# Simulation of softwood lignin gasification in supercritical carbon dioxide

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**Abstract:** The abundant and renewable lignin resource has attracted increasingly attention. Supercritical carbon dioxide has excellent properties in catalytic gasification. In this paper, a molecular model of softwood-lignin was established to as a reactant. ReaxFF molecular dynamics simulation method was used to simulate the gasification of softwood in supercritical carbon dioxide environment with nano-platinum particles as catalysts. The method of slow temperature rise (80K/ps) was adopted, and the system was studied at a constant temperature 1700K. The cleavage of different bond at the initial stage of reaction were studied, and the different gasification production under the action of catalysts in supercritical carbon dioxide were analyzed and compared with the non-catalyst condition. The result shows with the addition of catalyst, the amount of $CO_2$ cracking increases, the number of $H_2$ and CO molecules produced was increased, and the reaction rate increases.

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## 1. Introduction

Global warming and energy crisis are two serious problems that need to be solved in the world [1-5]. Biomass is a kind of renewable energy with broad prospect, which has attracted more and more attention because of its extensive resources and renewable characteristics [6-8]. The direct combustion of biomass caused serious pollution, and to utilization of biomass with clean and efficient approach is a worth widely concerned issue [9,10].

Lignin is one of biomass, with abundant reserves that is second only to cellulose on earth, and it is the only nature non-oil resource which can provide renewable aromatics. However, the current development and utilization of lignin is much less than the others biomass such as cellulose and hemicellulose. And it is the most difficult depolymerization substances in biomass duo to the natural complexity connection and high stability of the structure units.

Supercritical carbon dioxide ($CO_2$) refers to the temperature and pressure of $CO_2$ are both higher than its critical temperature (Tc= 304.1K) and critical pressure (Pc= 7.38MPa), which has excellent performance, and it is an advanced energy conversion method to using supercritical $CO_2$ in catalytic gasification. $CO_2$ has many advantages, such as non-toxic, non-polluting, non-combustible, and compared with other supercritical fluids, the supercritical conditions of $CO_2$ are easier to achieve. Apply supercritical $CO_2$ to the field of chemical reaction can be less energy consumption, lower equipment requirements. Supercritical $CO_2$ can be used as a medium in reaction, compared with organic solvent, it can eliminate the resistance of gas-liquid interface and greatly improve the reaction rate. And by adjusting the temperature and pressure, the viscosity and density of supercritical $CO_2$ can

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be changed, thereby affecting the conversion rate and selectivity of reactants and the solubility of products. When the reaction is over, the pressure can be reduced to normal pressure to separate and recover $CO_2$. In addition, supercritical $CO_2$ can also be used as a reactant to directly participate in the reaction, which still has a broad space for development [10,11].

Recently, more and more studies have been conducted using supercritical fluids to gasify biomass, the gasification of biomass can improve the double pressure of energy and environment, that is, reduce the use of fossil fuels, and improve the utilization rate of resources. As far as we know, in generally the supercritical fluids medium in gasification process is supercritical [12-15], and although there are some research about using supercritical carbon dioxide to gasify lignin [10,11], it is not enough and still lack of the study from microscopic mechanism aspect. The microcosmic mechanism study can further understand the reaction and promote the development of experiment research, it is worth to be paid more attention.

In this paper, the ReaxFF molecular dynamics simulation was carried out to simulate the process of softwood lignin catalytic gasification in supercritical carbon dioxide to reveal the microcosmic mechanism. The nano-platinum particle was used as catalyst. The different gasification production under the action of catalysts in supercritical carbon dioxide was analyzed and the results are compared with no catalyst system at the same condition.

