AN EVALUATIVE COMPARISON OF LIGNOCELLULOSIC PYROLYSIS PRODUCTS DERIVED FROM VARIOUS PARTS OF POPULUS DELTOIDES TREES AND PANICUM VIRGATUM GRASS IN AN INDUCTIVELY HEATED REACTOR

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ABSTRACT

Poplar is considered a suitable resource for production of renewable fuels and chemicals due to its rapid growth and tolerance to environmental stresses. Switchgrass is also extensively studied for biofuel production due to its use as a resource-efficient low-input plant and ability to grow and thrive in diverse weather or soil conditions. In this study, fast pyrolysis of biomass obtained from various parts (main stem, secondary stems, branches) of eastern cottonwood (*Populus deltoides*) and switchgrass (*Panicum virgatum)* was carried out in an inductively heated reactor. Devolatilization rates (ranging from 450 °C to 600 °C) were initially obtained to determine their decomposition kinetics and estimate process parameters (temperatures and times) suitable for their pyrolysis in an inductively-heated reactor. The effect of temperature (450 °C, 500 °C, 550 °C) on pyrolysis product yields and composition was investigated. Results indicate that activation energies ranged from 9.2 to 13.5 kJ/mol, while pre-exponential constants ranged from 0.23 to 0.51 s^{-1}. The maximum quantity of bio-oil of 39.8% ± 9.50 was obtained from poplar stem at 450 ^{0}C whereas the least amount of 33% was obtained from poplar branch at 550 ^{0}C. The highest amount of bio-oils of 34% from switchgrass was obtained at 450 ^{0}C. Water content in the bio-oil obtained from switchgrass was significantly higher than those from poplar tree parts. The GC-MS results showed that bio-oil compositions are similar among the various parts of poplar trees, with phenols being the dominant chemical specie for all bio-oil samples analyzed. With increasing temperature, an increase in furans is observed. Bio-oil fractions derived from biomass pyrolysis of the trunk and stems have higher HHV than those from switchgrass, with the average HHV of water-free bio-oils ranging from 17.4 - 19.4 MJ/kg. Overall process energy recovery from initial biomass reached a maximum of 80.1% in the case of cottonwood main stem pyrolyzed at 500 °C.

KEYWORDS: Cottonwood poplar; stem; branch; switchgrass; inductive pyrolysis; bioenergy

1. INTRODUCTION

Global challenges such as the disruption to the supply of limited fossil fuels, spikes in energy costs, consistent rise in world energy demand, and the need for lower greenhouse gas (GHG) emissions have informed substantial research efforts in the conversion of biomass into biofuels and other beneficial renewable products [1-3]. Biomethanation, fermentation and thermochemical methods are commonly used approaches to obtain biofuels from biomass products [4]. For instance, conversion of biomass into biogas, ethanol, and biodiesel can be done by microbial/enzymatic fermentations with the aid of physical and chemical pretreatment steps [5, 6]. Bio-oil, biochar and syngas are produced from biomass using entirely thermochemical conversion processes such as torrefaction, carbonization, hydrothermal liquefaction, gasification, and pyrolysis. These processes yield fuels with high-energy content with minimal environmental impact [3, 7]. The thermochemical conversion method to be used depends on the available raw material and the desired product. Pyrolysis is a valuable thermochemical process which converts biomass into combustible gas, bio-oil, and char in an oxygen-free environment within reactor temperatures range of 300 ^{0}C and 900 ^{0}C [8].

Fluidized bed reactors, ablative pyrolysis reactors, and fixed bed drop-type reactors are some of the several reactor systems that have been designed to optimize liquid oil reduction [9]. To obtain higher quantities of liquid oil from the pyrolysis process, several features have been identified as important, including rapid heating rates, high heat transfer-to-biomass rates, methodical control of the reactor temperature, rapid removal of the pyrolysis vapors from the reactor, and the rapid cooling of the vapors to make the bio-crude products [10]. Based on these features, an induction-heating reactor has proven to be a suitable alternative to carry out the pyrolysis process [9], as compared to other fast/flash pyrolysis systems due to its high-energy efficiency and low pollution rates [11]. The induction-heating system is designed to heat any ferromagnetic material placed within its coils by creating an oscillating magnetic field with the aid of an AC power supply. Since the heat is generated inside the material itself, during induction heating, and not from an external source, process objectives such as rapid heating rates and high energy efficiency are readily achieved. Although induction heating mechanism has been demonstrated to be effective both in the pyrolysis of biomass and subsequent bio-oil upgrading, major downsides of the mechanism include low performance efficiency and minimal tolerance for design flexibility or expansions [12].

The eastern cottonwood tree (*Populus deltoides*) is tree is one of the fastest-growing trees in North America and Europe [13], as it can grow up to 30 m tall and adapt to a wide gamut of soil and climatic conditions. Although eastern cottonwood is not a quality source of timber due to its fragile nature, it presents potential as a bioenergy crop due to its rapid growth, high rate of biomass production, and its high cellulose and low lignin contents [14]. These features are significant in the production of liquid fuels because the cellulose provides the substrate for liquid fuels whereas its low lignin content makes it suitable for various pretreatment processes [14]. It has been established that short-rotation woody crops (SRWCs) in which trees such as cottonwood are managed for rotations of 10 years or less have lower environmental footprints than fossil fuels [15]. The studies of the effect of pyrolysis on various parts of the cottonwood tree are limited to non-existent. In this paper, we compare the effect of induction-heating pyrolysis on the various parts of cottonwood tree – stem, branch, main trunk – using a laboratory scale induction heating reactor.

Switchgrass (*Panicum virgatum* L.) is a native warm-season grass used for hay and forage crops in the United States. Switchgrass has several characteristics which makes it suitable as a biomass energy crop in the US, including being native in North America, consistently growing in diverse planting conditions, producing average to high biomass yields on marginal soils [16], and existing as an environmental enhancement energy crop [17]. For these reasons, switchgrass is well positioned to be used as a bioenergy feedstock for pyrolysis, gasification, cellulosic ethanol production, and combustion for heat and electrical generation [18]. While there are several studies on ethanol production from these feedstocks [19-22], there is only limited published literature on the pyrolysis of cottonwood and switchgrass biomasses [23]. Moreover, there is a knowledge gap in terms of induction-based pyrolysis for both feedstocks. In this study, we aim to fill this gap by investigating devolatilization kinetics in inductively heated reactor to evaluate the yield and quality of the residual bio-oils. The process performance for the various parts of the poplar tree is critically compared, as from a practical perspective, depending on specific management of the trees, only select parts of the tree may be harvested for biofuel production.

