Effects of hydrolysis and oxidative hydrolysis pretreatments on upgrading of the water-soluble fraction of bio-oil via decarboxylation

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HIGHLIGHTS

- Water-soluble fraction of bio-oil was pretreated by hydrolysis/oxidative hydrolysis.
- Hydrolysis/oxidative hydrolysis could convert pyrolytic sugars into carboxylic acids.
- Such pretreatments reduced remarkably char formation during followed decarboxylation.
- The reaction pathways for conversion of the pyrolytic sugars were proposed.

GRAPHICAL ABSTRACT
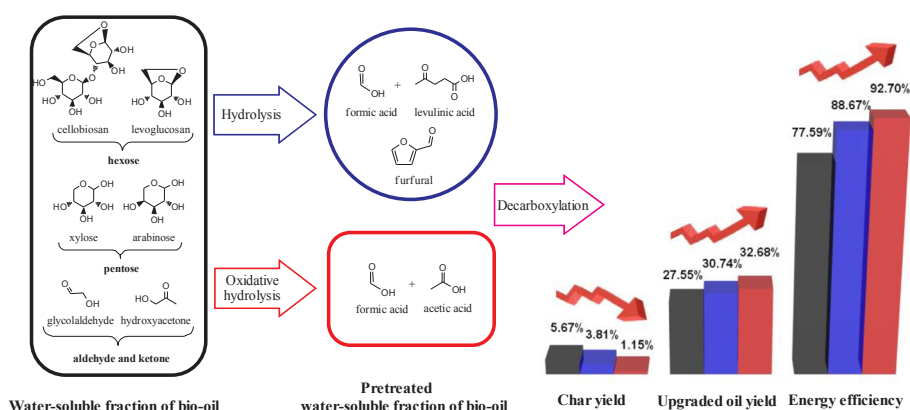
ABSTRACT

Conversion of the carboxylic acids in bio-oil into ketones via decarboxylation is a highly efficient approach for bio-oil upgrading. However, the char formation during decarboxylation is due to the existence of a considerable amount of pyrolytic sugars in bio-oil, which severely weakens the upgraded bio-oil yield and the energy efficiency. In this paper, two pretreatment approaches, hydrolysis and oxidative hydrolysis, were employed to solve this problem. The pyrolytic sugars in bio-oil were firstly enriched into the water-soluble fraction through water extraction, followed by hydrolysis or oxidative hydrolysis pretreatment before decarboxylation. With the aid of hydrolysis pretreatment, the upgraded bio-oil yield was increased from 27.55 to 30.74%, and the energy efficiency was increased from 77.59 to 88.67% after decarboxylation, whereas the char yield was decreased from 5.67 to 3.81% in comparison with the results without hydrolysis. In the case of oxidative hydrolysis pretreatment, the upgraded bio-oil yield and the energy efficiency were further enhanced to be 32.68% and 92.70% respectively, while the char yield was drastically decreased to only 1.15%. To clarify the effect of the pretreatment, two pentoses and four hexoses were used to investigate the reaction pathways for their conversion in the water-soluble fraction during hydrolysis or oxidative hydrolysis pretreatment. The experimental results showed that hydrolysis of the water-soluble fraction could effectively convert pyrolytic sugars to carboxylic

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acids. In contrast, oxidative hydrolysis could convert not only the pyrolytic sugars, but also most of the aldehydes and ketones in the water-soluble fraction into carboxylic acids. The reaction pathways for conversion of pentose and hexose into organic acids via oxidative hydrolysis were also investigated.

1. Introduction

Fast pyrolysis of biomass to bio-oil is one of the important techniques for biomass utilization, not only because its process is relatively simple, but also it is able to afford bio-oil in high yield [1]. However, bio-oil is a very complex mixture that contains a broad spectrum of oxygenated organic compounds, including acids, aldehydes, ketones, alcohols, sugars, phenols, esters, and water. It is not an eligible biofuel substitute for petroleum fuel because of its low heating value and strong corrosiveness, and thus not suitable for direct application in the internal combustion engine. To meliorate the bio-oil quality, various techniques have been examined, such as hydrogenation [2], catalytic cracking [3,4], treatment in supercritical fluids [5], esterification [6,7]. For example, Oh et al. [2] employed hydrogenation using activated carbon supported Pt and Ru catalysts to stabilize bio-oil. Although the bio-oil could be improved, the char yield was up to 6.10–14.90%. In the field of catalytic cracking, the vapors of beech sawdust pyrolysis oil were upgraded over Fe-modified ZSM-5 zeolite with a char yield range of 11.45–11.74% [3]. Ma et al. [4] reported that the co-catalytic cracking of the raw bio-oil mixed with kitchen waste oil could enhance the upgraded bio-oil yield, but associated with a char yield rang of 9.07–15.32%. Prajitno et al. [5] reported a non-catalytic method for bio-oil upgrading in supercritical ethanol. The addition of a large amount of solvent did not significantly depress the char yield (7.65–27.00%). Esterification enables bio-oil upgrading to carry out under mild reaction conditions, but the char formation is still unavoidable. The experimental results of Wu et al. [6] demonstrated that the char yields ranged from 11.00 to 29.80% under the catalysis of various acidic catalysts. To better improve the quality of the resulting bio-oil, coupling techniques were also attempted. In the case of in-line esterification with ethanol of the pyrolysis vapor, which was the precursor of bio-oil, the char yield reached up to 21.80–24.40% [7]. Although a combination of hydrogenation and esterification could boost up the hydrogen content and decrease the acidity of bio-oil, the char formation was not overlooked yet [8]. These results show that a common challenge confronted with these techniques is the high char formation in the upgrading process, overwhelmingly resulting from the pyrolytic sugars and the reactive aldehydes in bio-oil [9], which severely depresses the upgraded oil yield and the energy efficiency.

