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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.

ARTICLE INFO

Article history:

Received 20 August 2015
Received in revised form 24 October 2015
Accepted 25 October 2015
Available online xxxxx

Keywords:

Eastern redcedar
Pyrolysis
Cedar wood oil
Bio-oil

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 (α/β -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.

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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 CO₂ 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 evalu-

ate performance and properties of end-products obtained from pyrolysis of softwood and heartwood of eastern redcedar. Both analytical and lab-scale pyrolysis reactors were 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.

The GC contained a DB-5 capillary column (30 mL × 0.32 mm ID, 0.25 μm film thickness). The GC oven temperature was set to maintain 40 °C for 4 min, and then increased at a rate of 5 °C/min to 280 °C and held for 20 min. The injector temperature was held at 250 °C. The split ratio was set at 30:1. Helium (purity: 99.99 vol.%) was used as the carrier gas at a flow rate of 1 mL/min. Pyrolysis products were identified by comparing the mass spectrum with National Institute of Standards and Technology (NIST) mass spectral library.

2.4. Slow pyrolysis: Parr reactor

A commercial reactor (Series 4570 HP/HT, Parr Instrument Company, Moline, Illinois, USA) was used for slow pyrolysis study. The reactor vessel is made of 316 stainless steel with a volume of 0.5 L. The vessel was heated by a cylindrical ceramic fiber electrical heater using a controller (Series 4840, Parr Instrument Company, Moline, IL, USA). The temperature inside the vessel was monitored by a J-type thermocouple. A pressure transducer (0–5000 psi) was used to measure the pressure build-up inside the reactor.

Approximately 50 g of crumbled Eastern redcedar wood sample was loaded into the reactor vessel for each test run. Prior to pyrolysis, the reactor vessel was purged with ultra-high pure nitrogen gas (99.99 vol.%) at 10 psi for 20 min to create an inert atmosphere. The reactor was then heated to the set temperature (450 or 500 °C) at a constant heating rate of 6 °C/min. The pressure inside the reactor vessel was allowed to increase to 100 psi as the temperature and gas production increased. Pressure was maintained at 100 psi by opening the outlet gas valve manually by a quarter turn to release the producing gases. The reaction was maintained at the set temperature for 30 min. Then, the heater was turned off to allow the reactor to cool to room temperature.

The liquid product was collected from flasks under the condensers and weighed. The char collected in the reactor vessel was weighed. The yield of produced gases was measured by difference of weight percent. Gas sample was collected using a 0.5 L Tedlar sampling bag, and the composition was measured using a gas chromatograph (model CP3800, Varian Inc., CA) with a packed column (HayeSep DB-100/120, Alltech Associates, Inc., Deerfield, Ill.) and a thermal conductivity detector (TCD).

2.5. Pyrolysis product characterization

The bio-oil samples were kept in a refrigerator at 4 °C prior to analysis. The physical properties analyses, including moisture content, specific gravity, pH value and higher heating value were conducted according to ASTM standard (D 7544-12). The moisture content of bio-oil was determined by KF Titrino 701 (Metrohm USA Inc.) at Kansas State University following the ASTM D 1744 protocol using hydranal as titrant [11]. The specific gravity of the bio-oil was measured using a pycnometer (2 mL, ACE GLASS INC. Vineland, NJ) according to ASTM D891-09. The pH value of bio-oil sample was determined using a pH meter (Mettler Toledo) following ASTM D7544-12. The higher heating value (HHV) of bio-oil and bio-char was measured using a bomb calorimeter (model 6200, Parr Instrument Co., Moline, Ill.). Ultimate analysis of bio-oil and bio-char was performed using a Vario MICRO Elemental Analyzer (Elementar Analysemesysteme GmbH, Germany) at Kansas State University. All measurements were performed at room temperature, and each measurement was repeated twice, the average of which was recorded as the final value.

The main chemical components of bio-oil were analyzed by gas chromatography/mass spectrometry (GC/MS, Agilent 7890/5975). The analysis procedure was the same as used for the pyroprobe pyrolysis treatments. Bio-oil samples were prepared as 0.02 g/mL solutions in methanol, and were filtered through a 0.45 μm

micro-filter to remove the particles prior to injection into 5975 series mass selective detector. The *m/z* values corresponding to the fragment ions of the compounds were recorded for each compound. Bio-oil samples were fully scanned over an *m/z* range of 30–500.

2.6. Carbon balance and energy yield calculation

Carbon balance was performed to investigate the carbon distribution in bio-oil, biochar and syngas using Eq. (1).

$$\text{Total carbon} = (C_{\text{bio-oil}} \times Y_{\text{bio-oil}} + C_{\text{char}} \times Y_{\text{char}} + C_{\text{syngas}} \times Y_{\text{syngas}}) \times 100 \quad (1)$$

where

$C_{\text{bio-oil}}$ = carbon content in bio-oil (wt.%),
 C_{char} = carbon content in bio-char (wt.%),
 C_{syngas} = carbon content in syngas (wt.%),
 $Y_{\text{bio-oil}}$ = yield of bio-oil (wt.%),
 Y_{char} = yield of bio-char (wt.%), and
 Y_{syngas} = yield of syngas (wt.%).

