



## Mechanism study of degradative solvent extraction of biomass



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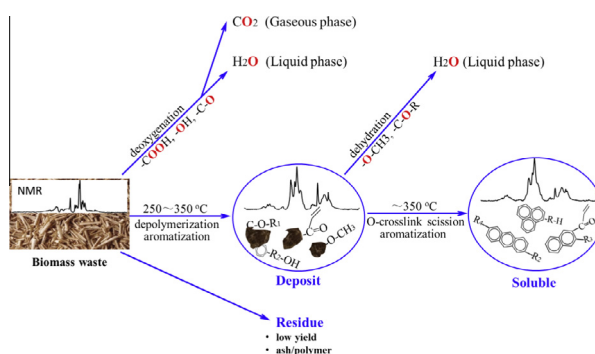
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### HIGHLIGHTS

- The residence time greatly affected the products yield distributions.
- The residence time exhibited considerable effects on the characteristics of the products.
- Prolonging the residence time can enhance the conversion from Deposit to Soluble.
- The reaction process can be divided into two stages.
- A conversion pathway of the degradative solvent extraction of biomass was proposed.

### GRAPHICAL ABSTRACT

Proposed conversion pathway of the degradative solvent extraction of biomass.



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### ABSTRACT

We have recently proposed a novel and effective degradative solvent extraction method to upgrade and convert various types of biomass feedstocks into high-grade carbonaceous materials under rather mild conditions. The feasibility of this method has been preliminarily proven in our previous work. However, the conversion mechanism of this process remains unknown. Hence, in this study the conversion process of the degradative solvent extraction of biomass was investigated in detail. A typical biomass (fir sawdust) was treated in 1-methylnaphthalene at 350 °C with the residence time from 0 to 90 min. Three solid products, which were the fraction soluble in the solvent at room temperature (termed Soluble), the fraction soluble in the solvent at treatment temperature but insoluble at room temperature (Deposit) and the unextractable fraction (Residue), were obtained. The products were then characterized by various analysis methods in detail. The oxygen, carbon and minerals in the raw biomass were mainly recovered as CO<sub>2</sub>/H<sub>2</sub>O, Deposit/Soluble, and Residue, respectively. With the residence time increasing from 0 to 45 min, the soluble yields increased obviously but the deposit yields decreased significantly. The yield variations of the Solubles and Deposits obtained at residence time longer than 45 min were not significant. The chemical structure and properties of Solubles were independent of the residence time, while those of Deposits varied obviously with residence time. According to the results, the conversion process of the degradative solvent extraction of biomass was proposed. The process can be divided into two stages. The first stage took place at heating up stage from 250 to 350 °C and the beginning of the isothermal stage at 350 °C. In this stage, the thermal extraction, deoxygenation and aromatization reactions of the raw biomass occurred significantly. The main product was Deposit. The oxygen was removed

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as CO<sub>2</sub> and H<sub>2</sub>O. At the second stage, the Deposit was further deoxygenated and converted into Soluble. In this stage, the Deposit underwent complex reactions, such as the cleavages of oxygen containing cross-links and slight aromatization reactions. The oxygen was mainly removed as H<sub>2</sub>O at the second stage.

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## 1. Introduction

The rapid depletion and excessive use of fossil fuels (coal, petroleum and natural gas) have brought in serious problems such as the energy crisis and environmental pollution (acid rain, greenhouse gases and particulate matter emissions). Intensive researches have been conducted to seek new and renewable energy resources as substitutes for fossil fuels. Biomass is one of the cheapest and most available renewable energy resources, which accounts for 14–15% of the world's total primary energy consumption [1]. Concerning its zero net emissions of carbon dioxide, renewable characteristic, low sulfur content, and low nitrogen content [2,3], biomass shows great potential in substituting fossil fuels. However, some inherent characteristics of biomass such as high moisture content, high oxygen content, and low bulk density, lead to its low calorific value, hydrophilic nature, high tendency of spontaneous combustion, inconvenience for transportation and storage, and create great challenges for the direct application by the conventional processing technologies (e.g. pyrolysis, gasification, and combustion). Hence, it is essential to dewater and deoxygenate biomass feedstocks prior to introducing them into conventional conversion processes. This is the so-called biomass upgrading.