Figure 1. Left: Naturally occurring cottonwood (*Populus deltoids*) tree. Right: Various parts of managed cottonwood tree – person holding main stem (largest of the shoots), secondary stems shooting from the stool, and branches (twigs and branches off the main and secondary stems)

2. MATERIALS AND METHODS

2.1. Materials

Eastern cottonwood and switchgrass biomass samples were collected at a research site in northeastern Louisiana as part of a larger project described in previous reports [24, 25]. Both biomass types were collected in the fourth year after planting at the retired agricultural site. Eastern cottonwood trees were trimmed and sorted based on the part of the tree from which the trimmings was collected viz-a-viz stem, branch, and main trunk. Switchgrass was cut and broken by hand into smaller pieces. All samples were ground with the aid of a mill able to produce particles of uniform size that are less than 1 mm in diameter. The measured particle size distribution of the ground biomass, alongside the moisture content determined gravimetrically according to ASTM C566 – 13 [26], was recorded. Moisture content of the biomass parts ranged from 2.2% wet basis for cottonwood stem to 4.8% wet basis for switchgrass. The milled biomass was placed in thin layer on trays and oven-dried overnight at 105 ^{0}C. The dried biomass was then stored in sealed plastic bags at low temperatures to minimize moisture absorption during storage until the experiments are ready to be run.

2.2. Equipment

For the initial experiments determining the devolatilization kinetics, a free-standing stainless steel reactor (a 10 cm long cylinder with an internal diameter of 2.54 cm), capped at one end and with a small opening at the other, was placed in an induction coil connected to an RF generator (2 kW max power, model Flex Heat 2, RDO Induction, LLC, Washington, NJ). The reactor was placed on a support system consisting of an fabric insulating layer, a quartz half-cylinder, and wood legs, all located on a balance (with resolution of 0.1 g) as shown in Figure 2 below. The balance (model #, Ohaus, Inc, CITY, STATE) was connected to computer that recorded the mass loss in real time.

For the second study which included gas and bio-oil collection and analysis, a low-frequency induction heater (RDO Induction L.L.C., Washington, NJ) with a power output of 5 kW was used to heat a 1.5-inch nominal diameter stainless steel reaction tube (which held the biomass) at various temperatures [9]. An infrared Omega iR2C PID controller (Omega Engineering, Inc., Stamford, CT) was used to control the power output of the induction heating system, with the aid of a 4–20 mA control signal to achieve and maintain the desired reactor temperature. The reaction tube was a 316 – stainless steel tri-clamp tube, 454 mm in length, with inner and outer diameters of 34.925 mm and 50.8 mm respectively. The biomass was compactly packed in the reactor which was placed within a ten-loop rubber-coated copper induction coil 285 mm in length and 59 mm inner diameter.

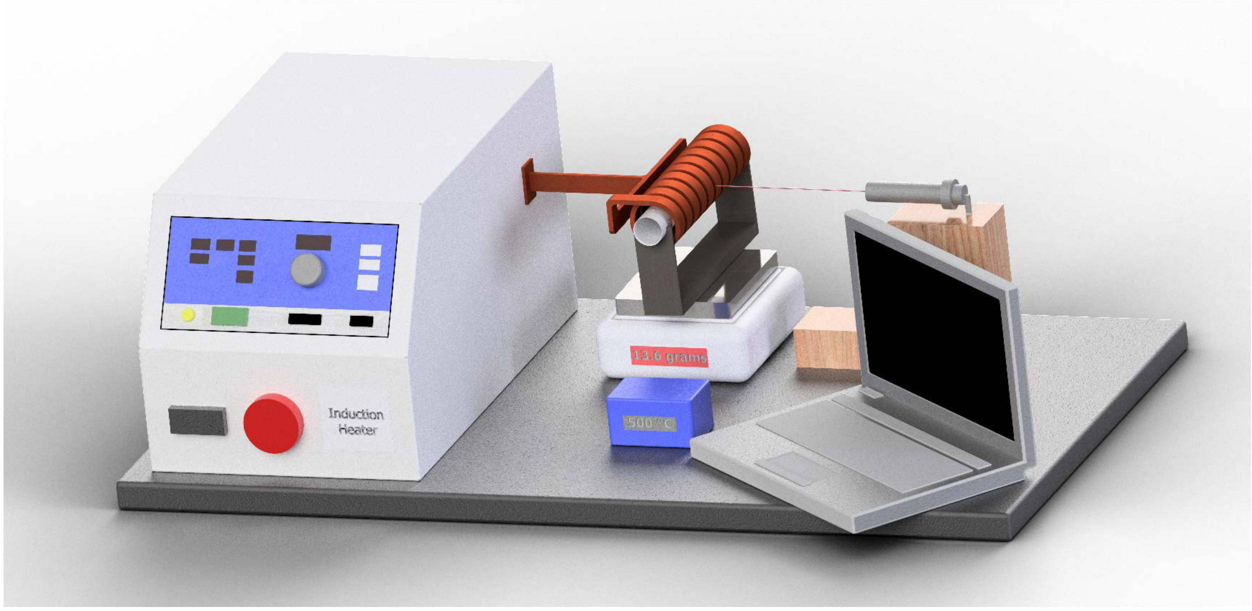

Figure 2. Autodesk Inventor drawing of pyrolysis system. The balance was only used for the collection of kinetic data.

The pyrolysis vapors were collected and condensed into liquid bio-oil as condensate using a system consisting of a round bottomed flask placed in an ice bath at 0 ^{0}C and an electrostatic precipitator (ESP) to prevent the dissolved liquid from vaporizing and prevent secondary reactions by reducing the system temperature [27, 28]. The ESP was specifically built for this study from a glass recipient (Technical Glass Products INC., Painesville, OH) and operated at a 15-kV power level with the aid of a Gamma High Voltage power supply (Gamma High Voltage Research, Ormond Beach, FL). The ESP exhaust was connected to a water-ethanol dual trap system and the resulting non-condensable, non-soluble gases were sampled and weighed.