Energy yield (%) was defined as the portion of energy that contained in the biomass feed recovered in the pyrolysis products (Eq. (2)).

$$\text{Energy yield (\%)} = \frac{\text{Product yield (wt.\%)} \times \text{HHV}_{\text{product}}}{\text{HHV}_{\text{biomass}}} \times 100 \quad (2)$$

where

$\text{HHV}_{\text{product}}$ = higher heating value of the pyrolysis products (MJ/kg), and
 $\text{HHV}_{\text{biomass}}$ = higher heating value of the biomass (MJ/kg).

3. Results and discussion

3.1. Characterization of eastern redcedar SW and HW

Physical properties and chemical constituents of eastern redcedar are listed in Table 1 [35]. Glucan, a polysaccharide of D-glucose, generally represents cellulose content. SW and HW had similar cellulose contents. Hemicellulose content was characterized by pentose (xylan and arabinan) and hexose (galactan and mannan). The total hemicellulose of SW was 19.2 ± 0.7 wt.%. Total hemicellulose content of HW was similar to that of SW. The lignin content of HW was not significantly different from that of SW. Extractives of HW were higher than that of SW. This discrepancy could be due to the transport of extractives from transition zone

Table 1

Chemical composition, proximate and ultimate analysis of SW and HW zones of eastern redcedar^a [35].

	Sapwood	Heartwood
<i>Chemical compositions (wt.%)</i>		
Glucan	34.7 ± 0.5	34.6 ± 0.0
Xylan (C ₅)	8.9 ± 0.2	8.5 ± 0.0
Arabinan (C ₅)	1.0 ± 0.0	0.7 ± 0.0
Galactan	2.6 ± 0.0	3.0 ± 0.1
Mannan	6.7 ± 0.4	7.4 ± 0.0
Lignin ^b	33.7 ± 0.4	34.3 ± 0.1
Extractives	4.0 ± 0.0	4.9 ± 0.2
<i>Proximate analysis (w.b. wt.%)</i>		
Moisture content	8.64 ± 0.25	9.42 ± 0.04
Volatile matter	72.13 ± 0.30	71.83 ± 0.30
Ash content	0.12 ± 0.06	1.14 ± 0.25
Fixed carbon	19.10 ± 0.24	18.28 ± 0.60

^a Values listed above are means ± standard error of two subsamples.

^b Acid soluble lignin and acid insoluble lignin are included in lignin content.

(between the SW and HW) to the HW zone [39]. The ash content of HW was significantly higher than that of SW. SW contained 1.5 wt. % higher fixed carbon content than HW.

3.2. Fast pyrolysis

The compositions of bio-oil obtained from pyrolysis of eastern redcedar can be categorized into eight groups: ketone, acid, anhydrous sugar, pyran, furan, phenol, guaiacol and nitrogen containing compounds according to functional groups. The distribution (area %) of the eight groups the two pyrolysis temperatures are shown in Fig. 1 (450 °C) and 2 (500 °C). The major compounds obtained from the two wood zones and two pyrolysis temperatures are provided in Table 2. All of the major bio-oil compounds found in bio-oil obtained from SW also existed in bio-oils obtained from HW but their quantities differed.

3.2.1. Fast pyrolysis: Effect of wood zone on bio-oil composition

Pyrolysis products obtained at 450 °C showed that anhydrous sugar (11.90% for SW, and 15.63% for HW) and guaiacol (40.80% for SW, and 38.20% for HW), primary products derived from depolymerization of cellulose and lignin structures, were the two most abundant species detected. This was consistent with the results of chemical composition analysis that glucan and lignin were the two dominant constituents in eastern redcedar wood. Levoglucosan and D-Allose were the two dominant sugar compounds. These two sugar compounds had relatively large standard deviations, which might be due to the variation in biomass constituents, especially cellulose between the biomass samples used. As reported by others [37], this variation also explains significant changes in the anhydrous sugar yield in the repeated experiments. Anhydrous sugar yield obtained from SW was not significantly different from that obtained from HW at 450 °C. Effect of wood zone on the total guaiacols yield was not significant but the wood zone significantly affected several guaiacol compounds. For example, 2-methoxy-4-propylphenol derived from HW (5.92 ± 1.88 area%) was significantly higher than that derived from SW, and 2-methoxy-4-(1-propenyl)-phenol-(Z) derived from SW was significantly higher than that derived from HW. There was no difference in total yield of furans from SW and HW. This can be attributed to the similar cellulose contents of both wood fractions (Table 1). Furans are mainly derived from levoglucosan, the primary pyrolysis product from cellulose, via dehydration, decarboxylation and decarbonylation [40]. Among furans, 3, 5-dihydroxy-2-methyl-4H-pyran-4-one was the only pentose derived pyran that was identified. Acetic acid was the only acid compound detected in the pyrolysis product of SW and HW. Acid compounds were thought to be mainly derived from the elimination of the active O-acetyl groups linked to the xylan chain [41]. Ketones derived

