

Effect of microwave-assisted organosolv fractionation on the chemical structure and decoupling pyrolysis behaviors of waste biomass

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ABSTRACT

Fast pyrolysis of waste biomass is a cross-coupling pyrolysis of its components (cellulose, lignin, hemicellulose and ash), resulting in the complex composition of bio-oil. Here, microwave-assisted organosolv fractionation (MOF) of waste biomass combined with decoupling pyrolysis is first proposed to overcome this challenge. MOF of waste eucalyptus was conducted in different solvents (organic acid, glycerol or ethylene glycol (EG)). The derived fractions were first characterized by Fourier transform infrared (FTIR) spectroscopy and two-dimensional heteronuclear single-quantum coherence nuclear magnetic resonance (2D HSQC NMR) and then pyrolyzed via thermogravimetric analyzer-mass spectrometry (TG-MS) and a pyro-probe reactor to exam their pyrolysis behaviors. The experimental results demonstrated that waste eucalyptus can be rapidly divided into xylose, high purity organosolv lignins (OL) and cellulose-rich fractions (CF) by MOF under mild conditions. Compared with the fast pyrolysis of raw waste eucalyptus, the decoupling pyrolysis of CF produced higher yields of levoglucosan, whereas the decoupling pyrolysis of OL can result in decreases in the yields of some phenols. MOF can boost the levoglucosan yields from CF by 464–502% compared to that of raw waste eucalyptus. The rank order of the solvents for the improvement in the levoglucosan yield was organic acid < glycerol < EG. This work proposed an efficient, integrated process for selectively producing platform chemicals from waste biomass that can compete with hydrolysis and catalytic conversion processes.

1. Introduction

Due to increasing concerns regarding fossil fuel shortages and climate change, waste biomass has emerged as a potential alternative to fossil fuel for the production of chemicals, liquid fuels, power and heat [1,2]. Fast pyrolysis of waste biomass is one of the most promising methods to convert solid waste into a high yield of a liquid product (as high as 70–75%), namely, bio-oil [3–6]. However, the poor thermal stability, low heating value and acidic pH value of bio-oil hamper its direct utilization as a liquid fuel [7–9]. Alternatively, bio-oil has been considered as an intermediate platform in a pyrolysis-based biorefinery for extracting desired value-added chemicals or producing transport fuels via further upgrading [10]. Biomass mainly consists of three major components: cellulose, hemicellulose, and lignin. Each of the three components exhibits a unique thermal stability and product distribution during a fast pyrolysis process [11,12]. Fast pyrolysis of waste biomass

is a cross-coupling pyrolysis of its components [13]. The interactions between the biomass components (cellulose, hemicellulose, lignin and ash) during fast pyrolysis can alter the production distribution from the fast pyrolysis of each individual component. As a result, bio-oil is an extremely complex mixture of water and organic compounds, including anhydrosugars, furans, phenols, aldehydes, ketones, carboxylic acids, alcohols, esters and oligomeric lignins [2,14–17]. Unfortunately, most organic compounds have very low concentrations, rendering their extraction or upgrading technically difficult and economically unattractive [18]. Therefore, improving the selectivity for the desired molecules from fast pyrolysis is the key to the successful development and commercialization of fast pyrolysis technology for value-added chemicals or transport fuels.

The most commercially valuable components extracted from bio-oil are pyrolytic sugars (e.g., levoglucosan) and phenols [19,20]. Levoglucosan has been identified as a renewable and versatile platform

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molecule for the synthesis of transport fuels and chemicals in a sugar-based biorefinery [21]. It is also a chiral building block for pharmaceuticals, such as antibiotics and antiparasitics [22]. Phenols can be used as raw materials for producing aromatics, resins, adhesives, binders, asphalt and so on. Pretreatment is one of the most common methods to improve the selectivity for targeted molecules from the fast pyrolysis of waste biomass. Pretreatment can alter the chemical composition and structure of waste biomass, improving the selectivity for targeted molecules in a subsequent fast pyrolysis. The major pretreatment methods include water washing, acid leaching, hydrothermal pretreatment, and torrefaction [23–25]. However, these pretreatment methods are effective in improving the quality of bio-oil. Finding a facile and low-cost pretreatment method to maximize the yield of pyrolytic sugars is still a bottleneck in a pyrolysis-based biorefinery.

Different from enzymatic saccharification, the high degree of polymerization and crystallinity of cellulose is beneficial to the formation of pyrolytic sugars [26–28]. Prior to a fast pyrolysis, the chemical structure of cellulose should be maintained as much as possible during a pretreatment. Hence, the crucial factors controlling the yields of pyrolytic sugars are the catalytic effects of alkali and alkaline earth metals (AAEM) and the biomass recalcitrance caused by the interaction of biomass components during fast pyrolysis. Microwave-assisted organosolv fractionation (MOF) could be an ideal pretreatment method for enhancing the yields of pyrolytic sugars because it could simultaneously realize the removal/passivation of AAEM and the effective deconstruction of raw biomass into cellulose, xylose and lignin fractions. After MOF, most AAEM remain in the lignin fractions and solvents [29–31]. Hence, new pyrolysis-based biorefinery schemes based on MOF combined with decoupling pyrolysis are proposed in Fig. 1.