2.3. Experimental procedure

To determine devolatilization kinetics and pyrolysis times, triplicate experiments were conducted without collecting products. Dried and ground cottonwood and switchgrass biomass were pyrolyzed in a batch induction pyrolysis system at four different reactor bed temperatures: 450, 500, 550, and 600˚C. Kinetic experiments indicated that the residence time after which the biomass recorded no change in mass was 15 minutes at most. The electric field impulses during active heating introduced transient effects in the mass balance sensor, resulting in significant noise in the signal. This noise was eliminated by performing a 20-second moving average on each data set and averaging the three replicates.

Analysis of Reaction Kinetics

The kinetic reactions were modeled using the Borchardt and Daniels method [29] which describes the dependence of the rate of reaction on the amount of material present as shown in Equation 1.

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \qquad (1)$$

Where: $\frac{d\alpha}{dt} = reaction\ rate\ (s^{-1})$, α = fraction reacted (dimensionless), $k(T)$ = rate constant at temperature T (s^{-1}), n = reaction order (dimensionless).

The rate constant $k(T)$ was determined by calculating the slope of the linear portion of the experimental mass loss data plotted versus time. The Borchardt and Daniels model also uses the Arrhenius equation to describe how the reaction rate changes as a function of temperature as shown in Equation 2.

$$k(T) = Ae^{-\frac{E_a}{RT}} \qquad (2)$$

Where: A = Arrhenius pre-exponential factor (s^{-1}), E_a = Activation energy (J mol^{-1}), T = Absolute temperature (K), R = Gas constant (8314 J mol^{-1} K^{-1}). E_a was determined by plotting $k(T)$ versus the ln of $1/T$ and determining the slope of the resulting line. Multiplying the slope by $-1/R$ gave E_a. A was then determined as the linear slope of a plot of $k(T)$ versus $e^{-Ea/RT}$.

A second set of studies was performed on the biomass in a similar, but larger reactor (30 cm long, 3.5 cm internal diameter), modified to allow for more biomass loads as well as for the collection of products. In order to account for the higher initial mass and the larger reactor, as well as to insure a complete pyrolysis, all experiments in the secondary study were uniformly run at a conservative residence time of at least 30 minutes. Based on our previously published work [28, 30], it was estimated that no additional benefits are derived from processing the biomass at 600 °C, thus these experiments were carried out only at 450, 500, and 550 °C. The dried biomass was weighed out in 25 g sizes and packed in the center of the pyrolysis reaction tube. The reaction tube was then placed in the induction coil, connected to the gas inlet and outlet, and in such a way that the laser light from the infrared PID controller would focus on the center of the tube.

All apparatus including the ESP condenser tube, round bottomed flask and connector stem were cleaned, dried and weighed. Nitrogen gas flowing at 1.0 L min^{-1} was bubbled through the inlet to purge the system of oxygen for 25 min. After purging, the induction heating system was turned on to pyrolyze the biomass while the nitrogen gas flow was maintained. The ESP, placed in an ice bath, served as a conduit for condensable vapors (bio-oil) into the collection flask, while non-condensable vapors were filtered out via the ethanol and water bubble outlet.

At the end of the experiment, the residue in the reaction tube was weighed to obtain the char yield. The content of the collection flask was weighed to determine the bio-oil yield. Obtained bio-oil yield was transferred to scintillation vials and stored at -20 ^{0}C to prevent secondary reactions until further analysis. The mass of the syngas was determined by difference according to the following:

Mass of syngas = Mass of biomass feedstock – (Mass of bio-oil + Mass of biochar) (3)

2.4. Characterization and analysis

Cottonwood and switchgrass biomass pyrolysis products were qualitatively analyzed to determine the chemical compositions of the various product fractions. The proximate analyses of the samples were carried out according to ASTM standards [moisture content (MC): ASTM E871-82; ash content (Ash): ASTM E1755-4582; volatile matter (VM): ASTM E872-82, while the fixed carbon (FC) content was determined according to FC (%) = 100% - [MC % + Ash % + VM %]. The ultimate analysis was carried out according to ASTM D5373 using an elemental analyzer 2400 Series 2 CHNS/O (Perkin Elmer, Inc., Waltham, MA). The solid char samples were analyzed for their Carbon, Hydrogen, and Nitrogen content using the same elemental analyzer. The ash content of each char resides was also tested to determine its Oxygen content. The liquid fraction was analyzed using three different analysis techniques: Karl Fischer titrations to determine water content, CHN elemental analysis, and GC–MS to identify the different compound groups in the liquid fraction. The detailed description of these processes has been provided [31]. High heating values of the liquid fractions were measured using bomb calorimeter (Parr Instrument Company, Moline, IL.) according to the procedure already described elsewhere [32].

2.5. Carbon and energy balances

The carbon balance (a primary component of the heating value) was performed to determine the carbon distribution in the pyrolysis products, which estimates the extent of temperature effects on individual component yields. The CHNO content of bio-oil and bio-char were analyzed using Perkin Elmer 2100 series elemental analyzer. The energy content of the biomass was obtained using the equation provided by Scholze and Meier to compute the higher heating value (HHV) of the liquid product using the CHN analysis, equivalent to that developed by Dulong [33]:

$$HHV\left(\frac{\mathrm{MJ}}{\mathrm{kg}}\right) = \left[338.2 * C\% + 1442.8 * \left(H\% - \frac{O\%}{8}\right)\right] * 0.001 \tag{4}$$

Where C, H, and O are mass fractions obtained from pyrolysis analysis.

Likewise, the energy content of the four biomasses were determined using the equations provided by Dulong and Vandralek [33], using the C, H, N, O, and ash contents of the feedstocks.