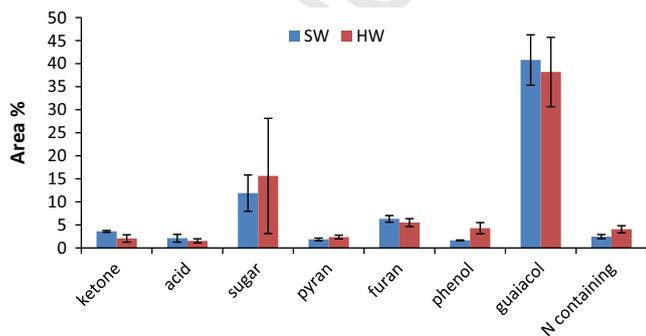


Fig. 1. Fast pyrolysis products of eastern redcedar wood at 450 °C (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

from SW and HW were significantly different. The total yield of phenols obtained from pyrolysis of HW was 4.30 ± 1.22 area%, which was significantly higher than that of SW. Phenols and guaiacols, lignin originated groups, were 42.46 ± 5.52 and 42.50 ± 8.64 area% in SW and HW pyrolysis products, respectively. Syringols were not detected in the pyrolysis product indicating that eastern redcedar wood lignin was composed of Guaiacol-Hydroxyphenyl (G-H) structure. Thangalazhy-Gopakumar et al. [37] also observed the absence of syringols in the pyrolysis products of pine wood. The absence of syringols was attributed to the lack of syringyl monomer in the pine lignin structures. Lignin structure in soft woods, such as pine wood and eastern redcedar were found to predominantly (over 95%) composed of G-units [42]. 1,4-dimethyl-3-pyrazolidinone (a heterocyclic oxygenated compound) was the only nitrogen containing compound.

3.2.2. Fast pyrolysis: Effect of temperature on bio-oil composition

Fig. 2 shows the product distribution of eastern redcedar at 500 °C. The total yield of lignin derived compounds from SW and HW increased to 47.38 ± 0.74 and 54.28 ± 2.61 area%, respectively. Phenols derived from both SW and HW increased significantly as the pyrolysis temperature increased from 450 to 500 °C. Phenols were mainly the result of decomposition of lignin oligomers and guaiacols. Both processes are thermodynamically favorable, therefore leads to an increase in phenols. Guaiacols from both SW and HW were not significantly affected by the temperature increase. Guaiacols and phenols from HW were significantly higher than that from SW. Furans from both SW and HW increased significantly as the pyrolysis temperature increased from 450 to 500 °C. The increase in temperature favored the degradation of levoglucosan and other anhydrous sugars.

Both HW and SW produced similar yields of lignin derived compounds at the low temperature (450 °C). Increase in temperature facilitated the depolymerization of lignin and levoglucosan in both SW and HW, leading to increased phenols, guaiacols and furans. At the high pyrolysis temperature (500 °C), lignin derived compounds from SW and HW were significantly different. As shown in Table 3, the interaction of temperature and wood zone was significant only on the yield of ketones. By comparing the ketone yield, it can be concluded that ketone yield was more sensitive to the variation in pyrolysis temperature than the variation in wood zone. The ketone yield was found to decrease with increase in temperature probably due to the increase in secondary pyrolysis reaction rates with increase in temperature, leading to formation of lighter gaseous compounds at 500 °C [43,44].

3.3. Slow pyrolysis

3.3.1. Slow pyrolysis: Effects of temperature and wood zone on pyrolysis products distribution

The yields of bio-oil, biochar and syngas obtained from slow pyrolysis of HW and SW and at 450 and 500 °C (shown in Table 4) were not significantly different, except that biochar yield obtained from SW was significantly higher than that from HW at 500 °C. Biochar and total volatile (bio-oil + syngas) yields were comparable with those reported from slow pyrolysis of woody biomass, such as pine and fir wood [45–47]. Bio-oil yields from slow pyrolysis reported in this study and literature [48] are typically much lower than bio-oil yield (up to 60 wt.%) from fast pyrolysis using auger and fluidized bed reactors at 500 °C [49,50]. The high bio-oil yields of fast pyrolysis are due to its high heating rate and short gas residence time. In an auger reactor system, biomass moves continuously through the auger and heated via the thermal conduction between the reactor wall and biomass with a temperature gradient of 100–150 °C, with a residence time of approximately 8 s [49]. Owing to the fluidizing medium, high heating rate can be achieved