For a bio-oil whatever kind of biomass derived from, the addition of certain water will make the bio-oil spontaneously separated into two phases, a water-soluble fraction (WSF) and an oil-soluble fraction. This phenomenon is called water extraction. Fractionation of bio-oil by water extraction is viewed as an important preliminary step for effective upgrading of bio-oil because it is capable of reducing the complexity of bio-oil and suppressing side reactions. Through this approach, most of the polar chemicals including the pyrolytic sugars, the carboxylic acids, and most of the aldehydes and ketones with small molecular weights can be enriched into the water-soluble fraction, while the nonpolar and weakly polar substances such as phenols and esters are kept in the oil-soluble fraction [10].

Recently, we found that upgrading the water-soluble fraction of bio-oil via decarboxylation could efficiently convert the carboxylic acids into ketones [11]. As a novel and effective method for bio-oil upgrading, decarboxylation is suitable for energy densification because it can remove the oxygen in the form of CO_2 rather than in the form of H_2O. As a result, the energy efficiency can be enhanced. Zhang et al. [12] reported the removal of organic acids in bio-oil via in-situ decarboxylation, in which the biomass pyrolysis vapor was allowed to pass through a $CaCO_3$ bed so as to capture the organic acids, with a removal

rate of acetic acid of 98.10%. The spent $CaCO_3$ could be regenerated by subsequent thermal decomposition of calcium salts of the organic acids into ketones. Wheeler's group surveyed the decarboxylation of the mixture of formic and levulinic acids in the presence of $Ca(OH)_2$. Interestingly, the major products were liquid hydrocarbons with high yields instead of ketones after the decarboxylation [13]. In terms of application, decarboxylation has been demonstrated in pilot scale [14] as a part of the MixAlco process which involves: (1) anaerobic fermentation of biomass into carboxylic acids, (2) neutralization of carboxylic acids to calcium carboxylates, (3) decarboxylation of calcium carboxylates to ketones, and (4) hydrogenation of ketones to mixed alcohols.

However, direct decarboxylation of bio-oils still suffered from the charring issue. The char formation in direct decarboxylation of an original bio-oil was as high as 9.20%. And it was still up to 5.67% even after water extraction [11]. One of the main reasons is that pyrolytic sugars are facile to take part in dehydration and carbonization reactions at high temperature and the content of these sugars usually accounts for more than 55 mg/g of bio-oil [15]. Due to their strong polarity, pyrolytic sugars are not easily to be isolated from the other polar compounds in bio-oil, but readily extracted into water-soluble fraction. Therefore, the pyrolytic sugars should be removed or transformed before upgrading the WSF.

Conversion of the pyrolytic sugars in bio-oil to valuable chemicals via fermentation has been examined. Unfortunately, the presence of phenols and carboxylic acids has inhibiting effect on the activity of bacterial strain and yeast. To remove the acids and phenols from the pyrolytic sugars and so as to alleviate their inhibiting effects, many approaches have been reported, such as neutralization of the acids with alkaline reagents [16], extraction of the bio-oil with organic solvents [17,18], and adsorption of the phenols over activated carbon [18]. But the usage of a large amount of alkaline reagents and organic solvents as well as the polluted activated carbon give rise to pollution concerns that must be taken into account from a viewpoint of green chemistry.

It is well known that biomass-derived carbohydrates can be converted to carboxylic acids in the presence of acid catalyst under hydrothermal conditions. One of the essential routes is acid-catalyzed hydrolysis of hexose-based carbohydrates to levulinic acid. As reported by Girisuta et al. [19], hydrolysis of cellulose at 150 °C using 1.0 mol/L H_2SO_4 as the catalyst could afford 60 mol% levulinic acid. Szabolcs et al. [20] compared the hydrolysis of various hexose-based carbohydrates to levulinic acid under microwave irradiation, including fructose, glucose, saccharose, cellobiose, cellulose, and chitosan. The highest yield (34.20%) was obtained from the hydrolysis of cellulose under the optimized conditions (170 °C, 2.0 mol/L H_2SO_4 and 50 min). In addition, several kinds of real biomass were also examined, such as wheat straw [21], cotton straw [22] and *Quercus mongolica* wood [23]. The above results indicated that levulinic acid can be obtained from various hexose-based carbohydrates and biomass. Deng et al. [24] proposed a four-step process for the acid-catalyzed conversion of cellulose into levulinic acid, which were: (1) hydrolysis of cellulose into glucose, (2) isomerization of glucose to fructose, (3) dehydration of fructose to HMF, and (4) rehydration of HMF to levulinic acid and formic acid. A few of kinetic models have also been established to describe the process of levulinic acid. A mathematical model was developed to predict conversion of cellulose to levulinic acid through glucose and HMF based on an irreversible pseudo-first order reaction [25]. Weingarten et al. [26] proposed a kinetic model for production of levulinic acid from glucose under homogeneous catalytic condition, which enables to determine the optimal operating conditions in reactor