



## Fast pyrolysis of beetle-killed trees

Guanqun Luo, Fernando L.P. Resende\*

School of Environmental and Forest Sciences, University of Washington, Box 352100, Seattle, WA 98195, United States



### ARTICLE INFO

#### Article history:

Received 6 April 2014

Accepted 16 August 2014

Available online 27 August 2014

#### Keywords:

Beetle-killed lodgepole pine

Decay-stage

Fast pyrolysis

Catalytic fast pyrolysis

HZSM-5

### ABSTRACT

In this article, we propose beetle-killed lodgepole pine (BKLP) as a feedstock for fast pyrolysis due to its low moisture and high energy content. To the best of our knowledge, no previous studies on fast pyrolysis of beetle-killed trees have been reported. Samples of healthy lodgepole pine and three decay-stage BKLPs were used as feedstock to investigate the effects of the decay stage on the performance of both non-catalytic and catalytic fast pyrolysis using a Py-GC/MS. Compared to the healthy tree, BKLPs were found to have slightly more extractives and less lignin. The decay stage, however, did not affect the product yield and selectivity for both non-catalytic and catalytic fast pyrolysis. A variety of oxygenated compounds were produced in non-catalytic fast pyrolysis, but most of those were converted into aromatic hydrocarbons in the presence of HZSM-5. For non-catalytic fast pyrolysis, the yield of char decreased from 22 wt.% to 11 wt.% as the pyrolysis temperature increased from 450 °C to 650 °C. The average HHV of volatile compounds was found to be around 26 MJ/kg. For the catalytic fast pyrolysis, the yield of hydrocarbons was as high as 40 wt.%, and the yield of char was as low as 5 wt.%. The average HHV of volatiles was found to be about 41 MJ/kg, which is close to the HHV of commercial gasoline and diesel (~46 MJ/kg). A high yield of toluene (11 wt.%) and xylenes (9 wt.%) was also observed in the catalytic fast pyrolysis process. Our work suggests that beetle-killed trees are a good feedstock for fast pyrolysis, because the bio-oil derived from the trees that have been dead for four years showed the same quality as that from the healthy trees.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Recently, climate change combined with unhealthy forest conditions have led to a large bark beetle outbreak in the western United States. Across the landscape from the West Coast through the Rocky Mountains, more than 41.7 million acres of conifer forests have been infested by bark beetles since 1996 and this number is expected to increase in the near future (5–10 years) [1]. Although bark beetles are natural components of western forest ecosystems; recent bark beetle epidemic with high levels of tree mortality has negatively impacted public benefits from forests [2]. Bark beetle-caused tree mortality may also change forest fuel distributions and therefore wildfire characteristics [3]. As bark beetle-killed trees decay and fall to the ground, surface fuel loads start to accumulate. Heavy surface fuel loads not only act as ladders to carry a surface fire into tree crowns but also increase the heat intensity and duration of the fire on the forest floor [2]. Thus, the potential for high-severity wildfire increases without changing the probability of fire

occurrence. What is worse, wildfires increase the susceptibility of trees to the bark beetle attack [2].

In order to minimize the wildfire hazard, beetle-killed trees should be properly disposed of. Traditionally, the forest industry uses pile or broadcast burning to dispose of forest residues, which unfortunately causes air pollution and wastes energy and nutrients [4]. Moreover, some undesirable properties of beetle-killed trees limit applications for solid wood and wood panel manufacturing. For example, mountain pine beetles carry a diversity of fungi on the surface of their bodies when attacking. The introduction and propagation of these fungi, mainly staining fungi, cause a bluish discoloration in the timber; consequently reducing the commercial value of infested trees for wood product manufacturing [5]. Additionally, staining fungi lower the wood moisture content, particularly for sapwood. Reid [6] found that the sapwood moisture content of beetle-killed trees decreased from 85 to 165% of oven dry weight to around 16% after one-year of attack. Once the moisture content falls below the fiber saturation point (30%, dry basis), checking and splitting are observed in the wood, making it improper for wood product manufacturing [7,8]. Low moisture content and high energy content, however, are excellent feedstock characteristics for bioenergy and biofuel production, because the costs of biomass drying could be reduced or even eliminated.