Table 2
Pyrolysis products of eastern redcedar wood from Py–GC–MS^a (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Chemicals	Group	SW450	HW450	SW500	HW500
<i>Cellulose/Hemicellulose derived compounds (area%)</i>					
Acetic acid	Acid	2.11 ± 0.84	1.55 ± 0.45	2.36 ± 0.41	2.00 ± 0.06
1,2-Cyclopentanedione	Ketone	2.58 ± 0.07	1.29 ± 0.41	–	–
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ketone ^b	1.18 ± 0.15	–	1.01 ± 0.16	–
4H-Pyran-4-one, 3,5-dihydroxy-2-methyl-	Pyran	1.87 ± 0.29	2.38 ± 0.40	1.66 ± 0.21	2.38 ± 0.37
2-Furanmethanol	Furan	1.03 ± 0.11	–	1.25 ± 0.67	–
Furfural	Furan	1.88 ± 0.23	1.80 ± 0.43	2.10 ± 0.49	2.28 ± 0.07
2-Furancarboxaldehyde, 5-methyl-	Furan	–	1.05 ± 0.43	–	1.07 ± 0.31
2(5H)-Furanone	Furan	1.77 ± 0.14	–	1.88 ± 1.01	1.10 ± 0.08
2(3H)-Furanone, 5-methyl-	Furan	–	–	2.08 ± 0.44	1.50 ± 0.82
5-Hydroxymethylfurfural	Furan	1.64 ± 0.28	1.87 ± 0.41	1.83 ± 0.21	2.46 ± 0.03
Glutaraldehyde	Sugar	1.27 ± 0.15	1.01 ± 0.22	1.43 ± 0.53	1.09 ± 0.07
Levogluconan	Sugar	5.43 ± 2.84	3.68 ± 1.57	6.56 ± 5.00	1.19 ± 0.73
D-Allose	Sugar	2.76 ± 0.60	9.13 ± 11.95	3.97 ± 2.54	6.34 ± 4.16
α-D-Glucopyranoside	Sugar	1.38 ± 0.96	1.82 ± 1.64	1.21 ± 0.19	1.81 ± 0.10
<i>Lignin derived compounds (area%)</i>					
P-cresol	Phenol	–	–	1.04 ± 0.06	1.19 ± 0.18
Catechol	Phenol	1.66 ± 0.09	2.32 ± 0.76	2.27 ± 0.52	3.73 ± 0.45
1,2-Benzenediol, 3-methyl-	Phenol	–	1.98 ± 0.24	1.64 ± 0.06	3.64 ± 0.32
Phenol, 2-methoxy-	Guaiacol	4.24 ± 0.87	3.44 ± 0.81	3.74 ± 0.04	4.17 ± 0.10
Creosol	Guaiacol	5.94 ± 1.35	6.56 ± 1.50	5.64 ± 1.16	9.21 ± 1.58
2-Methoxy-4-vinylphenol	Guaiacol	6.91 ± 1.03	6.39 ± 1.51	6.46 ± 1.05	7.87 ± 0.88
2-Propanone,1-(4-hydroxy-3-methoxyphenyl)-	Guaiacol	2.81 ± 1.83	2.45 ± 1.64	2.19 ± 1.12	1.62 ± 0.30
Apocynin	Guaiacol	1.33 ± 0.27	1.56 ± 0.68	1.55 ± 0.17	2.47 ± 0.30
Vanillin	Guaiacol	2.11 ± 0.30	1.94 ± 0.68	2.42 ± 0.32	2.57 ± 0.32
Eugenol	Guaiacol	1.37 ± 0.26	1.00 ± 0.26	1.35 ± 0.11	1.38 ± 0.10
Homovanillic acid	Guaiacol	2.20 ± 0.47	1.84 ± 0.81	1.88 ± 0.04	2.35 ± 0.32
Phenol, 2-methoxy-4-propyl-	Guaiacol	2.08 ± 0.72	5.92 ± 1.88	2.31 ± 0.41	5.63 ± 1.03
Phenol, 4-ethyl-2-methoxy-	Guaiacol	1.65 ± 0.70	1.96 ± 0.93	1.32 ± 0.31	2.54 ± 0.44
Phenol, 2-methoxy-4-(1-propenyl)-, (Z)-	Guaiacol	5.69 ± 1.22	1.67 ± 2.30	5.04 ± 1.06	4.55 ± 0.41
Phenol,4-(3-hydroxy-1-propenyl)-2-methoxy-	Guaiacol	1.73 ± 1.24	–	2.01 ± 1.92	–
<i>Nitrogen containing compounds (area%)</i>					
3-Pyrazolidinone, 1,4-dimethyl	Nitrogen	2.47 ± 0.44	4.06 ± 0.78	2.65 ± 0.21	4.31 ± 0.11
Total		69.82 ± 4.07	72.81 ± 0.91	72.38 ± 3.75	80.08 ± 3.77

^a “–” means the relative peak area percentage of the detected compound is less than 1%.

