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Pyrolysis of eastern redcedar: Distribution and characteristics of fast and slow pyrolysis products

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HIGHLIGHTS

- Wood zone (heartwood and sapwood) effects bio-oil composition.
- Cedar wood oil yield (α/β-cedrene) can be maximized through slow pyrolysis.
- Heartwood produced significantly more α/β-cedrene than sapwood.
- Slow pyrolysis yielded small molecules derived from primary pyrolysis products.

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ABSTRACT

Eastern redcedar is a problematic plant in Oklahoma due to its extinguished environmental flexibility and rapid expansion. Pyrolysis thermally converting solid biomass polymers into liquid fuel intermediate, solid char and gaseous products is one promising approach to use redcedar for the production of sustainable fuels. The objective of this study was to investigate effects of eastern redcedar wood zones (heartwood and sapwood), pyrolysis temperature (450 and 500 °C) and pyrolysis types (slow at lab-scale and fast at micro-scale) on distribution and composition of pyrolysis products. In fast pyrolysis conditions, the products were dominated by anhydrous sugars, phenols and guaiacols. The total yield of lignin-derived compounds from heartwood was higher than sapwood at 500 °C but not significantly different at 450 °C. In slow pyrolysis conditions, acetic acid and furfural were the two most abundant species in bio-oil. Slow pyrolysis products consisted of less branched compounds of phenols and guaiacols as compared to fast pyrolysis products. Cedar oil components (alpha/beta-cedrene) were only produced at slow pyrolysis conditions and its maximum yield (21.04 ± 1.08 area%) of was obtained from heartwood at 500 °C. Heartwood produced significantly more cedrenes than sapwood.

1. Introduction

Depletion of fossil fuels and increase in greenhouse gases emissions justifies the need to develop innovative energy technologies that are both alternative and sustainable. Biomass is considered as one of the potential energy resources that can maintain the energy and environmental sustainability mainly due to its abundance and CO_2 neutrality [1]. Biomass can be converted into fuels and energy through a number of different processes, among which thermochemical processes, namely gasification, pyrolysis and hydrothermal liquefaction, are promising technologies for production of renewable energies, fuels and chemicals [2,3].

Pyrolysis converts biomass into multiple fuel products like solids (biochar), liquid fractions (bio-oil) and gaseous products (syngas) by thermally decomposing biomass under a medium temperature (~600 °C) in an inert atmosphere [4]. The operation conditions (e.g. temperature, heating rate, and residence time) can be adjusted to maximize the production of each product. Production of bio-oil has received great interest since the liquid is easier to store and transport than solid biomass feedstock to use as fuel. Bio-oil can be used in several applications, such as: direct boiler combustion for heat and power; transportation fuels that substitute traditional fossil fuels; or platforms for chemical production because it is composed of numerous organic species [5]. The properties of bio-oil are distinctly different from fossil based resources. Its undesirable qualities such as low heating value, high moisture content, acidity, viscosity and chemical instability toward temperature cause significant challenges to the application of bio-oil as a

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fuel [6,7]. To obtain bio-oil with high yield and quality, considerable research [8–14] has been focused on designing and optimizing the pyrolysis conditions, such as increasing heating rates, using fine particle size feedstocks and decreasing residence time for heating and quenching. In addition, various reactor configurations and liquid collection systems have been developed and researched to improve the quality of bio-oil [8,15–17].

During pyrolysis, cellulose, hemicellulose and lignin follow different decomposition pathways, leading to different products. The cellulose and hemicellulose primarily degrade into anhydrosugars and then convert into furan compounds through dehydration and rearrangement reactions [18]. Lignin primarily depolymerizes into phenols and methoxyphenols, such as guaiacols and syringols. Methoxyphenols can be further converted into simple phenols through demethoxylation and cracking [19]. Pyrolysis performance and end-product quality were dependent on the biomass properties that can vary because of crop variety, production practices, and climate. Even in the same species of woody biomass, the chemical compositions of sapwood (SW) and heartwood (HW) zones are significantly different. HW is the outer part of wood with a darker color and older cambial age than SW. A radial decrease in lignin content with cambial age is usually observed in individual tree species, e.g. the lignin contents in teak HW and SW are 37.3 and 35.4 wt.%, respectively [20]. In addition, the lignin compositions, such as *H*-lignin (p-hydroxyphenyl subunits), *G*-lignin (guaiacyl subunits) and *S*-lignin (syringyl subunits) vary in different wood zones, e.g. the content of S-lignin is higher in HW than SW of teakwood [20]. The extractive content of HW is usually higher than that of SW [21], e.g. the total extractives in the HW of Acacia melanoxylon was about twice of that in the SW [22]. The extractives decrease pulp yield and increase the consumption of pulping chemicals in paper industry [23]. Thus, understanding the effect of chemical compositional diversity of wood zones on pyrolysis products is important for optimizing conditions that enhance effective utilization of both sapwood and heartwood fractions for bio-oil production through pyrolysis.