\* Corresponding author. Tel.: +1 206 221 1580.

E-mail address: [fresende@uw.edu](mailto:fresende@uw.edu) (F.L.P. Resende).

We propose fast pyrolysis, the rapid thermal decomposition of organic matter in the absence of oxygen, as a potential way to convert beetle-killed trees into bio-oil that could be further upgraded into commodity chemicals and fuels. Fast pyrolysis has been extensively studied for different feedstocks such as woody biomass (softwood and hardwood), agricultural residues (e.g. rice husk and wheat straw) and algae [9–12]. The products of fast pyrolysis include primarily a liquid that is commonly called bio-oil, permanent gases (i.e. CO, H<sub>2</sub>, CO<sub>2</sub>, and light hydrocarbons), and some solid char. Around 70 wt.% (dry basis) yield of bio-oil has been reported for fast pyrolysis of woody biomass [13]. Bio-oil is a mixture of hundreds of oxygenated compounds. Its high oxygen content results in some undesirable properties, such as high viscosity, high acidity, instability, and relatively low energy density; therefore, further upgrading of the bio-oil through a heterogeneous catalytic process is required before it can be used for the production of commodity chemicals and transportation fuels. Upgrading of bio-oil can be performed either in-situ or ex-situ. The in-situ upgrading process is called catalytic fast pyrolysis (CFP) and has drawn significant attention recently. During the CFP process, upgrading takes place immediately after the formation of pyrolysis vapors in a single reactor. Due to its short residence time, less char is produced compared to the ex-situ process, in which pyrolysis vapors are upgraded in a secondary reactor [14,15]. A variety of zeolites have been tested using CFP, including HY, SN-27, MSM-15, and HZSM-5 [16,17]. HZSM-5 is widely accepted to be the most effective and selective catalyst to produce gasoline-range hydrocarbons, which is mainly attributed to its acidity and network structure [18].

Lodgepole pine is one of the most prevalent tree species in the Pacific Northwest of the United States. It is also the main target of the mountain pine beetle (MPB, *Dendroctonus ponderosae*), out of the other varieties of pine species that coexist in this region [19]. To the best of our knowledge, there are no previous studies on fast pyrolysis of beetle-killed trees. The main goal of this study was to investigate the effects of different decay stages of BKLP on the performance (i.e. product yield and selectivity) of both non-catalytic and catalytic fast pyrolysis. The effect of non-catalytic fast pyrolysis temperature has also been studied.

## 2. Materials and methods

### 2.1. Materials

Lodgepole pine (*Pinus contorta*) samples were purchased from Forest Concepts, LLC, for use in this study. The samples were wood Crumbles® (2 mm × 2 mm) from: (i) green uninfected trees (LP); (ii) partially green but terminally infected trees (BKLP1); (iii) standing dead trees with red needles and intact bark (BKLP2); and (iv) standing dead trees without needles, and 2–4 years after death (BKLP3) (Fig. 1). All trees were collected from the same forest field in Steamboat Springs, Colorado, and were in the age range of 70–80 years old. Thus, we assumed that all the differences found between the four types of feedstock used in this study could be attributed to their unique stages of decay. The particle size of these wood Crumbles® was reduced to 40 mesh (420 µm) using a Thomas Wiley mill for the non-catalytic pyrolysis, in order to generate uniform decayed lodgepole pine samples which fit the small CDS pyroprobe tube. For the catalytic pyrolysis, the wood particle size was further reduced to 140 mesh (105 µm), which is the same particle size as the catalyst, generating a uniformly sized mixture of wood samples and catalyst. The catalyst was CBV2314 ZSM-5 (Zeolyst International, Si/Al = 23, ≤140 mesh) in the form of the ammonium salt. Prior to use, the catalyst was converted to the acid form, HZSM-5, by calcination at 600 °C for 5 h. Oxygenated and hydrocarbon compounds

used as standards were purchased from Sigma Aldrich and Fisher Scientific and used as received.