^b Values listed above are means ± standard deviation of three subsamples.

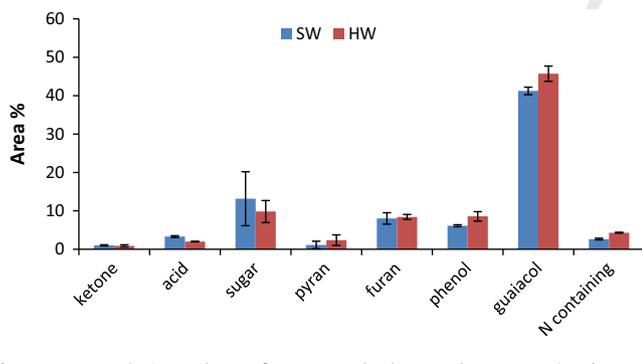


Fig. 2. Fast pyrolysis products of eastern redcedar wood at 500 °C (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

in fluidized bed with short gas residence time (<2 s). High heating rate and short gas residence time are believed to enhance the rapid fragmentation of biomass and mitigate the secondary cracking of tar [51], resulting in the high bio-oil yield. The Parr reactor system used in this study for slow pyrolysis was operated at a low heating rate (6 °C/min). In addition, the volatiles evolved from the reactor were in absence of any carrier gases.

3.3.2. Slow pyrolysis: Effects of temperature and wood zone on bio-oil properties and composition

All bio-oil samples were brown in color and heterogeneous liquids with two phases, the organic phase in the bottom and the aqueous phase on the top. The moisture contents of bio-oil samples

shown in Table 4 were higher (above 60%) than those reported in the literature (20–40 wt.%) [52]. High moisture contents reduce bio-oil energy content and also lead to the phase separation during the storage [53]. The carbon, hydrogen and oxygen contents of bio-oil samples ranged from 52.69 to 57.81 wt.%, 7.51 to 8.75 wt.%, and 33.32 to 38.91 wt.%, respectively and were comparable with the results previously reported [52,54]. The low heating values of bio-oil samples (shown in Table 4) were lower than those of bio-oil derived from forestry residue (21 MJ/kg dry basis) reported in the literature [52]. The low bio-oil pH could cause corrosion issues during the storage and transportation.

Bio-oils were mainly composed of carboxylic acids, ketones, furans, aromatics, phenols, guaiacols and olefins, as shown in Table 5.

Table 3

Results of two-way ANOVA analysis (*p*-values): Effects on pyrolysis temperature and wood zone one yields of pyrolysis product groups.

Groups	Temperature	Wood zone	Temperature * wood zone
Ketone	0.00	0.012	0.025
Acid	0.021	0.011	0.23
Sugar	0.61	0.96	0.44
Pyran	0.049	0.85	0.43
Furan	0.004	0.72	0.32
Phenol	0.00	0.001	0.84
Guaiacol	0.18	0.74	0.23
N containing Compound	0.45	0.00	0.90
Lignin derived compound	0.024	0.28	0.28

Table 4
Distribution of products from slow pyrolysis of eastern redcedar woods (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Products (wt.%)	SW450	HW450	SW500	HW500
Bio-oil	^A 35.9 ± 0.16 ^a	^A 33.2 ± 5.52	^A 33.4 ± 3.11	^A 34.3 ± 1.39
Biochar	^A 31.4 ± 1.41	^A 32.6 ± 2.62	^A 30.9 ± 0.42	^B 29.3 ± 0.14
Syngas	^A 32.7 ± 1.34	^A 34.2 ± 0.16	^B 35.7 ± 0.89	^A 36.4 ± 1.35

^a Means with the same letters under the same column are not significantly different at 5% level.

^a Values listed above are means ± standard deviation of two subsamples.

