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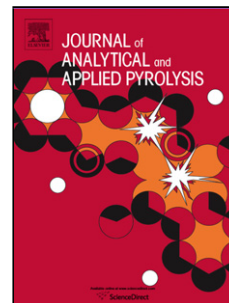
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Characterization of Bio-Oil, Syn-Gas and Bio-Char from Switchgrass Pyrolysis at Various Temperatures

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ABSTRACT

Pyrolytic conversion of lignocellulosic biomass, such as switchgrass and other agricultural residues, to bio-fuels is being considered for national energy security and for environmental advantages. Bio-oil, syn-gas and bio-char were produced and characterized from switchgrass at 400, 500 and 600 °C by pyrolysis. Bio-oil yield increased from 22 to 37%, syn-gas yield increased from 8 to 26%, and bio-char yield decreased from 48 to 25% with increases of pyrolysis temperatures from 400 to 600 °C. Bio-oil heating value was 36.3 MJ/kg, density was 920 kg/m³ and viscosity was 10 cST. GC-MS study indicated that the bio-oil contained 37% oxygenates that can be upgraded to transportation fuel in future research. Syn-gas compositional analysis shows that, with increasing pyrolysis temperature, CO₂, CO, C₂H₄ and C₂H₆ contents increased, whereas H₂ and CH₄ contents decreased. Part of the syn-gas consisting of H₂, CO and CO₂, when converted to syn-fuel, can be beneficial to the environment; sulfur free, presence of oxygenates results in less CO emissions and ozone to the atmosphere. Bio-char may be used as a co-product to enhance soil quality, and for carbon sequestration. Analysis of elemental composition and physical properties of bio-char show increase in carbon content, decrease in oxygen, hydrogen, and nitrogen content, and increase in surface area and pore volume with increases of pyrolysis temperature. The optimized pyrolysis process for bio-oil production in this study will help meet future goals of oil upgrading to produce transportation fuel.

Keywords: pyrolysis, renewable energy, bio-oil, syn-gas, bio-char, switchgrass, fuel

1. Introduction

Renewable energy from biomass has received increased interest due to the growing concerns over declining fossil oil reserves and increases in energy demand and costs [1,2]. Biomass is: energy crops used as fuel, such as fast-growing trees or switchgrass; agricultural residues and by-products such as straw, sugarcane fiber, and rice hulls; residues from forestry, construction, and other wood processing industries [3,4]. These biomass sources are considered as clean energy [5]. Biomass contains negligible amounts of nitrogen, sulfur and ash compared to conventional fossil fuels, which results in lower emissions of SO₂, NO_x, and soot than do conventional fossil fuels [6,7]. In addition, CO₂ released from biomass is resolved into plants by photosynthesis. Switchgrass (*Panicum virgatum*), a high-yielding perennial crop, has been designated as an energy biomass by the US Department of Energy because of its high biomass productivity for renewable sources of fuel and electricity generation [8–10]. Perennial grasses have various advantages over annual crops. These are: lower establishment costs [11]; reduced soil erosion [12]; increased water quality [13]; excellent conservation attributes; good compatibility with conventional farming practices [14] and enhanced wildlife habitat [15]. Also, there has been extensive research on improving switchgrass productivity, including management field trials, breeding, tissue culture and physiological or genetic modifications [9,11]. Switchgrass, being a C₄ species (plant where, CO₂ is fixed into oxaloacetate containing four carbon atoms in mesophyll cell before entering the Calvin cycle of photosynthesis) has the anatomical and physiological characteristics of C₄ grasses [16]. Therefore, it can better withstand drought, high temperature, nitrogen and CO₂ limitations, and further, low water loss by the plant allows it to grow for more than 10 yrs in an arid environment [17,18].