3. RESULTS AND DISCUSSION

3.1. Reaction Kinetics

The mass loss data (Figure #) indicated a clear relationship between the process temperature and both the overall process time and the rate at which this mass loss occurs. In all cases, a higher temperature resulted in a more rapid decomposition. With the exception of secondary stems, which seemed to converge toward the same value (18.5% to 19%) indifferent of the process temperature, the final char content decreased with an increase in temperature. For cottonwood main stem the range was 12.1 to 26.2% and for branches was 16.3 to 24.6%, whereas for switchgrass the range was 14.6 to 34.6%. This higher stability at lower temperatures compared to cottonwood indicates the different internal structure of switchgrass, containing more ash-type compounds binding the organic carbon more tightly into the matrix and resisting decomposition.

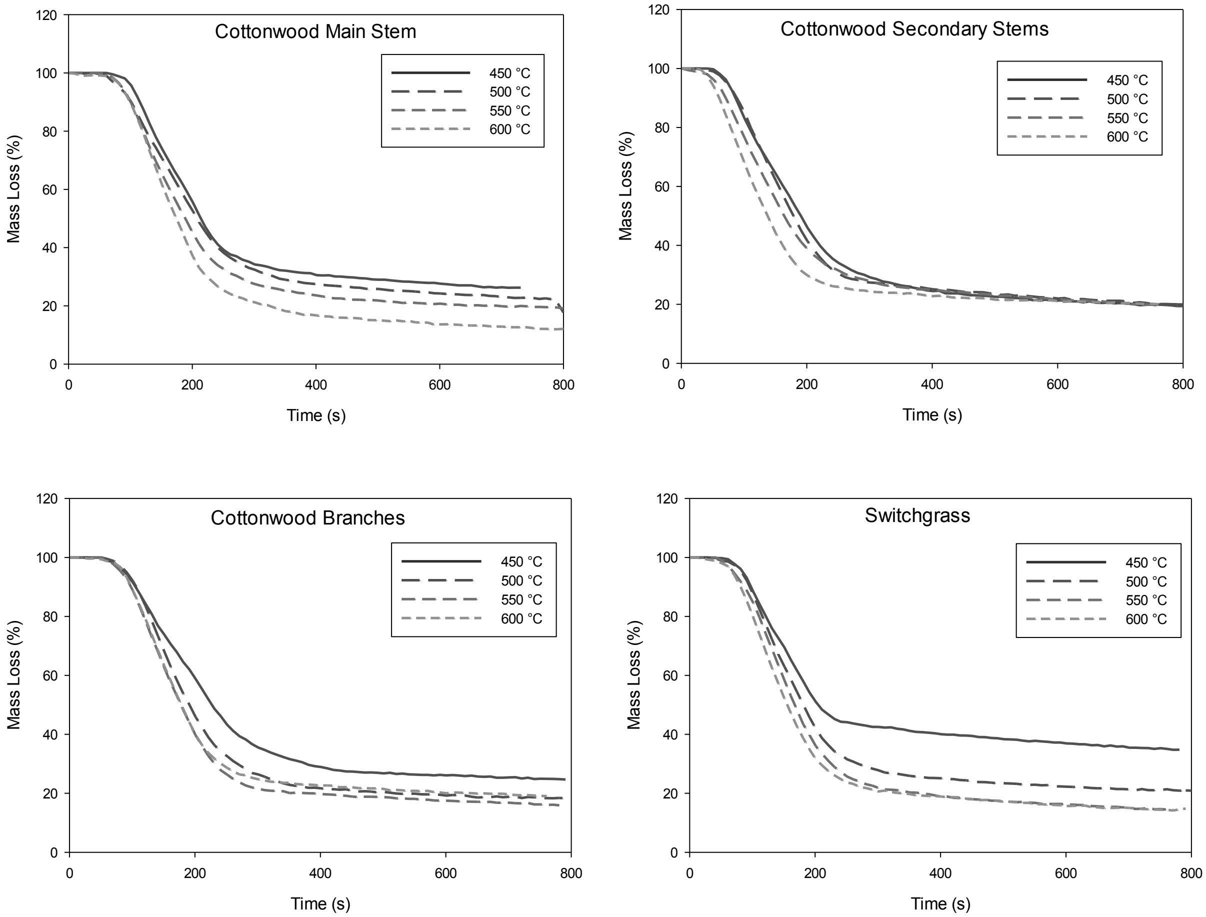

Figure #. Mass loss in the inductively heated reactor for the four biomasses under investigation.

The devolatilization kinetic rates are presented in Table x. As expected, in general mass loss rates increase with temperature for all samples tested. The activation energies and pre-exponential constants calculated using the Borchardt and Daniels model are also presented in Table x. Compared to values presented in literature by Sadaka *et al.* [34] for TGA analysis, these values are markedly different (9.2 to 13.5 kJ/mol in this study vs. 234.5 to 300.3 kJ/mol in [34]). Similarly, the pre-exponential constants are multiple orders of magnitude smaller (0.23 to 0.51 s^{-1} in this study vs. 2.26E+13 to 3.94E+18 s^{-1} in [34]). These differences are explained by the specific experimental conditions. In the study by Sadaka et al. [34], the kinetic parameters were calculated using the Kissinger method [35], on an extremely small sample (milligram in size) compared to what is presented in this study (12 g). The TGA method also uses for calculation different heating rates as a parameter, rather than different temperatures. Thus, the results cannot be directly compared due to the differences in samples sizes, reactor configurations, and method of heating. When compared to similar size samples and reactors, conventionally heated in a furnace [36] (personal communications), the activation energies and pre-exponential constants are in the same range. For white poplar (a similar but different subspecies of *Populus*) E_a and A were determined to be 30.5 kJ/mol and 4.7 s^{-1}, respectively [36] (personal communications). Also, recent data on food court waste in similar size and reactor systems [37] indicate E_a of 21.32 kJ/mol, A of 6.1 s^{-1} for induction heating vs. E_a of 30.75 kJ/mol and A of 10.9 s^{-1} in conventional heating.

Table 1: Values of the thermal decomposition rate constant k(T), activation energy and Arrhenius pre-exponential factor for fractionated Cottonwood (main trunk, secondary stem, and branches) and Switchgrass undergoing fast pyrolysis in an inductively heated reactor.