Acetic acid and furfural were the most abundant species identified in the bio-oil compounds. For example, acetic acid and furfural accounted for approximately 18 and 22 area%, respectively, for all bio-oil compounds identified from SW at pyrolysis temperature of 450 °C. Similar findings have also been observed in beech wood derived bio-oils [55]. Acetic acid was expected to form by primary decomposition of monosaccharides derived from hemicellulose [56]. The substantial quantity of acetic acid was responsible for the high bio-oil acidity as shown in Table 4. Ketones detected in bio-oils were 1-hydroxy-2-butanone, cyclopentanone and 2-methyl-2-cyclopenten-1-one, which confirm findings in the literature [57,58]. Furan derivatives were dominated by furfural; derived from ring-open and rearrangement of monosaccharides in hemicellulose [56]. The observation of aromatic hydrocarbons was the major qualitative difference between the identified compounds from the fast and slow pyrolysis. The reaction mechanisms of aromatics production from lignocellulosic biomass has been well documented [19,40,59,60]. Aromatics are derived from a series of reactions such as decarbonylation and oligomerization associated with furan compounds [40]. Lignin is a minor contributor to the production of aromatics even though its chemical structure is built on aromatic phenols blocks. Noticeable compositional differences on lignin derived products were observed between the fast (Table 2) and slow pyrolysis runs (Table 4). Guaiacols, especially those derived directly from degradation of lignin monomers (e.g. 2-Methoxy-4-vinylphenol, Vanillin, 2-methoxy-4-(1-propenyl) -phenol(Z)-, etc.), were the dominant lignin derived groups detected from fast pyrolysis runs, while simple phenols were the major chemical group for the slow pyrolysis runs. The qualitative difference could be due to the additional cracking of primary lignin derived products when exposed to the thermal environment. Alpha/beta-cedrenes were two hydrocarbon isomers sharing the formula C₁₅H₂₄, which were commonly identified in essential oils [61] as well as cedar wood oil [26]. Significant quantitative differences between alpha and beta-cedrene were observed between the bio-oils produced in the slow pyrolysis runs. Also, HW produced significantly more total cedrenes than SW, suggesting that HW is more suitable than SW for extraction of this value-added chemical. It should be noted that these two species were not detected in the fast pyrolysis runs. These results indicated that slow pyrolysis were more favorable for the extraction of alpha/beta-cedrenes than fast pyrolysis, one of the main components of cedar wood oil.

Table 5
Characteristics of bio-oil obtained from slow pyrolysis of eastern redcedar wood^b (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Bio-oil sample	Moisture (wt.%)	C ^a (wt.%)	H ^a (wt.%)	N ^a (wt.%)	O ^a (wt.%)	Higher heating value ^a (MJ/kg)	pH	Specific gravity
SW450	^A 84.16 ± 4.10	^A 68.98 ± 14.91	^A 7.11 ± 0.08	^A 0.21 ± 0.14	^A 23.71 ± 15.13	^A 31.00 ± 5.24	^A 2.52 ± 0.21	^A 1.01 ± 0.001
HW450	^B 77.64 ± 7.62	^A 53.27 ± 19.58	^A 7.24 ± 1.19	^B 0.11 ± 0.01	^A 39.38 ± 18.40	^B 17.42 ± 7.96	^A 2.45 ± 0.06	^A 1.02 ± 0.01
SW500	^B 79.31 ± 0.08	^A 52.69 ± 2.34	^B 8.30 ± 0.47	^B 0.10 ± 0.00	^A 38.91 ± 2.80	^B 14.19 ± 6.69	^A 2.38 ± 0.04	^A 1.00 ± 0.02
HW500	^B 78.9 ± 2.16	^A 57.81 ± 3.86	^B 8.75 ± 0.23	^B 0.12 ± 0.05	^A 33.32 ± 3.58	^B 17.29 ± 7.07	^A 2.36 ± 0.08	^A 1.02 ± 0.01

^a Means with the same letters under the same column are not significantly different at 5% level.

^a Values are converted to dry basis.

^b Values listed above are means ± standard deviation of two subsamples.

3.3.3. Slow pyrolysis: Effects of temperature and wood zone on properties of biochar and syngas

Table 6 summarizes the elemental analysis and energy content for both unprocessed and biochar eastern redcedar SW and HW. Comparing the unprocessed components, HW had higher carbon content than SW. The C/H and O/C molar ratios for HW were 0.74 and 0.71, respectively, while these ratios were 0.73 and 0.77, respectively, for SW. The energy content of unprocessed HW was significantly higher than that of unprocessed SW. Pyrolysis led to a significant increase of carbon content and a significant decrease of hydrogen and oxygen content in the biochar compared with the unprocessed sample, as indicated in Table 6. The C/H ratios of biochar obtained at 450 °C were 2.34 and 2.7 for SW and HW, respectively, which were comparable to wood waste results reported in literature [52]. The carbon and oxygen content variation that resulted from pyrolysis also contributed to the significant increase in the biochar heating value, e.g., the heating value of SW biochar obtained at 450 °C increased 58% compared with that of unprocessed SW.

A statistical analysis (unpaired *t*-test) was performed to evaluate the effects of SW and HW on the derived biochar compositions. The results showed that biochar obtained from HW contained significantly higher carbon and lower oxygen contents than that obtained from SW for both temperatures investigated. Comparing the carbon, hydrogen and oxygen content of SW and HW before and after pyrolysis, it was determined that the extent of variation (increase/decrease in percent) was similar, indicating that biochar composition differences between SW and HW could be attributed to the unprocessed sample chemical composition.