Pyrolysis, rapid decomposition of organic materials in the absence of oxygen, is a promising thermal approach that can be used to convert biomass into energy in the forms of liquid bio-oil, solid bio-char, and syn-gas composed of H₂, CO, CO₂ and lower molecular weight hydrocarbon gases [16,19,20]. There are various advantages of pyrolysis over other methods of energy conversion; these are drastic reduction of solid residue volume [21], carbonaceous matrices containing heavy metals are relatively resistant to

natural lixiviation [22,23], high energy value oil and gas products that can be potential fuels, and lower temperature of the process in comparison to incineration, thus limiting gas pollutants due to absence of air lowering dioxins [24]. Various pyrolysis oil combustion demonstrations have been carried out, including applications such as boilers, diesel engines, and gas turbines [25,26]. However, there are some problems with bio-oil. These are high acidity, high viscosity, high water content and high inorganic content [27-29]. There has been ongoing research on production, reactor design, pyrolysis conditions [30,31], characterization [32,33], quality improvement [34,35], utilization [36], and feasibility of bio-oil generation by pyrolysis, with the goal of using it as transportation fuel [37].

Pyrolysis co-products, bio-char and syn-gas, have many potential uses that add to the economic viability of the production of bio-oil as a fuel [38– 41]. Bio-char has several prospective applications, including enhancement of soil quality [42], sequestration of carbon to mitigate global climate change [43], improvement of soil water and nutrients retention [44], and reduction of water contamination and soil erosion [38,43]. Past studies that assessed bio-char as combustion fuel to fire the pyrolysis system [45], to treat tetracycline (TC) and chlortetracycline (CTC) used for growth promotion and therapeutic purposes in livestock production [46], and to provide energy for drying feedstock in combustors [47]. The utility of syn-gas, a co-product from biomass pyrolysis, has been demonstrated in the combined heat and power (CHP) industry [48]. Part of the syn-gas consisting of H_2 , CO and CO_2 , when converted to syn-fuel, can be beneficial to the environment; sulfur free, presence of oxygenates results in less CO emissions and ozone to the atmosphere [41]. Furthermore, through various technologies, fuels of widely varying compositions can be selectively synthesized that have high engine performance characteristics and energy efficiencies. Fischer-Tropsch synthesis [49–51] may be used to selectively convert syngas to higher molecular weight hydrocarbons using catalysts [52–54]. Depending on the pyrolysis gas composition and economics of the available catalysts, a pathway to liquid fuel can be selected.

There have been many studies of switchgrass bio-oil production by pyrolysis, reactor design, pyrolysis conditions, product characterization, and quality improvement. However, few studies have fully characterized the pyrolysis process and the products resulting from pyrolysis at different temperatures. By

characterizing the pyrolysis process and its' products (bio-oil, syn-gas, and bio-char), the chemical composition and physical behavior of bio-oil can be better understood for further upgrading studies. The objectives of this switchgrass pyrolysis study were to assess the effects of different pyrolysis temperatures on the resulting bio-oil, syn-gas and bio-char production, as well as to characterize the products, and the distribution of mass and energy of all the pyrolysis products.

2. Experimental

2.1. Biomass

Switchgrass samples provided by the Soil and Crop Sciences Department, Texas A&M University, were harvested in Pecos, Texas. Switchgrass feedstock was ground in a Wiley mill using a 2 mm screen. It had a moisture content of 8.4% prior to pyrolysis.

2.2. Feedstock characterization

National Renewable Energy Laboratory (NREL) standard biomass analytical protocol was followed for structural compositional analysis (cellulose, hemicellulose, lignin, extractives). Proximate analysis; moisture Content (MC), volatile combustible matter (VCM) and ash were determined by ASTM D 3173, ASTM E 3175 and ASTM E 1755, respectively. The balance was fixed carbon. Ultimate analysis (C, H, N, S, O) was performed using the Ultimate Analyzer Elementar, Vario Micro Cube, 15102013. Heating value was determined using the Bomb Calorimeter, Parr 6200 Calorimeter and Parr 6510 water handling system.

