

# Co-processing of pyrolysis vapors with bio-chars for *ex-situ* upgrading



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## ABSTRACT

Co-processing of woody biomass with two bio-chars (bio-chars made from switchgrass and red oak bark) was studied as a way of upgrading the pyrolysis vapors. The clean woodchips were pyrolyzed with and without bio-chars under atmospheric pressure at the target temperature of 500 °C. The co-processing with both bio-chars showed a significant influence on the bio-oil yields, moisture content and pH value of bio-oils. However, the vapor-upgrading process significantly decreased the carbon yield in the bio-oil when using switchgrass bio-char was used for co-processing. The bio-oil yield decreased from 49.31% (non-bio-char) to 44.81% with the switchgrass bio-char and to 48.68% with the bio-char from the red oak bark. The lost mass of bio-oil ended-up in the gaseous phase as reflected in an increased content of carbon dioxide and carbon monoxide. The gaseous-phase composition of hydrogen increased from 0.82% to 3.74%, of carbon dioxide from 21.16% to 32.33%, and of carbon monoxide from 16.49% to 23.19% with the addition of the switchgrass bio-char compared to non-bio-char pyrolysis.

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## 1. Introduction

Renewable energy has received much attention in recent years as a result of increasing fossil fuel costs, limited fuel sources and environmental concerns. Comparing to other clean energy resources, biomass is an exclusively sustainable renewable resource capable of producing petroleum-like products due to its hydrocarbon content [1]. Current biomass conversion technologies for hydrocarbon production involve a combination of biological, biochemical and thermochemical processes [2].

Pyrolysis is one of the most promising thermochemical technologies as it can potentially transform cheap, local, and abundant lignocellulosic biomass into useful solid, liquid and gas products, when processed at temperatures between 400 °C and 650 °C in the absence of oxygen [3]. The pyrolysis technology is further classified into slow pyrolysis and fast pyrolysis, depending on heating rate and residence time. Traditionally pyrolysis with relatively slow heating rates ranging from 0.1 to 1 °C/s and unrestricted residence time from minutes to hours, is considered as slow pyrolysis.

Conversely, a fast pyrolysis occurs when the biomass is heated at a rate of 10–1000 °C/s with short residence time [4]. Fast pyrolysis claims to produce high bio-oil yields and is considered more advantageous than slow pyrolysis [4]. Chemically, during the pyrolysis process, the biomass decomposes into condensable volatile species, gasses and solid residue, also called bio-char. The volatile species are condensed in the form of a dark viscous liquid known as bio-oil or pyrolysis oil [5].

The bio-oil produced by biomass pyrolysis can be used as an alternative energy resource and it may be directly burned for various applications [6]. However, the polymerization reactions of the polyphenols in the bio-oil occur during prolonged storage [7]. These processes gradually change the properties of bio-oil. The polymerization reactions are intensified when the bio-oil is exposed to light, oxygen and temperatures above 80 °C. As a result, the viscosity of bio-oil increases from about 10 to 10,000 cp [7]. Also, bio-oil has lower pH and higher solid and moisture contents than crude oil leading to storage, corrosion and combustion issues [7].

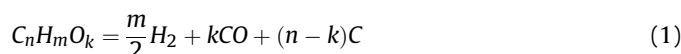
Catalytic upgrading the volatiles prior to their condensation is currently considered as the most promising method to minimize the negative characteristics of bio-oil [8]. During the catalytic upgrading process, the moisture and oxygen contents of bio-oil are minimized, molecular weight is reduced, and some bio-oil mass is

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reduced in favor of char and gaseous species [9]. The ideal catalyst should be highly active, selective to particular products, resistant to deactivation, readily recycled and cheap. Different catalysts have different reaction mechanisms. Currently, researchers are focusing on hydrodeoxygenation (HDO) reactions and cracking using zeolites. However, both of these have drawbacks. HDO requires large quantities of  $H_2$  at relatively high pressure while zeolite cracking produces relatively low bio-oil yields [1]. Chen et al. [10] pyrolyzed pine wood at 350 °C with several additives (NaOH,  $Na_2CO_3$ ,  $Na_2SiO_3$ , NaCl,  $TiO_2$ , HZSM-5,  $H_3PO_4$  and  $Fe_2(SO_4)_3$ ). During the pyrolysis, the main pyrolysis processes were expressed as follows:

Basic pyrolysis gasification reaction [11]:



Further secondary gasification reactions:



According to Chen et al. [10], the alkaline sodium additives (NaOH,  $Na_2CO_3$ , and  $Na_2SiO_3$ ) have the most noticeable effect by decreasing the formation of  $CH_4$  and  $CO_2$  and increasing that of hydrogen. The mineral concentration of red oak bio-char is dominated by potassium, magnesium and calcium. These alkaline minerals have chemical characteristics similar to alkaline sodium [10].