Material	$k(T)$ (s^{-1})				E_a ($J\ mol^{-1}$)	A (s^{-1})
	450 °C	500 °C	550 °C	600 °C		
Cottonwood – Main stem	0.40	0.37	0.43	0.52	9,198	0.37
Cotonwood – Secondary stems	0.36	0.45	0.41	0.44	5,502	0.51
Cottonwood - Branches	0.32	0.46	0.48	0.48	13,507	0.23
Switchgrass	0.38	0.46	0.50	0.50	10,023	0.42

3.2. Product yields

The results show the volatile matter, fixed carbon, ash content, and moisture present (dry basis) in the raw biomasses and resulting bio chars (Table 1). These values are comparable with results presented in literature for similar biomasses [34].

Table 2: Proximate and ultimate analysis of biomass (in %).

Biomass		Cottonwood stem	Cottonwood branch	Cottonwood main trunk	Switchgrass [38]
Proximate analysis	% Volatile matter	66.9±19.15	70.83±8.25	65.85±2.75	73.57±0.27
	% Fixed carbon	23.42	19.05	23.67	20.26±0.35
	% Ash content	1.53±0.19	1.75±0.13	2.14±0.29	6.17±0.09
	% Moisture	8.15±0.09	8.37±0.03	8.34±0.10	7.22±0.49
Ultimate analysis	% C	48.5	49.0	48.5	47.3
	% H	5.9	6.1	6.0	5.7
	% N	0.6	0.8	0.7	0.5
	% O	43.2	41.4	43.0	43.6

The product yields from cottonwood stem, trunk, and branches, and switchgrass were investigated to better understand the effects of reaction temperature on yields (Figure 3). All biomasses show a decrease in char yield as temperature increased from 450 °C to 550 °C. However, an unexpected spike in char yield was observed for cotton wood main stem from 450 °C to 550 °C, which eventually reduced at 550 °C. For the cottonwood main trunk, char yield increased with temperature increase of 450 °C to 500 °C but reduced beyond that range. Char yield was however uniform at all experiment temperatures for cottonwood branches. Also, char yield decreased as temperature increased in the cases of cottonwood stem and switchgrass. All biomasses exhibited a decrease in char yield as the temperature increased from 450 °C to 500 °C. However, cottonwood branch displayed the lowest decrease in char yields (0.75%) with respect to temperature as compared to the other three biomasses, with the absolute percentage decrease in char yield from 450 ^{0}C to 550 ^{0}C being 18.31%, 12.0% and 9.1% for cottonwood main stem, cottonwood stem, and switchgrass respectively. The small statistical significance in char yield for cottonwood branches shows that cottonwood branches are more rapidly converted to char at lower temperatures than switchgrass other biomasses and/or the other cottonwood tree parts. Sadaka *et al.* [34] reported char yields for cottonwood in the range of 36.9 – 45.7%, and 38.7% for switchgrass, higher that was was found here, but those experiments were performed only at

400 °C, a lower temperature which is expected to lead to a higher char yield. The individual yields as percentages of total product for char, bio-oils and gases at different temperatures for each biomass sample are presented in Figure 3.

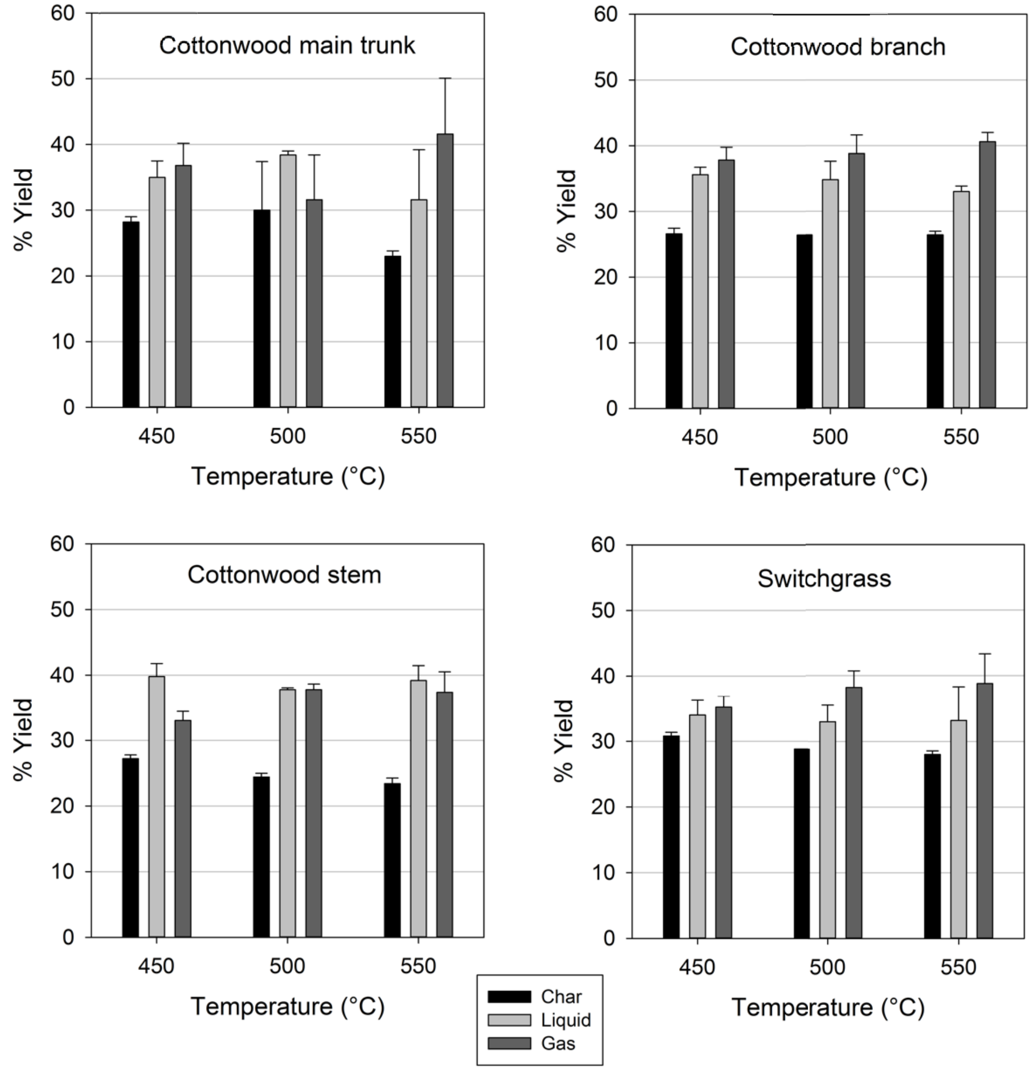

Fig. 3: Yields of char, liquid bio-oil, and gas as % of total products from pyrolysis of biomasses derived from cottonwood main trunk, branch, and stem; and switchgrass.

