of the most importance for the process of biomass/lignite/furfural gasification in supercritical water (SCW). Because given proper supercritical water reaction condition furfural can be converted into gas products such as H<sub>2</sub>, CO and CH<sub>4</sub>. Or else, furfural is converted into tar or char. Therefore, the conversion mechanisms of furfural appeared to be important [30–33].

Molecular simulation was believed to be a useful tool to reveal the reaction mechanism [34,35]. Zhang [36–38] investigated the reaction mechanism of coal gasification in SCW and concluded that SCW molecule clusters weaken C (ring)-C (ring) bond efficiently and the main source of hydrogen originated from the molecule clusters. Salmon [39,40] investigated the pyrolysis process of brown coal via ReaxFF reactive molecular dynamics simulation and found the depolymerization and restructuring of the coal model in the simulation. The investigations above was mainly about the reaction mechanism and product distributions especially for coal, and information reported on furfural was limited. To focus on furfural for the detailed supercritical water gasification process at the atomic level, this paper utilized ReaxFF and DFT to investigate the supercritical water gasification process to reveal the reaction mechanism.

## Computational method

The DFT and ReaxFF combination method was employed in this work to investigate the process of furfural pyrolysis and gasification in SCW. The work was conducted via Amsterdam Density Functional (ADF) software supplied by SCM Inc. The furfural model and water model were optimized using the ADF module in the ADF software. The thermodynamic analysis was utilized to calculate the cracking energy of different bonds. The model optimization and thermodynamic analysis were all conducted by DFT [41]. The DFT calculations were at the level of the generalized gradient approximation using the Becke–Lee–Yan–Parr function and the DZP basis set was utilized [36,42]. For the sake of cooperation, three reaction systems were designed as listed in Table 1. The initial structure of three systems were built using ReaxFF module in ADF software. For eliminating possible surface effects, periodic boundary conditions were used to the 3-D model [41]. Limited by the computational simulation time, researchers often

**Table 1 – The parameter setting of three simulation systems for reaction conditions.**

System	Furfural (molecules)	Water (molecules)	Pressure (MPa)
Pyrolysis	200	0	0.1
Steam gasification	200	500	0.1
SCW gasification	200	500	25

choose a much higher temperature, compared to the experimental one, to conduct the simulation [40,43–48]. Goddard studied the pyrolysis of lignite at different temperature, and concluded that high temperature did not affect the reaction paths in contrast to the distribution of reaction products. Therefore, the simulated temperature was set as 1800 K in order to ensure that the reaction can be carried out smoothly in the simulation time [35,40].

Geometric relaxation was conducted on the systems as follows [49]: Firstly, the temperature of the system was slowly raised from 0 K to 300 K at a rate of 5 K/ps. Then, the temperature was increased from 300 K to 600 K at a rate of 5 K/ps and the NVT ensemble (i.e., constant atomic number, volume and temperature) was used [41]. The system after NVT-EM (Energy Minimization) simulation was used as an initial model for the subsequent simulations. Then, uniform heating process with 20 ps was carried out from 600 K to 1800 K and the NPT ensemble (i.e., constant atomic number, pressure and temperature) was carried out for 500 ps. The time step was set to be 0.25 fs for all simulations.

## Results and discussion

### Reaction pathway of furfural gasification in SCW

Furfural is an important intermediate product in the process of biomass decomposition. As an important intermediate, furfural provides a promising, abundant platform for biomass fuel which includes furan, 2-methyltetrahydrofuran, 2-methylfuran, furfuralcohol, tetrahydrofuran and so on [50]. So it is necessary to study the reaction pathway of furfural gasification in SCW. The reaction pathways can be predicted in ReaxFF molecular dynamics simulation and the energy barrier of the reaction can be obtained by the thermodynamic analysis by DFT. The reaction pathways of furfural gasification in SCW are shown in Fig. 1. Commonly speaking, the ring-opening reaction was the rate-determining step in the thermal chemical process, and the ring-opening reaction occurred at the C (4)–O (6) bond between the oxygen atom in the heterocyclic ring and the carbon atom connecting to the aldehyde group. The cracking energy was calculated to be 266.49 kJ/mol. Then the bond cracking happened at C (2)–C (3) bond and the furfural structure decomposes into two fragments. Afterwards, the two fragments would decompose into small molecules, such as H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> and so on in SCW gasification process. By atomic tracing method it was observed that more than 70% H<sub>2</sub> originated from SCW. SCW molecules can form clusters and provide OH radicals to fragments to produce H<sub>2</sub>. Afterwards, H radicals in SCW

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