Syngas obtained from pyrolysis of eastern redcedar contained four major species, H₂, CO, CH₄ and CO₂ (Table 7). The gross calorific value of the syngas was estimated using the individual gas component higher heating values given in literature [62]. The syngas obtained from HW had a significantly higher gross calorific value (GCV) than that from SW. This could be due to the high yields of CO and CH₄ and low yield of CO₂ in the syngas obtained from HW pyrolysis. Phan et al. [47] reported that syngas obtained from waste wood composition at 650 °C pyrolysis temperature contained 30.5 vol.% CO, 44.7 vol.% CO₂, 7.0 vol.% H₂, and 14.7 vol.% CH₄ with a GCV of 12.6 MJ/Nm³, which was comparable to the GCV of syngas obtained from HW at 500 °C in this study. Researchers also observed CO and CO₂ maximize at temperature of 500 °C, whereas hydrogen continue to increase with pyrolysis temperature.

3.3.4. Slow pyrolysis: Carbon and energy balances

The percentages of carbon transferred from biomass into bio-oil, biochar and syngas during the pyrolysis process was estimated using Eq. (1), and the results are shown in Table 8. Over 90 wt.% of carbon transfer was achieved in the pyrolysis products, with most being retained in the biochar. The secondary tar cracking instigated by the slow pyrolysis condition could have promoted the production of syngas and reduced the production of liquid, hence low carbon transfer into bio-oil was expected. Fig. 3 shows the

Table 6

Composition of bio-oil from slow pyrolysis of eastern redcedar woods^a (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Chemicals	Group	SW450	HW450	SW500	HW500
<i>Cellulose/hemicellulose derived compounds (area%)</i>					
Acetic acid	Acid	18.18 ± 1.45	11.25 ± 1.52	18.15 ± 0.16	9.75 ± 1.84
Propanoic acid	Acid	2.42 ± 3.17	2.42 ± 0.36	3.42 ± 0.62	2.32 ± 0.85
1-Hydroxy-2-butanone	Ketone ^b	2.54 ± 0.31	1.49 ± 0.28	2.09 ± 0.66	1.21 ± 0.26
Cyclopentanone	Ketone	2.92 ± 0.28	1.79	3.58	1.54 ± 0.13
2-Cyclopenten-1-one, 2-methyl-	Ketone	4.42 ± 0.46	1.56 ± 0.56	2.58 ± 0.91	1.51 ± 0.25
Furfural	Furan	22.69 ± 0.40	26.20 ± 2.16	20.10 ± 3.39	21.80 ± 3.23
2-Furanmethanol	Furan	3.61 ± 1.54	–	1.47 ± 0.26	–
Ethanone, 1-(2-furanyl)-	Furan	0.99 ± 0.15	–	–	–
2-Furancarboxaldehyde, 5-methyl-	Furan	3.16 ± 0.57	4.46 ± 0.97	2.94 ± 0.21	4.43 ± 0.38
<i>Lignin derived compounds (area%)</i>					
Toluene	Aromatic	1.97 ± 1.02	–	–	–
p-Xylene	Aromatic	1.90 ± 0.14	1.65 ± 0.59	1.54 ± 0.51	1.77 ± 0.67
Phenol	Phenol	4.27 ± 2.08	3.04 ± 0.12	3.25 ± 1.24	3.55 ± 1.30
Phenol, 2-methyl-	Phenol	2.43 ± 0.79	2.54 ± 0.19	1.83 ± 0.39	2.71 ± 2.07
p-Cresol	Phenol	1.31 ± 0.68	1.67 ± 0.63	–	–
Phenol, 2-methoxy-	Guaiacol	10.34 ± 1.63	7.98 ± 0.67	10.13 ± 1.82	5.22 ± 0.03
Creosol	Guaiacol	4.28 ± 0.02	5.71 ± 0.33	4.24 ± 0.14	4.34 ± 0.61
<i>Cedar oil compounds (area%)</i>					
(–)-alpha-cedrene	Olefin	8.39 ± 1.12	12.97 ± 1.08	8.65 ± 1.46	18.15 ± 0.74
(+)-beta-cedrene	Olefin	2.27 ± 0.32	1.93 ± 0.93	1.81 ± 0.10	2.89 ± 0.34

^a “–” means the relative peak area percentage of the detected compound is less than 0.5%.

^b Values listed above are means ± standard deviation of two subsamples.