Bio-oil yield for poplar main stem was 38.4% at 500 ^{0}C while bio-oil yields were highest for the secondary stems, branches and switchgrass at 39.8% ± 0.019, 35.6% ± 0.011, and 34% ± 0.023

respectively, all at 450 ^{0}C. Bio-oil obtained from poplar secondary stems had the greatest yield of 39.8% ± 0.019 on average, while that obtained from poplar branch was least in bio-oil yield at 34.5% ± 0.011. It can thus be inferred that more quantities of bio-oil can be derived from poplar stems compared to branches. Bio-oil yields decreased as temperature increased, reaching a lowest value of 31.6% for cottonwood main stem and 33% for both cottonwood branch and switchgrass at 550 ^{0}C. The highest bio-oil yield of 39.8% was obtained from cottonwood secondary stems at 450 ^{0}C (Fig. 3). The maximum bio-oil yield for other biomasses were 38.4% at 500 ^{0}C for cottonwood main stem, 35.6% at 450 ^{0}C for cottonwood branch, and 34% at 450 ^{0}C for switchgrass. Published data for bio-oil yield obtained in a conventional reactor at 400 °C (lower than what is reported here) indicate bio-oil yields of 33-35% for cottownwood and 29.5% for switchgrass [34], which are lower than what is reported in the present work. It is therefore concluded that maximum bio-oil yields are obtained at temperatures in the range of 450-500 °C. Sadaka *et al.* [34] did not perform pyrolysis studies for yield determination at other temperatures, except 400 °C, so a clear comparison between conventional and induction heating cannot be made.

Volatile matter is released in larger quantities and at a higher rate as pyrolysis temperatures increase up to a certain point [1, 39]. Pyrolysis at this temperature range results in optimum extraction of the volatile condensable elements from biomass feedstock [40]. Beyond this temperature, volatile matter undergoes secondary tar reactions such as thermal cracking [41], and decomposes into incondensable gases and molecules small enough to escape at room temperature or even lower, thus reducing bio-oil yield [42].

All biomasses showed an increase in gas yields as pyrolysis temperature increased from 450 ^{0}C to 550 ^{0}C. Cottonwood stem displayed the highest percentage increase in gas yields of 13.33%

while cottonwood main stem (13.04%), switchgrass (11.43%), and cottonwood branch (7.41%) respectively trailed behind. This trend of increasing gas yields with temperature was expected as more gases are produced upon the more complete breakdown of biomasses at higher reaction temperatures as indicated by previous studies [30, 43-45]. The ideal operating conditions for highest overall energy efficiency are discussed in the energy balance section of this study.

3.2. Water Content of the Liquid Fraction

The water yield of the bio-oil was determined by performing Karl Fischer titrations on the liquid fractions as shown in Fig 4. Initial moisture content of the biomasses has been reported in Table 2.

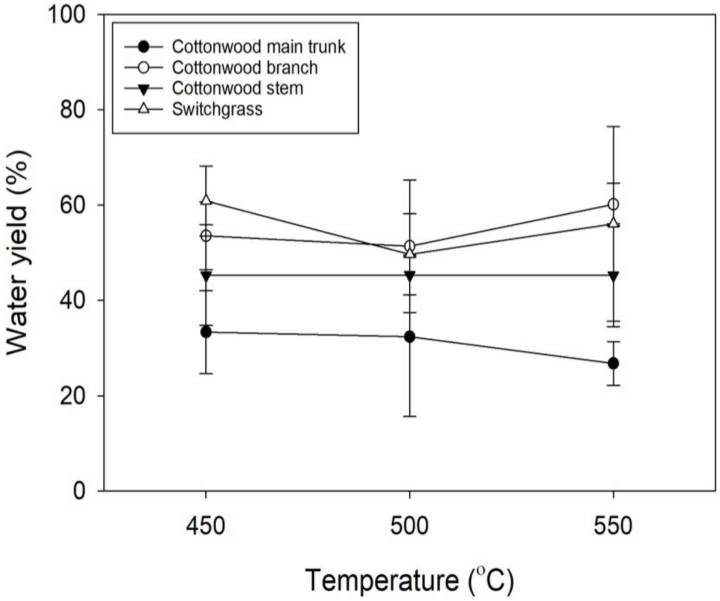

Fig. 4: Water content of the bio-oil as a fraction of the total liquid mass with respect to temperature for the different feedstock.

It was necessary to ascertain the water content in the bio-oil (both from the feedstock and pyrolysis process) due to its negative impact on the bio-oil's heating value [46]. For the cottonwood main stem, the water yield reduced with temperature increase, as was the case with cottonwood stem, although there was a minor spike at 500 ^{0}C. The range of water yields from the various biomasses were 26.75% to 33.32% for cottonwood mainstem, 51.35% to 60.13% for cottonwood branch, 45.3% on average for cottonwood stem, and 49.66% to 60.85% for switchgrass. Thus, the water yields from switchgrass was notably higher than that from cottonwood which agrees with the chemical compositions of both materials outlined in literature [28, 47]. Lignin, which has been proven to be present in switchgrass in larger quantities compared to switchgrass, produces water when dehydrated via pyrolysis reaction [48]. It was also observed that cottonwood main trunk had the highest liquid yield with a corresponding low water content compared to other poplar parts and switchgrass. Cottonwood main trunk harnesses vascular tissues to transport water and nutrients from the soil to other parts for overall tree growth. While pyrolysis temperature, heating rate, and particle size have been determined as key factors influencing bio-oil yield [49, 50], this phenomenon in cotton wood main trunk is indicative of its richness nutrients which are in relatively lower quantities in other tree parts such as the stem or branch.

