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Conversion of Biomass into High-Quality Bio-oils by Degradative Solvent Extraction Combined with Subsequent Pyrolysis

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ABSTRACT: The rapid depletion of fossil fuels has attracted more attention being geared toward the fast pyrolysis of biomass to produce bio-oils. However, the produced bio-oils usually contain high water, oxygen, and acid contents and low calorific values, which have limited their wide application. Therefore, in this study, a novel two-stage method combining degradative solvent extraction with subsequent pyrolysis was proposed to improve the quality of derived bio-oils. The raw biomass was initially dewatered and deoxygenated using a degradative solvent extraction method to obtain a low-molecular-weight extract (named "Soluble"). The Solubles were then pyrolyzed at 500 °C to prepare bio-oils. The carbon contents and calorific values of bio-oils produced from the Solubles were as high as 90.09% and 44.63 MJ/kg, respectively, which were 1.5−2.0 times higher than those from the raw biomasses. In addition, the water and oxygen contents of bio-oils from the Solubles were significantly lower than the bio-oils from the raw biomasses. Furthermore, the bio-oils from the Solubles contained much fewer corrosive and reactive acids and more value-added aromatic hydrocarbons compared to those from raw biomasses. In summary, the quality of the bio-oils produced from the Solubles was obviously superior to the bio-oils from the direct pyrolysis of the raw biomasses. It was shown that degradative solvent extraction combined with subsequent pyrolysis is an effective method to convert raw biomasses into high-quality bio-oils.

1. INTRODUCTION

With the fast depletion of fossil oils, renewable resources are increasingly considered as potential substitutes for energy production.[1] Among various renewable resources, biomass is the only sustainable carbon resource that can be directly converted into fuels or chemicals via biochemical conversion processes (such as hydrolysis and fermentation) and thermochemical conversion processes (such as pyrolysis, gasification, liquefaction, and hydrothermal carbonization).[2−6] Fast pyrolysis of biomass has been growingly taken as a promising technology, which converts biomass feedstock into bio-oil, char, and gas products under an inert atmosphere in a very short residence time (<2 s).[7−11] The bio-oils, whose yield can reach up to 60%, have shown the potential to be used as fuels in furnaces or engines and feedstocks for value-added chemical production.[12] The bio-oils, however, are always not suitable for direct commercial application. As a result of the high oxygen contents of biomass, the bio-oils produced from direct pyrolysis of biomasses are a complex mixture consisting of hundreds of oxygenated compounds with high water and oxygen contents (35−45%), high corrosive acid contents, and low calorific value.[13,14] These drawbacks have limited the widespread application of the bio-oils.

Various methods have been developed to improve the quality of bio-oils, such as hydrotreating of the produced bio-oils, catalytic reforming of pyrolysis vapors, emulsification, and thermochemical pretreatment of biomass prior to pyrolysis, such as torrefaction.[15−18] Generally, these methods are found to be effective for bio-oil upgrading to some extent. However, there are some issues needed to be resolved for the practical utilization of these methods, such as complicated equipment, severe conditions, catalyst deactivation, and ash-related problems.

Recently, a novel method, named degradative solvent extraction (DSE), has been put forward by the authors to achieve the deoxygenation and upgrading of a diversity of biomass wastes.[19,20] In this method, the biomass feedstocks were treated as a nonpolar solvent at a mild temperature (lower than 350 °C). Raw biomasses are decomposed and separated into three major solid products: an unextractable component (named "Residue") and two extracts (one is a solvent-insoluble component at ambient temperature, termed "Deposit", and another is a solvent-soluble component at ambient temperature, termed "Soluble"). The solid Soluble is then acquired by evaporating the solvent using vacuum distillation. The Soluble exhibits a high carbon content (more than 80%), low oxygen content (less than 15%), and moderate molecular weight of approximately 300. Furthermore, the Solubles contain nearly no moisture and ash. In view of the favorable properties of the Solubles, it seems highly feasible for further pyrolysis of the Solubles to produce high-quality bio-oils for fuels or chemical precursors.

Therefore, in this study, the feasibilities of a two-stage conversion of biomass feedstocks (combining the DSE with

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