2.3. Pyrolysis

Pyrolysis was carried out in a Parr Instrument Co. pressure reactor. The reactor was purged with nitrogen prior to the pyrolysis runs and then filled with 360 g of switchgrass for all experiments. Pyrolysis was conducted at three temperatures; 400, 500 and 600 °C, and build pressure in the reactor was kept constant at 100 psi. The temperature of the reactor was raised at 6 °C (± 0.3)/min to the final temperatures of pyrolysis (400, 500 and 600 °C), and this heating rate was consistent for all experiments. The reaction

time was 20 min (± 3) or until no significant gas release was observed. After 20 min of retention time, temperature of the reactor was set to cool to room temperature. The oil was condensed by a chiller and was collected for further analysis. Syn-gas was measured by water displacement and was collected over time for compositional analyses. Bio-char was collected for mass and energy balance and was further analyzed. All experiments were performed in triplicate.

2.4. Product characterization

Bio-oil water content was determined by ASTM E 203 by Karl-Fischer (K-F) titration, 701 KF Titrino, Metrohm Brinkmann. Viscosity of the bio-oil was determined by ASTM D 445, using Kinematic Viscosity Bath, Koehler Instrument Company, INC. GC/MS analysis of bio-oil was performed on a Shimadzu GCMS-QP2010 Plus equipped with an Agilent 5973 mass selective detector (MSD). The GC column used was a DB-WAX 122-7032, 30-cm long with 0.25 mm ID and 0.25 μm film. The oven was programmed to hold at 45 $^{\circ}\text{C}$ for 4 min, ramp at 3 $^{\circ}\text{C}/\text{min}$ to 280 $^{\circ}\text{C}$ and hold there for 20 min. The injector temperature was 250 $^{\circ}\text{C}$, and the injector split ratio was set at 30:1. Carrier gas helium flow rate was 1 mL/min. The bio-oil samples were prepared as 10% solution in chloroform. For quantification of components, relative response factors were determined relative to the internal standard [55]. Proximate and ultimate analyses and heating value of bio-oil were determined using the protocol stated above under Feedstock Characterization.

Syn-gas samples were collected at the different pyrolysis temperatures and were analyzed on the SRI 8610 C Gas chromatograph. The columns for the syn-gas analyses were molecular sieve 13x and shin carbon ST. The detector for H_2 gas was HID and for all other syn-gas components was TCD. The oven was programmed to hold at 55 $^{\circ}\text{C}$ for 8 min, ramp at 20 $^{\circ}\text{C}/\text{min}$ up to 250 $^{\circ}\text{C}$ and hold for 15 min. Both detectors were maintained at 150 $^{\circ}\text{C}$. A mixture of standard gases was used as the internal standard for quantification.⁵⁶ The heating values from gas compositional analyses were then calculated based on higher heating values of CO , H_2 , CO_2 , CH_4 , C_2H_4 , C_2H_6 .

Bio-char from different pyrolysis temperatures were tested for their heating values and for proximate and ultimate analyses using the protocol stated under feedstock characterization. Bio-char surface area

and pore volume were measured using the Brunauer-Emmett-Teller (BET) analyzer on a Nova 4200e, Quantachrome Instrument in an automated volumetric nitrogen adsorption apparatus at 77 K. Bio-char samples were degassed at 300 °C for 12 hours before adsorption measurements.

2.5. Energy balance calculation

Energy input in to the pyrolysis system was calculated based on the biomass energy (8524 BTU/lb) and the heat energy (3.42 BTU/s) supplied to the system. Energy output was the total energy from bio-oil, syn-gas and bio-char (refer to 2.2 for heating value/energy content calculations). Further, the energy loss in the system was total energy output subtracted from total energy input.