## 2. Materials and Methods

Molecular dynamics simulation is an effective method to revealing microscopic phenomena that are difficult to do experimentally supplement studies, which has been widely used in many research [16-24]. The approach of ReaxFF molecular dynamics simulation has been successfully used to describe chemical reaction in numerous previous works [25-28], such as the decomposition and combustions process of toluene and cyclic compounds. A version force filed for C/H/O/Pt was adopted in this work. [29] The energy of the ReaxFF field is expressed by Formula (1), including bond energy, over coordination energy, three-body valence angle strain energy, four-body torsional angle strain energy, Van der Waals interaction energy and electrostatic interaction energy, the $E_{specific}$ represents system specific terms that are not generally included, unless required to capture properties particular to the system of interest, such as lone-pair, conjugation, hydrogen binding, and so on.

$$E = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{Coulomb} + E_{specific} \qquad (1)$$

The molecular model of carbon dioxide and a typical softwood lignin ($C_{160}H_{180}O_{58}$) consisting of 14 guaiacyl units, one $p$-hydroxyphenyl unit, and one syringyl unit, linked by C−C or C−O-C bonds was constructed by the Material studio software [30], as shown in Figure 1. The Density functional theory (DFT) approach was used optimized initial molecular model to get a more suitable structure. In all following figures, the hydrogen atoms described by blue ball, the carbon atoms described by black ball, and the oxygen atoms described by red ball. There are 321 Pt atoms in the PtNPs catalyst, which was established into a sphere with a radius of 1.0 nm with the densest packing of face-centered cubic (fcc) [31]. Then, a cubic cell with periodic boundary conditions was constructed to establish the initial

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structure and eliminate the surface effect, and the catalyst nanoparticles placed in the center of the simulation system. The optimized structure of the simulation system was exhibited in Figure 2. In reactive process, the simulation of the bond breaking, and bond formation were implemented with bond order. Each pair of atoms connected independently and using Electronegativity Equalization Method to evaluate the atomic charges. [32] The method of slow temperature rise (80K/ps) was adopted from 325K and the target temperature was 1700K, When the 1700K was reached, a constant temperature simulation was implemented, and the whole simulation process lasts for 3ns. The time step was set as 1fs, verlet algorithm was adopted for the numerical integration of the motion equation, and berendsen method was adopted for the temperature control of the system.
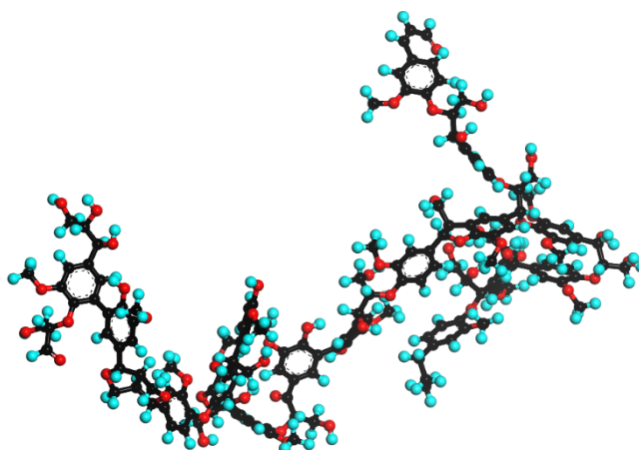


**Figure 1.** Alder's softwood lignin model ($C_{160}H_{180}O_{58}$).
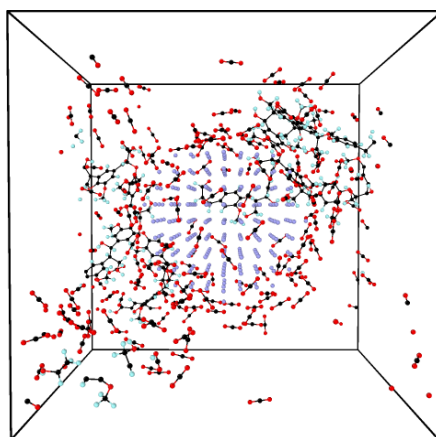


**Figure 2.** Simulation system with PtNPs.

## 3. Results

Lignin macromolecule is composed of multiple monomers, and the connection between monomers is mainly by ether bond (C-O-C) and carbon-carbon bond (C-C). In addition, C-H bond is mostly in the outermost layer of lignin molecule and will also begin to crack at the beginning of the reaction. Therefore, this work statistic the changes of the number of three kinds of bond in lignin molecule at 1700 K in the Figure 3. In the initial phase of the reaction, the C-O-C bond is reduced to zero very quickly which means that the C-O-C fracture process is proceeding very quickly. This is