3.3. Characterization of char

The elemental analyses of char yields were compared to the CHNO analysis of their respective raw biomasses (Table 2). The values obtained for both raw biomass and the carbonized (char) form are in the same range as those reported in literature for cottonwood and switchgrass pyrolized in conventional reactors [34]. The minor differences can be attributed to the different pyrolysis temperature (400 °C vs 450-600 °C in the present study).

Table 3: CHNO analysis of char yields from the induction pyrolysis of cottonwood main trunk, branch, stem, and switchgrass compared to the CHNO analysis of their respective raw biomasses.

Biomass	Temperature (°C)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen* (%)
Cottonwood main trunk	Raw biomass	48.5	6.0	0.7	43.0
	450	69.3 ± 4.65	3.0 ± 0.09	0.7 ± 0.30	25.3 ± 4.26
	500	74.7 ± 0.80	2.4 ± 0.24	0.4 ± 0.01	20.7 ± 0.57
	550	74.8 ±0.25	2.7 ± 3.87	0.5 ± 0.68	20.3 ± 0.06
Cottonwood branch	Raw biomass	49.0	6.1	0.8	41.4
	450	70.5 ± 0.47	2.9 ± 0.15	0.8 ± 0.05	23.0 ± 0.37
	500	74.3 ± 1.36	2.5 ± 0.04	0.8 ± 0.13	19.7 ± 1.27
	550	75.8 ± 0.17	2.5 ± 0.13	0.8 ± 0.02	18.1 ± 0.28
Cottonwood stem	Raw biomass	48.5	5.9	0.6	43.2
	450	74.4 ± 0.88	3.1 ± 0.11	0.8 ± 0.01	19.8 ± 0.98
	500	77.0 ± 0.38	2.4 ± 0.00	0.6 ± 0.00	18.2 ± 0.38
	550	77.8 ±0.24	2.3 ± 0.17	0.8 ± 0.06	17.2 ± 0.35
Switchgrass	Raw biomass	47.3	5.7	0.5	43.6
	450	65.2 ± 0.51	2.8 ± 0.52	1.0 ± 0.28	28.2 ± 0.29
	500	69.3 ± 1.30	2.4 ± 0.17	0.8 ± 0.06	24.7 ± 1.41
	550	66.8 ± 0.62	1.8 ± 0.02	0.9 ± 0.05	27.6 ± 0.69

* Calculated by difference on ash-free basis

The carbon content for cottonwood main stem reduced with increasing temperature from 32.22% at 450 °C to 31.58% at 550 °C. The unburned cottonwood branch sample has a carbon content of 48.95% almost twice (53.5%) that of the char when pyrolyzed at 550 °C – the highest reduction of all the biomasses. This significant reduction indicates that the oxygen content in the cottonwood branch biomass, which represents a major percentage of total unburned biomass CHN content, was significantly reduced by the pyrolysis process. Similarly, other biomasses exhibited a decrease, albeit lesser, in their carbon content from 450 to 550 °C with 31.8% and 33.8% for cottonwood main stem and stem products respectively. However, switchgrass showed a remarkable deviation – the pyrolysis process increased its carbon content from 47.29% unburned to 66.83% when processed to a 550 °C temperature, accounting for 41.3% increase in carbon content. This behavior connotes that the oxygen content of the switchgrass biomass, which represents most of the remaining mass in the CHN content of the unburned biomass, has depleted due to the pyrolysis process. Thus, its oxygen content reduced by 30.14% as against a remarkable increase in oxygen content for the other biomasses. This increase in carbon content is a result of the increasingly condense carbon matrix caused by the pyrolysis process [29].

3.4. Characterization of liquid fraction

The bio-oil liquid fraction was dehydrated and characterized using CHN (Table 4) and GC-MS (Table 5) analyses. The liquid products from the GC-MS spectra were analyzed to quantify the peak areas of major compound groups namely: furans, ketones, alcohols, acids, phenols, and carbohydrates. The data revealed that bio-oils obtained from all biomasses yielded high concentration of phenolic compounds, which have earlier been reported. This is because phenolics naturally occur in trees which contain high lignin content. The phenolic yields are highest in the liquids derived from cottonwood main stem and stem; this can be explained by the presence of higher lignin amounts in tree stems than other parts [51]. Sadaka et al. [34] did not report the analysis of the liquid obtained from similar biomasses at 400 °C in a conventional reactor, so no comparison can be made with respect to bio-oil quality and composition.

Table 4: CHN analysis of the change in composition of the bio-oil fractions of cottonwood main trunk, branch, stem, and switchgrass as a function of temperature.

Biomass	Temperature (°C)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen* (%)
Cottonwood main trunk	450	32.2 ± 1.59	8.4 ± 0.63	0.2 ± 0. 06	59.2 ± 1.02
	500	32.3 ± 1.97	8.7 ± 0.22	0.1 ± 0.04	58.9 ± 1.78
	550	33.1 ± 4.93	8.9 ± 1.03	0.1 ± 0.04	57.9 ± 3.95
Cottonwood secondary stems	450	29.1 ± 0.27	8.8 ± 0.48	0.1 ± 0.00	62.0 ± 0.74
	500	28.3 ± 0.69	8.3 ± 0.48	0.1 ± 0.01	63.3 ± 0.32
	550	31.7 ± 3.74	7.9 ± 0.72	0.2 ± 0.08	60.3 ± 3.91
Cottonwood branch	450	28.0 ± 1.81	9.5 ± 0.89	0.1 ± 0.01	62.3 ± 0.92
	500	22.2 ± 2.47	8.9 ± 0.07	0.1 ± 0.02	68.7 ± 2.42
	550	22.8 ± 1.87	9.4 ± 0.55	0.1 ± 0.01	67.6 ± 2.43
Switchgrass	450	28.4 ± 0.33	7.8 ± 1.13	0.9 ± 0.14	63.4 ± 0.93
	500	30.5 ± 9.28	7.9 ± 0.02	0.9 ± 0.10	60.7 ± 9.36
	550	27.6 ± 0.98	8.1 ± 0.20	1.0 ± 0.05	63.3 ± 0.96

* Calculated by difference

Table 5: Quantification of products from GC-MS analysis of the liquid fractions from cottonwood main stem (CWMS), branch (CWB), secondary stems (CWSS), and switchgrass (SG).