Table 7

Characterization of bio-char from slow pyrolysis of eastern redcedar woods (S/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Bio-char sample	C (d.b. wt.%) ^a	H (d.b. wt.%)	O (d.b. wt.%)	N (d.b. wt.%)	S (d.b. wt.%)	Higher heating value (MJ/kg)
Unprocessed SW	46.45	5.33	47.64	0.19	0.16	^A 19.84 ± 0.077
Unprocessed HW	48.23	5.44	45.96	0.21	0.15	^A 20.22 ± 0.13
SW450	^A 84.35 ± 2.19	^B 3 ± 0.14 ^b	^A 11.45 ± 2.48	^A 0.45 ± 0.07	^A 0.4 ± 0.15	^B 31.36 ± 0.40
HW450	^B 87.4 ± 0.28	^A 2.7 ± 0.3	^B 8.95 ± 0.21	^A 0.4 ± 0.1	^A 0.4 ± 0.1	^B 33.77 ± 2.19
SW500	^A 85.8 ± 2.97	^A 2.4 ± 0.2	^A 10.85 ± 2.90	^B 0.35 ± 0.07	^B 0.35 ± 0.07	^C 29.98 ± 2.50
HW500	^B 88.88 ± 0.45	^A 2.6 ± 0.15	^B 7.75 ± 0.07	^B 0.35 ± 0.07	^A 0.4 ± 0.1	^D 32.95 ± 0.17

^a Values are dry base ash free.

^b Values listed above are means ± standard deviation of two subsamples.

^{*} Means with the same letters under the same column are not significantly different at 5% level.

Table 8

Composition of syngas obtained from slow pyrolysis of eastern redcedar woods (S/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Sample	H ₂ (vol.%)	CO (vol.%)	CH ₄ (vol.%)	CO ₂ (vol.%)	Gross calorific value (MJ/Nm ³)
SW450	^A 3.09 ± 1.04 ^a	^A 34.65 ± 1.33	^A 11.16 ± 1.13	^A 51.11 ± 0.83	^A 9.21 ± 0.75
HW450	^A 3.01 ± 1.05	^B 37.27 ± 0.89	^B 14.51 ± 1.77	^B 44.56 ± 4.62	^B 10.87 ± 0.95
SW500	^B 3.92 ± 0.73	^A 34.70 ± 0.97	^B 14.31 ± 1.22	^C 47.07 ± 0.99	^B 10.58 ± 0.70
HW500	^A 3.14 ± 0.09	^C 40.42 ± 1.34	^C 16.41 ± 2.60	^D 40.03 ± 4.04	^C 12.04 ± 1.22

^a Values listed above are means ± standard deviation of two subsamples.

^{*} Means with the same letters under the same column are not significantly different at 5% level.

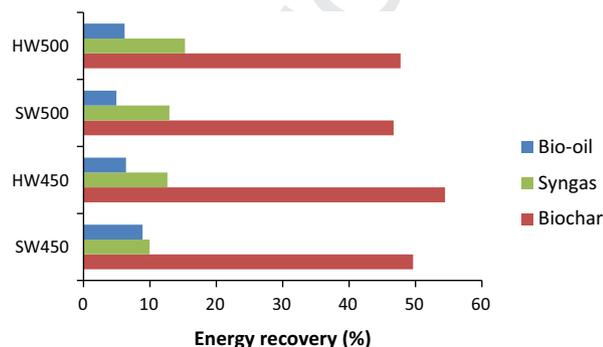


Fig. 3. Energy recovery for pyrolysis of eastern redcedar wood in slow pyrolysis runs (SW/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Table 9

Carbon balance of the products obtained from slow pyrolysis of eastern redcedar woods (S/HW450/550 = sapwood/heartwood pyrolyzed at 450/500 °C).

Sample	Carbon in bio-oil (wt.%)	Carbon in biochar (wt.%)	Carbon in syngas (wt.%)	Total (wt.%)
SW500	7.84	57.08	27.00	91.92
HW500	8.82	54.00	27.73	90.54

distribution of energy transferred to the pyrolysis products of eastern redcedar wood. Much of the energy (up to 50%) was retained in the biochar after pyrolysis. Less than 10% of the energy transferred to bio-oil. The low bio-oil energy yield could be associated with its high moisture content (see Table 9).

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4. Conclusions

This study investigated the pyrolytic behavior of eastern redcedar heartwood (HW) and sapwood (SW) in two process conditions (fast at micro-scale and slow pyrolysis at lab-scale) and at two temperatures (450 and 500 °C). Eastern redcedar wood was characterized by a G-H type lignin because of lack of S-lignin units in bio-oil. In fast pyrolysis conditions, bio-oils produced were dominated by primary products, such as anhydrous sugars, phenols and guaiacols. At 450 °C, ketones in bio-oils obtained from SW produced was significantly higher than that obtained from HW. There was no significant difference on the total yield of lignin-derived products from SW and HW; however, SW yielded less phenols and more guaiacols than HW. When temperature increased to 500 °C, HW yielded more lignin-derived products than SW.

Bio-oils produced from slow pyrolysis were dominated by small molecules, such as acetic acid, furfural and simple phenols that are derived from the decomposition of primary 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.

Acknowledgement

This project was funded by the South Central Sun Grant Initiative and Oklahoma Agricultural Experiment Station.

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