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because the C-O-C bond has the lowest bond dissociation energy, and it requires less energy to break than the other two bonds. The fracture of the C-C and C-H bonds continues throughout the whole reaction phase, because of the large amount of the two bonds.
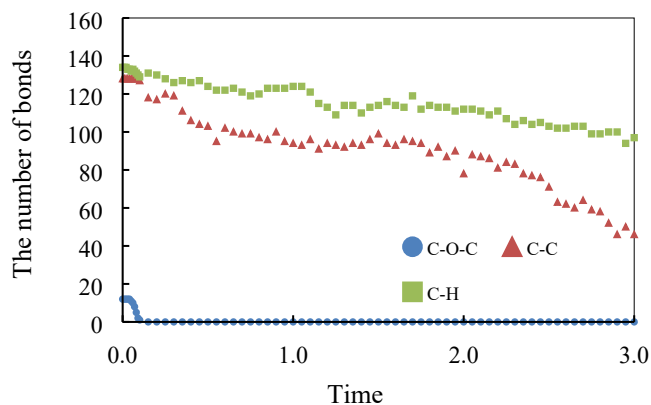


**Figure 3.** The change of connection bonds number over simulation time

With the broken of lignin, the molecular fragments with benzene ring gradually appeared in the process of C-O-C crushing. And then the benzene ring breaks up into a C chain. This process is much slower than breaking the C-O-C bond. The initial cleavage of most benzene rings in lignin is shown in Figure 4 and it is also the two most common morphological changes of benzene rings.

The internal bond structure of benzene ring is broken, and the six-membered ring is cracked into a five-membered ring. Alternatively, the benzene ring can be broken by an external atom, such as the O atom connected to the benzene ring inserted between the adjacent C-C bonds to form a 7-member ring.
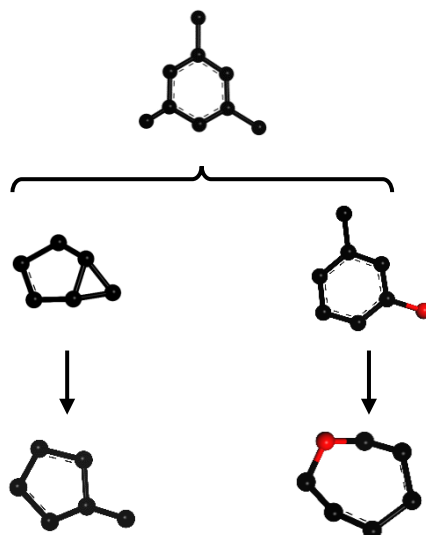


**Figure 4.** Typical initial cleavage pathways of benzene rings

With and without catalyst, the number of $CO_2$ molecules changes with reaction time, as shown in Fig. 5. At the lower temperature, the number of $CO_2$ molecules barely changes, after 0.015ns, the number of $CO_2$ molecules decreases rapidly. When the catalyst is not added, the number of $CO_2$ is reduced to about 182 and then decreased very slowly. When the catalyst is added, the number of $CO_2$ is

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still reduced after 0.015ns and reaches the dynamic equilibrium after 0.5ns, and the number of molecules is stabilized at about 143. It could be concluded from that after the addition of catalyst, the amount of $CO_2$ cracking increases, and the catalyst has a promote catalytic effect on the cracking rate of $CO_2$.
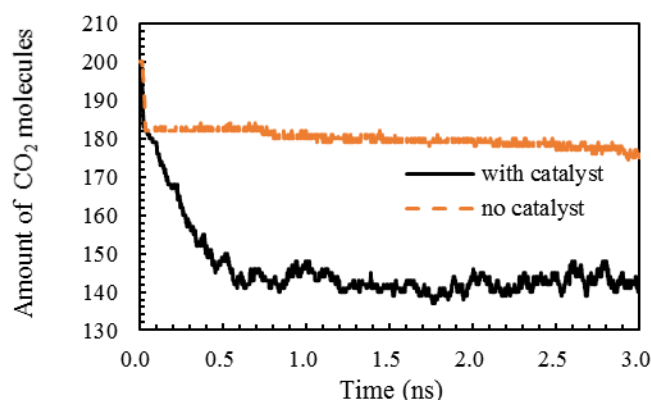


**Figure 5.** Left of $CO_2$ molecules amount

There are many products appeared in this reaction. Every different product relies on different chemical reactions. Among them, the main products, CO and $H_2$, were discussed in the Figure 6 and Figure 7, To investigate the detailed producing of the main products, the detailed molecular amount information for the two main products were recorded and exhibited.

