

Selective chemical recovery from biomass under hydrothermal conditions using metal oxide nanocatalyst

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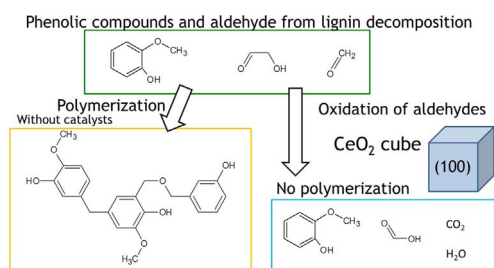
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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Hydrothermal treatment
Cellulose
Lignin
Monte Carlo simulation
Polymerize suppression
Cubic CeO₂ catalyst

ABSTRACT

This paper has two parts: The first part covers the review of previous researches on biomass fractionation based on mechanistic and kinetic viewpoints. Since the major components of biomass are cellulose and lignin, fractionation of each component is discussed. Kinetics and reaction mechanism of cellulose hydrolysis, glucose fractionation, and decomposition are also summarized. Based on the results of these basic studies, new processes of aldehyde recovery from cellulose/glucose and cresol addition method for fractionation from lignin are introduced. The second part of this paper proposes a new approach (original research) to decompose lignin and biomass with CeO₂ nanocatalysts fabricated by supercritical hydrothermal synthesis method. Char formation decreased, and liquid product yield increased when the nanocatalyst, {001} surface exposed cubic CeO₂ was used. This is probably because of the suppression of Friedel-Crafts reaction due to the oxidation of aldehydes, which could be the bridge molecules of phenolic structures.

1. Introduction

Global warming caused by increasing CO₂ emissions is the most critical issue facing the world today. The transition from fossil fuels to renewable energy sources including photovoltaic, wind/tide energy, hydropower, geothermal energy, and biomass is of great importance to address the global warming problem. Biomass is regarded as a carbon-

neutral resource; it is synthesized in the nature from CO₂ and H₂O by solar energy. Even though the combustion of biomass emits CO₂ and H₂O, the net CO₂ emissions are considered zero. A variety of biomass conversion processes have been proposed to date and are being developed for energy harvesting processes.

Reducing the energy and materials consumption in the life cycle of a product, from production to the waste treatment step is another critical

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<http://dx.doi.org/10.1016/j.supflu.2017.09.032>

Received 19 June 2017; Received in revised form 29 September 2017; Accepted 29 September 2017
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aspect of controlling CO₂ emissions. Recycling of used materials should be less energy consuming than producing the materials using natural resources [1,2]. Waste treatment is responsible for high CO₂ emissions; especially, the incineration of polymer wastes emits large quantities of CO₂ into the atmosphere. However, if those chemical products could be synthesized from biomass, including food wastes or the waste from biomass conversion processes, CO₂ emissions could be reduced significantly. Thus, the use of (waste) biomass as a materials resource leads to the reduction of CO₂ emissions from the life cycle of polymer production.

Different from the petroleum-based chemical production, the use of water as a reaction solvent for the materials produced from biomass, which is hydrophilic in nature, should be quite natural and environmentally friendly. In general, acid or base catalysts are used to control the reactions. However, high-temperature compressed water can serve as either an acid or a base catalyst because water dissociates to protons and hydroxyl ions greatly around its critical point [3]. In addition, water density of the high-temperature compressed water that can affect the reaction kinetics can be tuned continuously by controlling the pressure and temperature. Moreover, water molecules themselves work as an acid or a base catalyst as well as a nucleophile in supercritical water hydrolysis [4].

Furthermore, the reaction rate changes significantly near the critical point because of the solvent effect originated from the difference in the electrostatic interaction due to the change in the dielectric constant of water [5]. Thus, subcritical and supercritical water are regarded as effective solvents for transforming biomass into specific chemical products [6–9]. The use of heterogeneous catalysts that work in high-temperature water improves the reaction system towards the selective recovery of products from biomass materials, where the design of a catalyst is critical. Recently, it was demonstrated that nanocatalysts which expose most active crystal face could be synthesized by using supercritical water [10,11]. Sub- and supercritical hydrothermal processes have a high potential to fractionate and transform biomass into specific chemicals.