Biomass	CWMS			CWSS			CWB			SG		
Temperature (°C)	450	500	550	450	500	550	450	500	550	450	500	550
Furans	5.0	5.8	7.2	6.3	6.1	8.4	6.0	8.4	9.6	16.5	17.8	16.9
Ketones	5.6	9.9	2.9	6.9	8.8	3.5	8.1	4.6	8.5	5.6	5.6	3.8
Alcohols	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.8	0.0	3.9	0.0	0.0
Acids	0.0	9.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.5	0.0
Phenols	73.4	59.1	81.9	76.3	75.5	79.2	69.6	70.6	69.4	62.2	62.1	72.6
Others	16.0	15.7	8.0	10.6	9.6	8.9	16.3	12.6	12.5	11.7	13.1	6.7

3.4. Energy balance

Using the elemental analysis of each sample the specific energy content (Higher Heating Value – HHV and Lower Heating Value – LLV) was calculated for each feedstock and reaction product according to Scholze and Meyer equation above. For industry application the LHV is the relevant parameter, but for the purpose of this research the HHV is of interest and it is further discussed. The specific energy of the raw switchgrass is approximately 16.36 MJ/kg, whereas for the different parts of cottonwood is around 17.5 MJ/kg, with small variations between the different parts of the trees. The specific energy of the char (HHV) varies between 20.2 to 26.5 MJ/kg with no significant influence of the process temperature on it. This values are similar with those obtained in other studies on similar biomass [34]. Thus, the only factor influencing the total energy delivered is the char yield as a reaction product, and not its composition. The specific energy of the oil ranges between 5.9 MJ/kg to 11.5 MJ/kg. In this case the process temperature has a strong influence on the specific energy content of the oil. For example the

Cottonwood branch oil has a minimum of 5.9 MJ/kg at 500°C while at 450°C the specific energy content is about 9.8 MJ/kg.

Table 6. Specific energy content of the initial biomass and reaction products

Parameter Sample	Temperature °C	HHV (dry basis) MJ/kg	LHV (dry basis) MJ/kg	Total Energy content kJ	Energy Ratio Products / Feedstock %
Cottonwood main stem		17.304	15.95	398.74	-
Char	450	23.203	22.525	159.93	40.11
	500	24.993	24.451	183.38	45.99
	550	25.532	24.922	144.55	36.25
Oil	450	12.333	10.436	91.84	23.03
	500	12.854	10.889	104.54	26.22
	550	13.593	11.583	103.09	25.85
Cottonwood secondary stems		17.124	15.792	394.80	-
Char	450	26.064	25.364	172.47	43.26
	500	26.222	25.68	156.65	39.29
	550	26.528	26.009	153.45	38.49
Oil	450	11.357	9.369	93.69	23.50
	500	10.13	8.256	78.43	19.67
	550	11.262	9.478	92.89	23.30
Cottonwood branches		17.906	16.529	413.22	-
Char	450	23.879	23.224	155.60	39.02
	500	25.182	24.618	162.48	40.75
	550	25.978	25.414	167.73	42.07
Oil	450	11.922	9.777	87.02	21.82
	500	7.941	5.931	51.60	12.94
	550	9.064	6.941	57.61	14.45
Switchgrass		16.358	15.07	376.76	-
Char	450	21.005	20.372	156.87	39.34
	500	22.445	21.903	157.70	39.55
	550	20.211	19.805	138.63	34.77
Oil	450	9.515	7.753	65.90	16.53
	500	10.766	8.982	74.55	18.70
	550	9.605	7.776	64.54	16.19

The obtained energy (as reaction products) was refered to the input energy of the sample. As it may be noticed in Table 6 above, the main energy component of the reaction products is contained by the char (36 to 43% of the wood energy). The oil contains between 13 and 26% of the wood energy, while the rest is contained by the pyrolysis gas. The overall energy conversion efficiency (Table 7) varies between 61% - 80% depending both on feedstock and pyrolysis temperature. The values in Table # indicate that maximum energetic value is obtained from cottonwood main stem processed at 500 °C.

Table 7. Energy conversion efficiency of the process

	Temperature °C	Energy of reaction products kJ	Energy conversion efficiency %
Cottonwood main stem	450	288.57	72.37
	500	319.52	80.13
	550	289.24	72.54
Cottonwood secondary stems	450	299.37	75.83
	500	273.08	69.17
	550	283.94	71.92
Cottonwood branches	450	280.62	67.91
	500	252.88	61.20
	550	266.14	64.41
Switchgrass	450	257.97	68.47
	500	270.66	71.84
	550	241.97	64.22

4. CONCLUSION

In this study, fast batch inductive-heating pyrolysis of cottonwood main stem, stem, branch, and switchgrass were conducted in a fixed-bed induction heating system. Kinetics experiments showed that three temperatures (450, 500, and 550 °C) could be used to perform proximate and ultimate analyses on all biomasses. It was discovered that char yield and carbon content decreased with increasing temperatures for all the biomasses except for switchgrass, in which the carbon content increased as the temperature increases. The highest bio-oil yield of 39.8% was achieved by cottonwood stem at 450 ^{0}C, while the maximum bio-oil yields for cottonwood main stem (38.4%), cottonwood branch (35.6%), and switchgrass (34%) were recorded at 500 ^{0}C, 450 ^{0}C, and 450 ^{0}C respectively. Bio-oil outputs from cottonwood branch and switchgrass were significantly higher than cottonwood's stem parts because of the pyrolysis of lignin present in the latter which provide mechanical support, strength, and rigidity for the plant walls and therefore increased the bio-oil yield at a mid-range temperature of 500^{0}C, enough to extract the liquid, but not extreme to cause secondary reactions. Water content of the bio-oil yield from cottonwood main stem was the lowest, for which there was a uniform reduction of water content from 450 ^{0}C to 550 ^{0}C, as against the haphazard trend noticed for liquids from other biomasses. The GC-MS showed that for all poplar biomasses, most of the bio-oils comprised of phenolic hydrocarbons with minimal acid and alcohol content. The pronounced presence of phenols in the poplar biomasses can be explained by the presence of lignin in those parts, as compared to switchgrass with relatively lower lignin content. Rather, slightly higher content of furans was noticed in the case of switchgrass which was non-existent in bio-oils from other biomasses.

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