



# Fast pyrolysis of potassium impregnated poplar wood and characterization of its influence on the formation as well as properties of pyrolytic products



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## HIGHLIGHTS

- Potassium influence was characterized during fast pyrolysis of lignocellulosic biomass.
- Potassium lowered thermal decomposition temperature of biomass.
- Char formation as well as its agglomeration were also promoted by potassium.
- Potassium facilitated chemical reactions, such as dehydration and demethoxylation.
- Aromatic compounds were identified from non-condensable gas fraction.

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## ABSTRACT

TGA results indicated that the maximum decomposition temperature of the biomass decreased from 373.9 to 359.0 °C with increasing potassium concentration. For fast pyrolysis, char yield of potassium impregnated biomass doubled regardless of pyrolysis temperature compared to demineralized one. The presence of potassium also affected bio-oil properties. Water content increased from 14.4 to 19.7 wt% and viscosity decreased from 34 to 16.2 cSt, but the pH value of the bio-oil remained stable. Gas chromatography/mass spectroscopy (GC/MS) analysis revealed that potassium promoted thermochemical reactions, thus causing a decrease of levoglucosan and an increase of small molecules and lignin-derived phenols in bio-oil. Additionally, various forms of aromatic hydrocarbons, probably derived from lignins, were detected in non-condensed pyrolytic gas fractions.

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## 1. Introduction

Lignocellulosic biomass is considered a renewable and eco-friendly energy source that contributes to the reduction of carbon dioxide emissions. It can be utilized for electricity, heat, bio-fuels and chemical materials via thermochemical processes such as pyrolysis, gasification and combustion. Among those processes, fast pyrolysis has been the focus of promising methods to obtain liquid fuel, referred to as 'bio-oil' (Mohan et al., 2006). During the fast pyrolysis process, polymeric constituents of biomass are thermally degraded into numerous small molecules and converted mostly to volatile vapors that can be condensed to form bio-oil, char and non-condensable gas. The main product, bio-oil, is a complex mixture of water, solid particles and hundreds of organic

compounds that belong to acids, alcohols, ketones and multifunctional compounds (Kim et al., 2011; Milne et al., 1997). Bio-oil has several potential uses including heat and power for boilers, diesel engines and gas turbines, as well as transportation fuels and chemical resources (Czernik and Bridgwater, 2004). A pyrolysis co-product, bio-char, is also available to use for enhancement of soil quality, as a precursor of activated carbon (Azargohar and Dalai, 2006) and as a pollutant absorbent (Liu et al., 2011).

In general, the yield and physicochemical properties of pyrolytic products are closely related to future industrial applications. A large number of studies have reported that these properties are intensely affected by various factors of not only biomass feedstock but also processing conditions, i.e. heating rate, pyrolysis temperature and residence time (Demirbas, 2004; Kim et al., 2011; Onay, 2007). One important feature of biomass is the presence of inorganic metals such as K, Mg, Ca and Na, etc. The amount of inorganic metals ranges from less than 1% in lignocellulosic biomass to 15%

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in herbaceous biomass, depending on the type of biomass and its growing conditions (Agblevor and Besler, 1996). These inorganic metals, which indigenously exist in biomass, also influence the characteristics of pyrolytic products.

Previous studies have shown that inorganic metals may act as catalysts in the thermal behavior of biomass, char formation and pyrolysis product distribution (Eom et al., 2011, 2012a; Mourant et al., 2011; Nowakowski and Jones, 2008; Wang et al., 2010). These inorganic metals in biomass enhance char formation and the decomposition of biomass at lower temperatures. In addition, degradation of levoglucosan, an anhydrosugar formed from carbohydrates, is dramatically promoted (Eom et al., 2012a). Inorganic metals also have an effect on the physicochemical properties of bio-oil, especially viscosity, water content and chemical components (Mourant et al., 2011). Moreover, bio-oil and bio-char produced from fast pyrolysis of biomass are bound to contain high levels of inorganic metals. Accordingly, estimation of their contents in pyrolytic products could be important for their practical use and storage stability (Agblevor et al., 1994).

Therefore, it is essential to understand not only the catalytic effect of potassium but also its behavior during pyrolysis, in order to ensure optimal production and quality of pyrolytic products. However, there is still a lack of analysis regarding the fundamental reactions between inorganic metals and biomass and most of studies have focused on analytical pyrolysis, not on fast pyrolysis which is a practical process for production of bio-oil. In addition, there is even less information about metal distributions among pyrolytic products depending on temperature. In this study, potassium, which is abundant in biomass cell walls, was chosen as a representative inorganic metal, and potassium impregnated yellow poplar woods were prepared at various concentrations. Research focused on the investigation of the catalytic effects of potassium on pyrolysis behavior and on the characterization of essential pyrolytic products. Furthermore, distributions of inorganic metals in the pyrolytic products were also examined to study the behavior of inorganic metals during pyrolysis.