Although bio-char has not been used as a catalyst in pyrolysis process, it has been successfully used in phenol and toluene cracking, biodiesel esterification catalysis and methane reforming [12–15]. Mani et al. (2013) used pine bark bio-char pyrolyzed slowly at 900 °C as a low-cost catalyst to decompose toluene. In this work, the catalytic conversion of toluene was studied in a continuous-flow packed-bed reactor system in the temperature range of 550–900 °C under atmospheric pressure under nitrogen. Streams of toluene and water vapor were added to the carrier gas (nitrogen) by two syringe pumps. The mixtures of nitrogen, toluene and water were then transported through a static mixer to the reactor, enclosed in a furnace, containing a 0.45 m preheating zone, followed by 0.03 m of catalyst (3.8 g catalyst or bio-char). A

fractional conversion of 94% toluene was achieved via the bio-char catalyst [12]. In another study, Dehkhoda et al. [13] mixed 20 g of hardwood bio-char with 200 ml concentrated sulfuric acid (98%, Sigma) to prepare a sulfonated bio-char catalyst. The catalyst was very active in the esterification of free fatty acids and alcohols. To study the possibility of directly converting biogas to syngas, Dominguez et al. [15] used pyrolyzed bio-char pellets from coffee hulls as a potassium-rich catalyst during gasification of a mixture of  $CH_4$  and  $CO_2$  (1:1 ratio). The study indicated that the gasification of  $CH_4$  to  $H_2$  increased with high conversion of  $CH_4$  being achieved. In addition, the addition of bio-char may potentially lead to hydrogen formation during pyrolysis as it contains catalytic inorganic minerals [10,16,17].

Inspired by the demonstrated catalytic activities of bio-chars in other applications, this paper investigates the potential for upgrading pyrolysis vapors from raw wood chips using bio-chars (from red oak bark and switchgrass) and its effects on the yield and composition of various pyrolysis products. The objective of this research was to compare the influence of bio-chars on *ex-situ* pyrolysis vapor upgrading during woodchip pyrolysis. In addition, the effects of bio-char loading were studied by changing the bio-char-to-biomass ratio from 0.1 to 0.4 (by wt.). The term “bio-char” has been used here for the pre-pyrolyzed switchgrass and red oak bark added to the raw wood feedstock for co-processing of pyrolysis vapors while the term “char” describes the residual solid product of the pyrolysis of woodchips.

## 2. Method and measurements

### 2.1. Materials

Fresh samples of mixed hardwood wood chips, mostly flat and 0.475 cm–1.27 cm long, were collected from a nearby sawmill. Samples of switchgrass were collected from a field where it was being grown for research purposes. Red oak bark was collected from a log of red oak harvested from the West Virginia University (WVU) Research Forest. All the samples were oven dried for 24 h at 103 °C before pyrolysis.

### 2.2. Pyrolysis reactor description

Pyrolysis experiments as well as bio-char production experiments were performed in a cylindrical fixed bed reactor with a 22.86 cm diameter and 25.40 cm height (Fig. 1). The reactor was

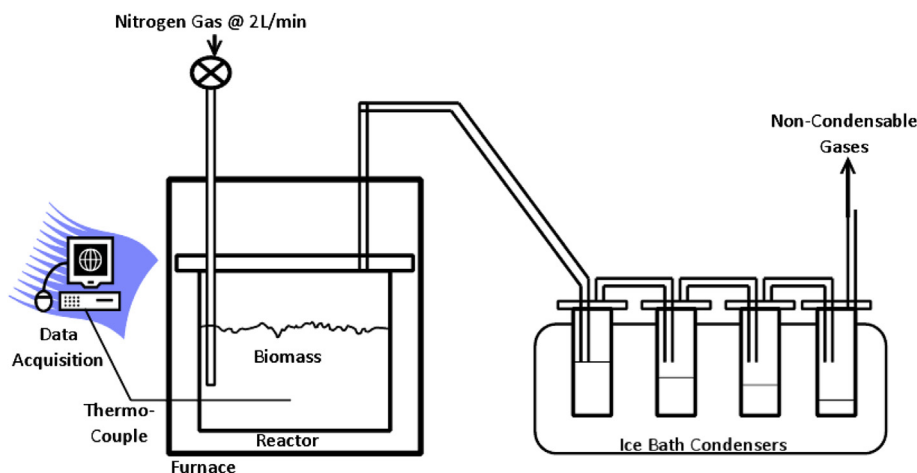


Fig. 1. Experimental set-up used in pyrolysis includes pyrolysis reactor holding biomass, nitrogen flow, location of thermocouple, and set of condensers.

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