Eastern redcedar is native to the Eastern United States [24,25]. More than seven million acres of Oklahoma is occupied by eastern redcedar [26]. The continued spread of eastern redcedar has created severe negative impacts on the local ecosystems, such as loss of native plants and birds, reduction of forage production and livestock handling, impacts on soil hydraulic properties, and increased severity of wildfires [27–29].

Current utilization of eastern redcedar has mainly focused on cedar wood oil extraction, which is used in the production of fragrances, essential oils, insecticides and antifungals [26,30]. Several techniques have been used to recover cedar wood oil, including steam distillation, solvent extraction and super critical fluid extraction. Oil yield depends primarily on the techniques used and the properties of the wood. On average, oil yield from eastern redcedar ranges from 1 to 4.6 wt.% [31]. These low oil recovering rates are a concern. Therefore, the development of alternative conversion techniques and processes with high efficiency, such as biomass pyrolysis, is critically needed. Multiple valuable products, such as fuels, chemicals, syngas and char, can be produced simultaneously from biomass pyrolysis process. The pyrolysis-derived bio-oil could either be upgraded to transportation fuel in biorefineries or used for chemical extraction. Biochar, a porous material, can be used as a source of carbon sequestration, soil amendment and contaminants adsorbents for water and soil [32]. Syngas could be burned for heat and power, or converted into chemicals through fermentation or Fischer–Tropsch synthesis [2]. Moreover, pyrolysis process is less energy intense as compared to steam distillation [26].

To date, there is limited information on pyrolysis of eastern redcedar for fuels production. The purpose of this study was to evaluate performance and properties of end-products obtained from pyrolysis of softwood and heartwood of eastern redcedar. Both analytical and lab-scale pyrolysis reactors were be used to perform fast and slow pyrolysis study, respectively.

2. Materials and methods

2.1. Biomass characterization

Eastern redcedar SW and HW crumbles were obtained from Forest Concepts, LLC (Auburn, WA, USA). The SW and HW were ground separately using a Wiley Mill (Thomas Model 4 Wiley® Mill) in Biosystems and Agricultural Engineering Laboratory at Oklahoma State University, using a 0.5 mm screen size. The ground samples were stored in zip-lock bags at room temperature.

Compositional analysis of eastern redcedar SW and HW including extractives, carbohydrates and lignin content was conducted following National Renewable Energy Laboratory (NREL) protocols [33,34]. Detailed procedures were previously reported [35,36]. Moisture, volatile matter and ash contents of SW and HW were determined according to ASAE standard S358.2, ASTM D3175 and ASTM E1755-01, respectively. The fixed carbon content was calculated by dry basis weight percentage difference. The ultimate analysis was performed using an elemental analyzer (Exeter Analytical CE-440, Chelmsford, MA, USA) at Midwest Microlab following ASTM D3176. The higher heating value (HHV) was measured with a Parr 6200 Bomb Calorimeter (model A1290DDEB, Parr Instrument Co., Moline, Ill).

2.2. Experimental design

Pyrolysis runs were carried out in a factorial design with two treatments, redcedar wood zones and pyrolysis temperatures for both fast and slow pyrolysis. The two wood zones were sapwood and heartwood. Pyrolysis temperatures were 450 and 500 °C. Fast pyrolysis runs were replicated three times and slow pyrolysis runs were replicated twice.

2.3. Fast pyrolysis: Py–GC/MS

A commercial pyroprobe (model 5200, CDS Analytics Inc.) attached to a gas chromatography/mass spectrometry (Agilent 7890GC/5975MS) system was used for fast pyrolysis of eastern redcedar wood. The probe had a computer-controlled heating element and held a sample in the middle of a quartz tube (25 mm length, 1.9 mm ID). The actual temperature difference between the filament and sample varies 50–125 °C depending on the filament temperature [37,38]. The temperature difference between the filament and sample was not measured during the study and was assumed to be 100 °C based on the literature [37]. Prior to pyrolysis, the ground eastern redcedar sample was screen sieved, and material with a particle size less than 106 μm was oven dried for 24 h. About 1 mg of the dried sample was loaded into the pyroprobe. The sample was then pyrolyzed to a filament temperature of 600 °C with a heating rate of 1000 °C/s and maintained for 3 min. The volatiles evolved from biomass pyrolysis were conveyed from the probe into an adsorbent (Tenax-TA™) trap using ultrapure helium (99.99 vol.%), and the trap temperature was maintained at 40 °C. The condensable bio-oil components were captured by the trap, and the permanent gases were purged from the trap using helium. The bio-oil components were evaporated by heating the trap to a temperature of 300 °C, and the gases were pumped into GC/MS through a heated transfer line for volatile component analysis.

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