### 2.2. Feedstock characterization

Chemical constituents (i.e. extractives, carbohydrates, and lignin), moisture content (dry basis) and ash content of the four types of feedstocks were measured, according to “Standard Biomass Analytical Procedures” developed by the National Renewable Energy Laboratory [20]. To measure the extractives, ethanol was used as a solvent. High-performance liquid chromatography (HPLC, Dionex ICS-3000) was used for monomer sugar analysis. CHN elemental analysis of the feedstock was performed using an elemental analyzer (Series II 2400, PerkinElmer), and the oxygen content was calculated by difference.

### 2.3. Fast pyrolysis

Fast pyrolysis experiments were carried out using a commercial micro-pyrolyzer (Pyroprobe model 5200, CDS Analytical Inc.). The pyroprobe contained a computer-controlled heating element (a platinum coil), which held an open-ended quartz tube (25 mm × 1.9 mm I.D.). Powdered samples were loaded in the middle of the tube with loose quartz wool packed at both ends. According to the CDS manufacturer's manual, the actual temperature inside the quartz tube is estimated to be about 100 °C lower than the temperature of the heating element. The pyrolysis temperature reported in this study is the set-up heating element temperature.

Feedstock amounts used in the fast pyrolysis experiments were weighed with an autobalance (AD 6, PerkinElmer) with an accuracy of 0.1 µg. Samples of LP and three decay-stage BKLPs (0.5 mg, 420 µm) were pyrolyzed at a temperature of 550 °C and a heating rate of 1000 °C/s. Fast pyrolysis of representative feedstock, BKLP3 (the highest stage of degradation), was also conducted at temperatures of 450 °C and 650 °C to evaluate the effect of temperature. For each experiment, the probe temperature was held for 45 s to minimize the temperature gradient inside the quartz tube. For the CFP process, only LP and BKLP3 were used as feedstocks. Prior to pyrolysis, LP and BKLP3 (105 µm) were evenly mixed with HZSM-5 (105 µm) at a catalyst-to-biomass ratio of 20. In order to avoid saturating the analytical detector (see Section 2.4), 0.1 mg of the LP and BKLP3 samples were used in CFP. CFP was operated at 550 °C with a holding time of 45 s and a heating rate of 1000 °C/s. The pyroprobe interface temperature was set to 300 °C. Triplicates were employed at each condition; error bars shown in later figures express the standard deviations. The solid residues from non-catalytic fast pyrolysis and CFP are defined as char and coke, respectively. The yields of char or coke were calculated by weighing the mass of samples before and after pyrolysis, taking the moisture content of the quartz wool and HZSM-5 catalyst into account.

### 2.4. GC/MS analysis

Pyrolysis vapors were carried with high-purity helium via a transfer line (300 °C, 1 m in length) to a gas chromatograph (GC, 2010 Plus, Shimadzu) that was equipped with a mass spectrometer (MS, QP2010 Ultra, Shimadzu). The chromatographic separation of pyrolysis products was achieved on a SHRXI-5MS column (30 m × 0.25 mm I.D. × 0.25 µm film thickness, Shimadzu). An injection temperature of 300 °C and a split ratio of 125:1 were used. The GC oven was programmed to hold at 35 °C for 2 min, followed by heating to 200 °C at 5 °C/s, holding at this temperature for 4 min. The GC oven was then ramped at 5 °C/s to a final temperature of 300 °C that was kept for 5 min. The mass spectra were recorded in the electron ionization mode over a mass per charge (*m/z*) range

Download English Version:

<https://daneshyari.com/en/article/1197294>

Download Persian Version:

<https://daneshyari.com/article/1197294>

[Daneshyari.com](https://daneshyari.com)