



# Enhancement of biomass conversion in catalytic fast pyrolysis by microwave-assisted formic acid pretreatment



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## HIGHLIGHTS

- Microwave-assisted formic acid (MA-FA) pretreatment can rapidly destruct biomass structure.
- MA-FA pretreatment selectively removes hemicellulose and lignin components of biomass.
- MA-FA pretreatment increases the valuable aromatic products in CFP of biomass.
- MA-FA pretreatment decreases the undesired coke formation in CFP of biomass.

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## ABSTRACT

This study investigated microwave-assisted formic acid (MW-FA) pretreatment as a possible way to improve aromatic production from catalytic fast pyrolysis (CFP) of lignocellulosic biomass. Results showed that short duration of MW-FA pretreatment (5–10 min) could effectively disrupt the recalcitrant structure of beech wood and selectively remove its hemicellulose and lignin components. This increased the accessibility of cellulose component of biomass to subsequent thermal conversion in CFP. Consequently, the MW-FA pretreated beech wood produced 14.0–28.3% higher yields (26.4–29.8 C%) for valuable aromatic products in CFP than the untreated control (23.2 C%). In addition, the yields of undesired solid residue (char/coke) decreased from 33.1 C% for the untreated control to 28.6–29.8 C% for the MW-FA pretreated samples. These results demonstrate that MW-FA pretreatment can provide an effective way to improve the product distribution from CFP of lignocellulose.

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## 1. Introduction

Lignocellulosic biomass is the most abundant and lowest cost biomass on the earth. It has therefore been considered an attractive feedstock for producing renewable energy, especially liquid hydrocarbon fuels for the transportation sector (Alonso et al., 2010; Huber et al., 2006). The overall goal of converting biomass to transportation fuels or fuel additives that can be used in conventional engines is (a) to remove the substantial oxygen content of biomass feedstock and (b) to create C–C bonds between biomass-derived intermediates to control the molecular weight of the final hydrocarbon products (Alonso et al., 2010). This objective can usually be achieved via two general steps: (i) conversion of solid biomass feedstock to a chemical platform and (ii) subsequent catalytic

upgrading of the chemical platform to the final hydrocarbon products, for example, gasification of biomass to syn-gas platform and subsequent Fischer–Tropsch synthesis of syn-gas to diesel fuels, or fast pyrolysis of biomass to bio-oil followed by zeolite upgrading or hydrodeoxygenation to produce hydrocarbons. In contrast to the conventional ways, the recently developed catalytic fast pyrolysis (CFP) technology can rapidly convert solid biomass feedstocks directly into gasoline range aromatic hydrocarbons (e.g., benzene, toluene, and xylenes) in a single step (Carlson et al., 2010; Park et al., 2010). CFP has therefore gained increasing attention as an effective processing option for producing transportation liquid fuels from biomass.

CFP involves rapidly heating lignocellulose in the presence of zeolite catalysts at temperatures of ~400 to 700 °C. Volatile intermediates (e.g., furans, acids, and phenolics) formed from the initial thermal decomposition of biomass then diffuse into the pores of zeolites, where they can be further converted to aromatic

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hydrocarbons via a series of zeolite-catalyzed reactions (e.g., cracking, deoxygenation, oligomerization, cyclization, and aromatization) (Carlson et al., 2010; Park et al., 2010). The whole conversion process can be completed in a single reactor at short reaction times (e.g., in seconds). CFP thus provides a very effective means that can accomplish both the oxygen removal and C–C coupling to yield high-octane liquid hydrocarbons (e.g., benzene, toluene, and xylenes) in a single step.

While CFP can rapidly convert biomass to aromatics, its carbon efficiency has yet to be improved to make the conversion process more economically competitive (Lazdovica et al., 2016; Li et al., 2013, 2015; Widayatno et al., 2015). It is well-known that natural lignocellulosic biomass consists of three major components, i.e., cellulose (40–50 wt.%), hemicellulose (25–35 wt.%), and lignin (15–20 wt.%) (Alonso et al., 2010; Huber et al., 2006). Many studies have demonstrated that among the three components, cellulose is the most amenable to thermal conversion and produces much higher aromatic yields (e.g., carbon yields of ~30 C%) in CFP than hemicellulose (~20 C%) and lignin (~7 to 10 C%) (Carlson et al., 2010; Li et al., 2012; Wang et al., 2014). Therefore, effective conversion of cellulose, which is the most abundant and easiest thermally-convertible component of biomass, is crucial for maximizing the carbon efficiency of aromatic production in CFP of natural lignocellulose.

However, cellulose strands are interlaced with hemicellulose and surrounded by lignin in the plant cell walls of natural lignocellulose (Alonso et al., 2010; Huber et al., 2006). The complex hemicellulose/lignin seal reduces the susceptibility of cellulose to thermal decomposition and inhibits the release of cellulose-derived volatile products from the plant cells for further catalytic upgrading, thus decreasing the conversion efficiency of cellulose to aromatics during CFP of natural lignocellulose (Jae et al., 2010; Yu et al., 2013). To enhance the conversion efficiency of biomass in CFP, several research groups have tested pretreatment of biomass by different means, e.g., hydrothermal extraction (Stephanidis et al., 2011), alkaline hydrolysis (Misson et al., 2009), and fungal degradation (Yu et al., 2013), to destruct the recalcitrant structure of plant cell walls and thus increase the accessibility of cellulose to thermal conversion in CFP. However, these pretreatment processes usually require high temperatures and pressures (e.g., ~150 to 200 °C and ~6 to 15 atm for hydrothermal extraction (Jae et al., 2010; Stephanidis et al., 2011) or long reaction times (several weeks for fungal pretreatment (Yu et al., 2013)).