3. Results and discussion

3.1. Feedstock characterization

Physical, elemental and structural analyses of the feedstock, switchgrass, used for all pyrolysis runs are presented in Table 1. These data were comparable to those of Boateng [45] and Adler [15]. Depolymerization and fragmentation of cellulose, hemicellulose and lignin form a multi-component bio-oil mixture; thus, structural composition is important [56]. Alkali metals contained in ash may act as catalysts for changing the depolymerization mechanisms during pyrolysis, resulting in changes in the composition of pyrolysis products [57]. However, we did not consider such catalytic behavior in this case because ash content is only 3.9%, and volatile content is high (84%) (Table 1). Low nitrogen content implies very low protein content in switchgrass. The heating value of switchgrass was 8,524 Btu/lb or 19.8 MJ/kg.

Table 1

Proximate, ultimate and structural analyses of biomass samples used for pyrolysis.

Proximate (wt%)	Switchgrass	Ultimate (wt%)	Switchgrass	Structural (wt%)	Switchgrass
Moisture	8.4	C	42	Cellulose	32
Volatile matter	84.2	H	6.1	Hemicellulose	19.2
Ash	3.9	N	0.4	Lignin	18.8
Fixed carbon	11.9	S	0.1	Extractives	18.5
		O	47.4		

3.2. Effects of pyrolysis temperature on products yields

Bio-oil, syn-gas and bio-char yields were determined at three pyrolysis temperatures; 400, 500 and 600 °C (Figure 1). With increase of the pyrolysis temperature, bio-oil and syn-gas yields increased, whereas bio-char yield decreased. Pyrolysis at 400 °C yielded 22% bio-oil and 8% syn-gas, whereas pyrolysis at 600 °C yielded 37% bio-oil and 26% syn-gas. Bio-char yield decreases from 48% at 400 °C to 25% at 600 °C (Figure 1). Pyrolysis products from oil seeds of other plants determined at different temperatures had trends similar to those obtained in this research [58]. Yang et al. [59] categorized pyrolysis in a 4-stage process where lignin degradation took place above 400 °C, while in the first 3 stages moisture evolution (<220 °C), hemicellulose decomposition (220-315 °C) and cellulose decomposition (315-400 °C) occurred. Higher temperature of pyrolysis results in higher heating rate and higher lignin degradation that may result in higher oil production [58,59]. On the other hand, increase in gaseous products at higher pyrolysis temperature of 600 °C is due to secondary cracking of the pyrolysis vapors and secondary decomposition of the bio-char [58]. A similar trend in gas production was reported in other studies [60,61]. For optimum production of switchgrass bio-oil and upgrading processes, we will pyrolyze samples at 600 °C in future research.

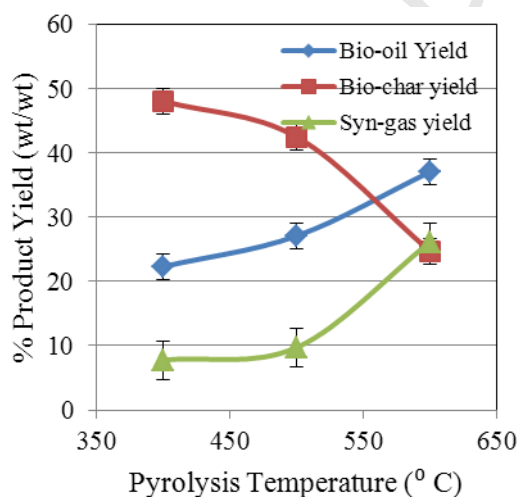


Fig. 1. Product; bio-oil, syn-gas and bio-char yields as a function of pyrolysis temperature.