## 2. Methods

### 2.1. Feedstock

Yellow poplar wood (*Liriodendron tulipifera*: **YP**) was used in this experiment as raw lignocellulosic biomass, which was kindly provided by the Korea Forest Research Institute, Seoul, Republic of Korea. The size of the biomass used was approximately 0.5 mm. The wood sample was dried in an oven at 75 °C overnight prior to pyrolysis, and the final moisture contents of the samples were ~2 wt%.

#### 2.1.1. Sample preparation

Inorganic elements in the cell wall of YP were removed by dilute hydrofluoric acid (HF, extra pure grade purchased from DUKSAN; demineralization). The demineralization process involved stirring a mixture of 3 wt% HF solution and 100 g of YP powder at 400 rpm for 1 h at room temperature. HF-treated YP was thoroughly rinsed with deionized water and then dried at 75 °C overnight (HF-YP).

To impregnate the demineralized biomass with potassium in this study, KCl ( $\geq 99.0\%$ , powder; Sigma-Aldrich) was used. HF-YP were immersed in KCl solution in the ratio of 10 ml/g biomass with increasing concentrations of salt at 0, 0.5, 1.0 and 2.0 wt% based on the biomass samples. Each mixture was placed on the magnetic stirrer at 200 rpm for 48 h at room temperature. After stirring, the sample was then filtered and dried in an oven at 75 °C overnight. The biomass sample treated with 0 wt% of salt

was called demineralized YP (**D-YP**) and the others were called **K-0.5**, **K-1.0** and **K-2.0**.

#### 2.1.2. Fundamental analysis of the samples

Elemental analysis (C, H and N) was performed using a US/CHNS-932 (LECO Corp., USA). Oxygen content was calculated by difference. Holocellulose, lignin and ash contents of the samples were obtained using NREL standard procedures (Sluiter et al., 2005, 2008). The amounts of inorganic elements in raw and potassium impregnated samples were measured by inductively coupled plasma-emission spectroscopy (ICP-ES) analysis, as described in a previous study (Eom et al., 2011). Prior to fast pyrolysis, the thermal decomposition behaviors of YP and potassium impregnated samples were determined by thermogravimetric and differential thermogravimetric analysis (TG and DTG analysis) using the Q-5000 IR instrument (TA Instrument, USA). Samples (~3.5 mg) were heated under N<sub>2</sub> gas flow at a heating rate of 10 °C/min in the range of 40–800 °C.

### 2.2. Fast pyrolysis

Fast pyrolysis of raw and potassium impregnated biomasses was carried out using a fluidized bed-type pyrolyzer, which has been thoroughly described in previous studies (Eom et al., 2012b; Kim et al., 2011). Pyrolysis was operated in duplicate under temperature conditions of 450, 500 and 550 °C. Residence time was adjusted to 1.3 s by inert nitrogen gas flow. Before the operation, the pyrolyzer was purged for 30 min with nitrogen to create an oxygen-free atmosphere. A sample was fed into the pyrolyzer in a rate of 2.5 g/min. Bio-oil and bio-char, which were the target products for analysis in this study, were recovered from each collector and the yield of pyrolytic products was calculated on a wet basis. The yield of char was calculated the sum of char in the reactor and char in the char collector because it usually remained in the reactor for potassium impregnated samples.

In addition, two extracting bottles filled with acetone were connected next to the electrostatic precipitator (see [Supplementary Fig. A](#)). The non condensable gas fraction formed during pyrolysis passed through them in order to extract acetone-soluble pyrolytic products contained in non-condensable gas. These products were called '**non-condensed pyrolytic compounds**' in this study.

### 2.3. Characterization of pyrolytic products

#### 2.3.1. Elemental analysis and higher heating value

Elemental analysis of bio-oil and bio-char was performed according to the same method mentioned above (Section 2.1.2) and their higher heating values (HHV) were estimated according to Sheng and Azevedo's (Sheng and Azevedo, 2005) correlation, as below:

$$\text{HHV (MJ/Kg)} = -1.3675 \times 0.03137 \times \text{C} + 0.7009 \times \text{H} + 0.0318 \times \text{O} \quad (1)$$

#### 2.3.2. Inorganic metals

To determine the behavior of inorganic metals during fast pyrolysis, their distribution in pyrolytic products was observed by quantifying the inorganic content of bio-oil and bio-char according to the same method described above (Section 2.1.2). Since some sand, which was the fluidized bed material in the pyrolyzer, passed over into the char collector with nitrogen gas during fast pyrolysis, bio-char was mixed with sand and was difficult to separate. Accordingly, ICP-ES analysis of sand was also performed as a control for sand-mixed bio-char and then the inorganic content of bio-char was calculated considering the amount of inorganic metals derived from sand by the weight of sand in each mixture.

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