The H radical all comes from the lignin molecule, so $H_2$ is also produced from the lignin molecule. As can be seen from Figure 6, there were very few $H_2$ molecules produced in the system without the addition of catalyst, but the number of $H_2$ molecules produced was significantly increased after the addition of catalyst, that is because the presence of catalyst accelerated the dissociation of H free radicals from lignin.
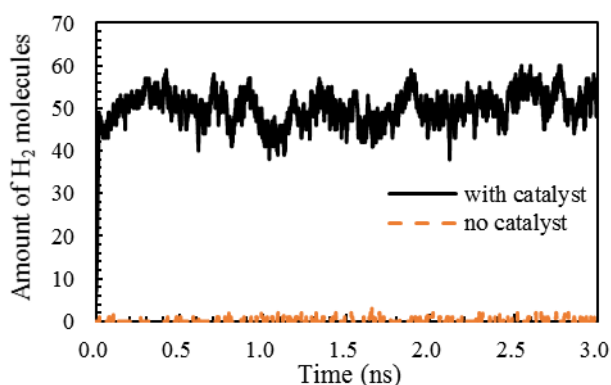


**Figure 6.** Evolution of $H_2$ molecules amount

As shown in Figure 7, there are almost no CO molecules appeared before 0.015ns, and the amount of CO increases rapidly after 0.015ns, because the reaction temperature increased to accelerates the reaction. For the condition without catalysts, the number of CO increases very slowly after the CO molecular amount reaching about 12. For the systems with catalysts, the CO molecular amount

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continuously increased to about 45 and then gradually decrease, that is because CO molecules are the adsorption of nano-catalyst particles to CO molecular.
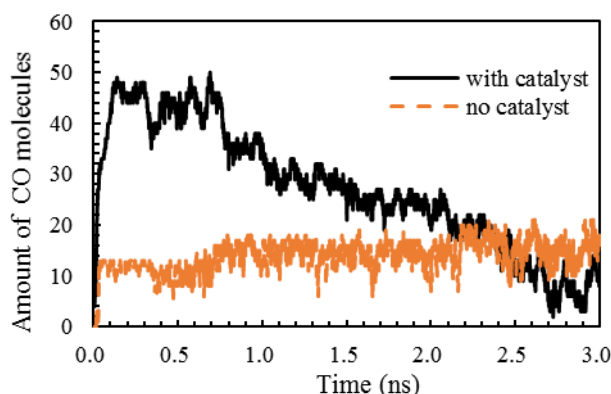


**Figure 7.** Evolution of CO molecules amount

## 4. Conclusions

This work studied the reaction process of a softwood lignin gasification in supercritical carbon dioxide with ReaxFF MD method. The initial evolution of softwood lignin is revealed, and the main products ($H_2$ and CO) are discussed. The effects of the nano-catalysts to the reaction are compared with that condition of no catalyst. During the gasification process, the C-O-C bonds of softwood lignin are broken at first, both dissociated of C-C bonds and the opening of benzene ring structures are proceed much more slowly than the processes of C-O-C bonds breakage. All $H_2$ is produced from the lignin molecule, meanwhile the CO is produced from lignin and $CO_2$. In the condition of with catalyst, the gas production is produced faster, and the number of $H_2$ and CO molecules was more than no catalyst. The catalyst accelerated the dissociation of H free radicals from lignin, and the amount of $CO_2$ cracking increases, and that shows the catalyst has a promote catalytic effect on the reaction rate. However, there are phenomenon of CO molecular adsorption by nano-catalyst, which still needs to be deeply studied.

**Conflicts of Interest:** The authors declare no conflict of interest.

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