To improve the efficiency of biomass pretreatment, this study tested microwave-assisted formic acid (MW-FA) extraction as a pretreatment of lignocellulose for CFP. Previous studies have shown that formic acid can selectively dissolve the hemicellulose and lignin components of biomass, but does not considerably affect the cellulose component (Chen et al., 2011; Zhang et al., 2010; Zhou et al., 2012). Formic acid extraction has therefore been used to destruct the recalcitrant of hemicellulose/lignin seal and thus improve the conversion of cellulose to sugars during enzymatic hydrolysis (Chen et al., 2011; Li et al., 2016; Zhang et al., 2016). Furthermore, when combined with microwave irradiation, the pretreatment time required to depolymerize biomass structure can be significantly reduced, e.g., from several hours for conventional formic acid extraction to <30 min for MW-FA extraction (Zhou et al., 2012). This is partly because microwave irradiation can break some bonds between the different components of biomass (Binod et al., 2012; Chen et al., 2011). More importantly, unlike conventional heating that heats biomass from the outside by thermal conduction, microwave irradiation heats up the biomass from inside out by dielectric heating (Binod et al., 2012; Chen et al., 2011; Wang et al., 2012). Consequently, microwave irradiation would cause abrupt increase in temperature and pressure inside the biomass

and thus result in thorough disruption of biomass structure (Binod et al., 2012; Wang et al., 2012). This greatly facilitates the penetration of formic acid into the internal structure of biomass, and thus improves the efficiency of formic acid extraction (Dong et al., 2014; Zhou et al., 2012). These previous studies indicate that acid extraction and microwave irradiation have significant synergistic effects on disrupting the recalcitrant structure of biomass, and can thus provide an effective way to enhance biomass conversion to sugars by enzymatic hydrolysis (Binod et al., 2012; Chen et al., 2012; Yemis and Mazza, 2012). However, to the best of our knowledge, no study has evaluated MW-FA pretreatment for biomass thermal conversion yet.

To this end, the main objective of this study was to investigate whether short duration of MW-FA pretreatment might provide a viable way to effectively depolymerize the recalcitrant structure of lignocellulose, and thus enhance the conversion of cellulose to valuable aromatic hydrocarbons in CFP. Beech wood was selected as a model compound of natural lignocellulose and treated by MW-FA extraction (microwave irradiation at 800–1200 W for 5–10 min in formic acid solutions). The raw and MW-FA treated samples were characterized with a variety of techniques to reveal how MW-FA pretreatment changes the chemical and structural properties of lignocellulosic biomass. The product distributions from non-CFP and CFP of the raw and MW-FA pretreated samples were compared to evaluate the effects of MW-FA pretreatment on the conversion of beech wood in fast pyrolysis.

## 2. Experimental

### 2.1. Materials

Beech wood powder was acquired from a furniture factory in Beijing. Commercial ZSM-5 zeolite (H type with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of 25, d<sub>50</sub> of 2 μm) was purchased from the Catalyst Plant of Nankai University (Tianjin, China). The morphological and chemical properties of the zeolite had been well characterized in our previous work (Zhou et al., 2014). All biomass and zeolite samples were crushed to pass a 140 mesh (<0.105 mm) sieve, and then stored in a desiccator before use. Formic acid (88%) was purchased from Tianjin Yongda Chemical Reagent Co. Ltd.

### 2.2. Microwave-assisted formic acid pretreatment of beech wood

MW-FA pretreatment of beech wood was conducted in a microwave synthesis system (NJL2-1 (2.45 GHz), Jiequan Co. Ltd., Nanjing, China) under atmospheric pressure. Approximately 7.5 g of beech wood powder and 300 mL of formic acid solution were added into a quartz flask (500 mL), which was then placed at the center of the microwave. The microwave was turned on for 5–10 min under 800 W or 1200 W irradiation. During the treatment, the mixture was stirred with a peddler. The solution temperature increased to the boiling temperature of formic acid solution (~108 °C) in ~4 and 6 min under microwave irradiation at 800 and 1200 W, respectively (see Fig. S1 in Supplementary data (SD)). After cooking, the mixture was filtered with a tared glass filter crucible. The collected solid residues were washed thoroughly with deionized water until the pH reached ~7. The washed solid residues were then dried at 65 °C overnight in a muffle furnace.

### 2.3. Biomass characterizations

The elemental compositions of raw and MA-FA treated beech wood samples were analyzed using an elemental analyzer (CE-440, Exeter Analytical, Inc. North Chelmsford, MA). The cellulose and hemicellulose contents of the samples were determined according to the procedures of Van Soest (Van Soest et al., 1991). The

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