Currently, the organosolv fractionation of waste biomass usually requires a high pressure and long residence time. Moreover, the effect of MOF on decoupling the pyrolysis behaviors of the derived fractions is not well understood. Here, the organosolv fractionation of waste eucalyptus in three types of green solvents (organic acid, glycerol and ethylene glycol) was conducted in a microwave reactor under mild conditions. Their derived fractions were subsequently pyrolyzed by thermogravimetric analysis-mass spectrometry (TG-MS) and pyroprobe reactors to investigate their decoupling pyrolysis behaviors and product distributions.

2. Experimental

2.1. Microwave-assisted organosolv fractionation of waste eucalyptus

The MOF of eucalyptus was carried out in a microwave reactor (MCR-3, Xingshuo, Guangzhou). The microwave reactor was operated at a frequency of 2.45 GHz with a power rating of 0–900 W. After the preliminary experiments, three types of green solvents (organic acid, glycerol and ethylene glycol) and their corresponding optimal pretreatment conditions were selected in this study because they can effectively destroy the three-dimensional structure of biomass under atmospheric pressure. Waste eucalyptus was purchased from a wood processing plant in Guangzhou. In organic acid-based MOF, 10 g of eucalyptus was mixed with a solution comprised of 59.5 g acetic acid, 25.5 g formic acid, 15 g deionized water and 1 wt.% H_2SO_4 . The mixture was heated to 108 °C by microwave irradiation and held there for 1.5 h under reflux. In glycerol- or ethylene glycol (EG)-based MOF, 10 g of eucalyptus was mixed with a solution containing 94.4 g glycerol or EG,

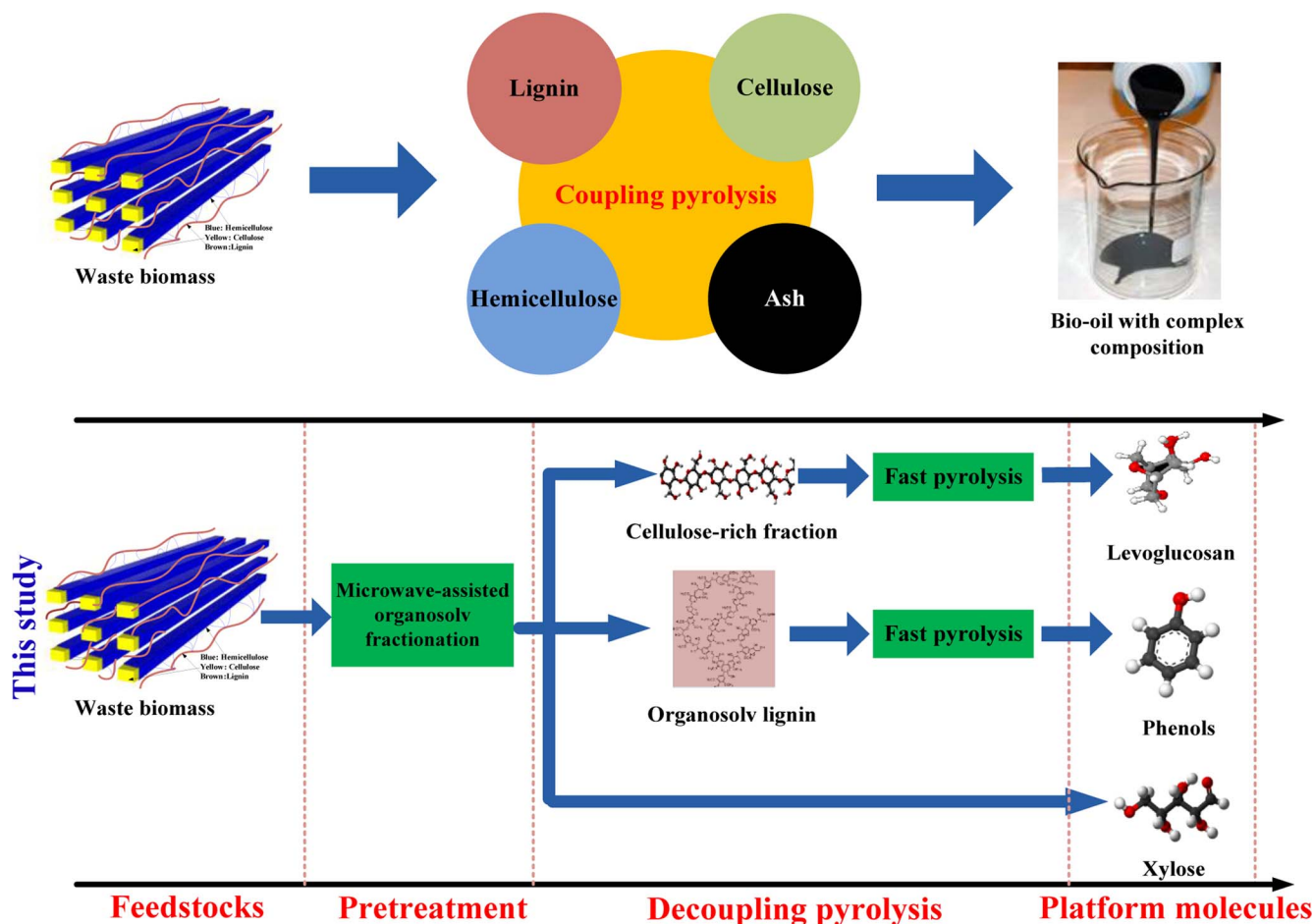


Fig. 1. New pyrolysis-based biorefinery schemes based on microwave-assisted organosolv fractionation of waste biomass combined with decoupling pyrolysis.

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