Processes to produce chemical products from biomass should be developed based on a better understanding of the mechanism of the biomass reactions in high-temperature water, for cellulose and lignin. In this paper, both aspects, namely the understanding of the mechanisms and kinetics and the proposal of a new process are introduced. This paper is composed of two parts: (1) A review of the previous studies on cellulose/glucose and lignin fractionation/transformation to recover chemicals showing the mechanism of those reactions in the sub and supercritical water. It includes the kinetic studies to determine the optimum conditions to recover chemicals. Mechanistic and kinetic studies for dissolution and hydrolysis of cellulose in high-temperature water, retro-aldol reactions of glucose into aldehydes, and the Friedel-Crafts reaction of phenolic compounds and aldehydes are explained. The process to recover glycolaldehyde or phenolic compounds is proposed based on those fundamental studies. (2) An original work to recover the chemicals from lignin, based on the understanding of the above reaction mechanism. We will show that an active catalyst, {001} face exposed CeO₂ nanocatalyst, synthesized in supercritical conditions oxidizes aldehydes to suppress the polymerization of phenolic compounds through Friedel-Crafts reactions.

2. Cellulose fractionation

2.1. Cellulose dissolution in high-temperature compressed water for rapid enzymatic hydrolysis

Cellulose, a major non-edible component of plants, can be a target resource for energy recovery; cellulose can be converted to ethanol. The first step of the process is to separate cellulose from lignin, another major component of biomass. Hemicellulose is also another major component of biomass, but, in this paper, the reaction of cellulose and

lignin was focused on. Since the insight into the reaction of cellulose and lignin is considered to lead to the understanding of the reaction of hemicellulose which has similar structure to cellulose composed of xylose and mannose not glucose and sometimes combined with lignin structure to form a complicated structure.

Cellulose separated from lignin is converted to glucose through enzymatic hydrolysis, followed by fermentation into ethanol. The first step, enzymatic hydrolysis, occurs on the surface of solid cellulose crystals and is extremely slow. Thus, this is the limiting step in the total biomass conversion reaction process and how to enhance this reaction is of great importance.

Cellulose is a crystalline solid under ambient conditions because of inter- and intra-molecular hydrogen bonds. If hydrogen bonds can be dissociated, cellulose can be dissolved in water. The melting point of cellulose is approximately 280 °C, which suggests that the hydrogen bond can be dissociated above that temperature. We have observed cellulose in high-temperature compressed water through a diamond anvil cell and a flow reaction system in which pressure can be controlled. As a result, solid cellulose disappeared around 300 °C, even for the highly crystalline cellulose called Avicel [12,13].

Under these conditions, hydrolysis occurs as well as the dissolution of cellulose crystals. To minimize the effects of hydrolysis on the dissolution of cellulose in high-temperature water, we employed a flow reaction system with a volume ranging from 0.03 to 5.27 cm³. The cellulose-water slurry was mixed with preheated water at the mixing point, and the slurry was rapidly heated to its reaction temperature. At the end of the reactor, cooling water was injected directly into the reaction stream to terminate the reaction. This rapid heating and quenching resulted in extremely short residence times with sufficient accuracy [12,13]. At a short residence time of 50 ms, at 380 °C and 30 MPa, a clear solution dissolved cellulose and the hydrolysis products as the main products, while the other products were minimized.

After maintaining the clear solution at room temperature for several hours, a white precipitate formed. The precipitate was identified by X-ray diffraction analysis as recrystallized cellulose, cellulose II. Scanning electron microscopy (SEM) showed that the size of the recrystallized cellulose was larger than that of the original cellulose [14]. The crystal structure of cellulose II differs from that of the original cellulose, cellulose I. These results suggest that cellulose is dissolved in high-temperature compressed water, although hydrolysis of cellulose still occurs. To evaluate the effect of hydrolysis, the degree of polymerization was evaluated. While the original cellulose had a polymerization degree of 250, the recovered cellulose had 50, and hydrolysis was successfully minimized by dissolving the cellulose in high-temperature compressed water using the flow reaction system.

Next, we introduced a hydrolysis enzyme-water suspension at the exit of the reactor. By mixing this water suspension and using an external cooling water jacket, the temperature of the exit solution rapidly fell to the room temperature. The hydrolysis reaction with this enzyme generated the hydrolysis products. Reaction rates were compared for the dissolved cellulose, recrystallized cellulose, and the original cellulose I. This dissolution treatment produced a reaction rate that is more than 700 times higher than that occurring in the original cellulose [15].

2.2. Hydrolysis rate of cellulose in high-temperature compressed water

As implied in the experiment of cellulose dissolution, hydrolysis and further decomposition occur in high-temperature compressed water. At 320 °C and 350 °C, most products were glucose decomposition products, namely erythrose, glycolaldehyde, glyceraldehyde, dihydroxyacetone, pyruvaldehyde, 1,6-anhydroglucose, 5-hydroxymethyl-2-furfural, and acids, obtained via the retro-aldol reaction of glucose followed by dehydration. The detailed mechanism of the decomposition of glucose, which is the hydrolysis product of cellulose, is explained in Section 2.3. However, at 400 °C, cellulose was converted 100% within 0.05 s and most products were the hydrolysis products, including

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