Two primary thermal treatment technologies (torrefaction and hydrothermal upgrading) have been employed to upgrade and convert lignocellulosic biomass into densified biochar or carbon material [4,5]. Torrefaction is the pyrolysis of biomass feedstocks between 200 and 300 °C under an inert atmosphere [6–9]. Hydrothermal upgrading is to treat the biomass feedstocks in a hot (180–300 °C) and pressurized water to produce biochar [5,10–12]. Generally, the properties of the biochar derived from torrefaction are greatly dependent on biomass feedstocks used. The carbon contents of the biochar are generally lower than 60%, and the oxygen contents are still as considerably high as 25–40% [13]. Besides, the ash contents of the biochars from torrefaction are higher than their raw biomasses, which can cause serious problems during further utilization. The hydrothermal upgrading of biomass is to produce biochar which generally has the carbon content ranging from 60% to 75% [4,12]. But it is generally carried out under subcritical or supercritical conditions with the pressure higher than 15 MPa. The severe conditions required for hydrothermal upgrading cause its poor practical applicability.

To overcome the disadvantages in the conventional technologies for biomass upgrading, the authors have recently proposed a novel method to dewater, deoxygenate and separate a wide variety of low grade carbonaceous resources, such as biomass wastes and low rank coals, into several fractions by degradative solvent extraction [14–17]. This method treats the carbonaceous resources in a non-polar solvent below 350 °C under an inert atmosphere by a specially designed autoclave. Three solid fractions are obtained, which are the fraction soluble in the solvent at room temperature (termed as Soluble), the fraction soluble in the solvent at treatment temperature but insoluble at room temperature (Deposit) and unextractable fraction (Residue). It was very interesting to find that the physico-chemical properties, chemical composition and structure of Solubles and Deposits prepared from various types of biomass feedstocks were extremely similar to each other,

respectively. The carbon contents and oxygen contents of Solubles and Deposits reached as high as 84.9% and as low as 7.3% respectively, significantly different from those of their raw material and similar to those of bituminous coal. It was also found that the low-temperature reactivity of Deposits and Solubles were significantly lower than those of their raw materials [18], demonstrating that the spontaneous combustion tendency of biomass or low rank coal is effectively suppressed by this method. Additionally, the utilization of the Solubles and Deposits obtained from biomass for liquid fuel production and carbon material preparation have been proved preliminarily in our previous work [19,20].

Much works have been performed in our previous study related to the degradative solvent extraction and the utilization of the products. However, the reaction process of this method has not been investigated in detail. In-depth understanding of this process would be rather beneficial for optimizing the treatment conditions and the development of this method. It is well known that the decomposition reactions during the biomass pyrolysis are complex, because the three major components of biomass (cellulose, hemicellulose and lignin) have different thermal decomposition characteristics [21]. Furthermore, the mechanisms of hydrothermal or solvothermal treatments of biomass are not clear. Thus, in this work a typical woody biomass was treated by the degradative solvent extraction at 350 °C. The yields, chemical composition and structure, physico-chemical characteristics of the products obtained at different residence time were investigated and compared in detail. The reaction mechanism of this process was then discussed.

## 2. Experimental

### 2.1. Samples and solvents employed

A fir sawdust (abbreviated as SD, from Hunan province, China) was employed as raw biomass material in this work. The proximate analysis and elemental compositions of SD is given in Table 1. A non-polar solvent, 1-methylnaphthalene (1-MN), was chosen as the solvent for the extraction.

### 2.2. Degradative solvent extraction procedure

It was found in our previous work that 350 °C was the proper temperature for the degradative solvent extraction of biomass [14,16]. So the degradative solvent extraction of SD was conducted at 350 °C in a specifically designed batch autoclave in this study. Fig. 1 shows the schematic diagram of the batch autoclave. The autoclave was equipped with a stainless filter device at the lower end and a valve which connected the autoclave reactor and the reservoir. The detailed procedure of the extraction experiments has been described in our previous papers [16,17]. Around 20 g raw SD (air-dry basis) and 300 mL of 1-MN were placed into the autoclave. After purging the autoclave sufficiently with N<sub>2</sub>, the autoclave was sealed with 0.2 MPa of N<sub>2</sub> and then heated up to 350 °C at an average heating rate of 5 K/min. The residence time at 350 °C were 0, 15, 30, 45, 60, and 90 min. The extracts along with the solvent were transferred to the reservoir through opening the valve immediately after the desired residence time. Therefore,

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