3.3. Bio-oil characterization

All properties of the bio-oil are affected by feedstock variation, production processes, reaction conditions, and collecting efficiency. Elemental analysis and properties of bio-oil from switchgrass pyrolysis at 600 °C were compared with gasoline and diesel (Table 2). The bio-oil was highly oxygenated (37%), which is consistent with results of other studies that show a range of 35-40% oxygen in bio-oil [55,65]. Oxygen is distributed among various compounds, depending on the resource of biomass and conditions of pyrolysis. Presence of oxygen results in lower energy density, high acidity and immiscibility with hydrocarbon fuels [56]. Moisture content of the bio-oil was 13%, resulting from the original feedstock moisture and the product of dehydration during pyrolysis reactions [66]. NREL (National Renewable Energy Laboratory) studies showed that additional thermal cracking of bio-oil improved its chemical and vaporization characteristics, resulting in lower water content and lower molecular weight [56,66]. The viscosity of our bio-oil is 10 cST, which is comparatively higher than viscosities of gasoline or diesel (Table 2). Studies of bio-oil viscosity showed that viscosity is lowered by high water content, low water insolubles, and alcohol presence/addition [67,68]. Heating value of the bio-oil obtained in this experiment is 36.3 MJ/kg, or 15,600 Btu/lb.

Table 2

Ultimate analysis and physical properties of switchgrass bio-oil.

Ultimate Analysis	Bio-oil (%)	Gasoline[62] (%)	Diesel [63,64] (%)	Properties	Bio-oil	Gasoline	Diesel
C	50	84.5	86.6	Heating value (mj/kg)	36.3	47.3	45.5
H	9.3	13.1	13.3	Moisture content (%)	13	<0.1	<0.1
N	1.5	-	0.0065	Density (kg/m ³)	920	723	838
S	0.6	<0.0001	0.11	Viscosity (Cst)	10	0.12	2.1
O	37	Not deter.	1.8				

Composition of the bio-oil from switchgrass pyrolysis is presented as whole bio-oil that has an aqueous phase (Figure 2). Distributions of the aqueous phase, bio-oil phase and the total of the two phases show that, at 400 °C, 4% of the whole bio-oil was oil phase and 19% was aqueous phase. The percentage of the oil phase increased with pyrolysis temperature to 7% at 500 °C and 12% for 600 °C. The aqueous

phase also increased to 20% and 25% for 500 and 600 °C pyrolysis, respectively. Due to the difference in density of the aqueous phase (1100 kg/m³) and oil phase (920 kg/m³), the two phases were easily separated. Compositions were used to categorize the oil phases as alkanes (Table 3), phenols (Table 4), aromatics; indene, methyl-indene, benzene, toluene, methyl-naphthalene (Table 5), and esters, acids, alcohols, ketones and other components (Table 6). Chemical composition of the aqueous phase of the bio-oil is further presented in Table 7.

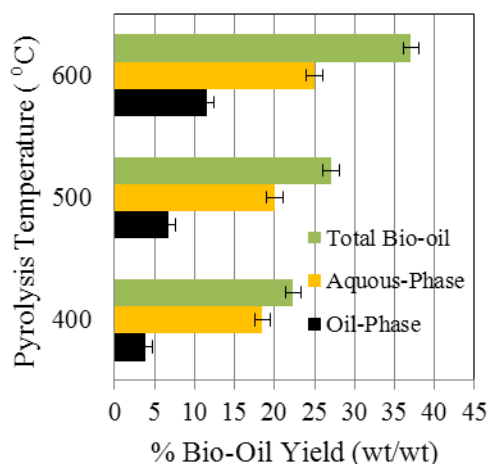


Fig. 2. Percentage of bio-oil and its aqueous phase from switchgrass at different pyrolysis temperatures.

Table 3

Branched hydrocarbon; alkanes detected in switchgrass pyrolysis oil.

Compound	%	Total %
Dodecane	7.3	
Undecane, 2,6-dimethyl-	1.3	
Octane, 3,6-dimethyl-	2.9	
Tridecane	2.6	
Dodecane, 2,5-dimethyl-	0.6	
Hexadecane, 1-bromo-	1.4	
Tridecane, 4-methyl-	0.3	
Decane, 3,8-dimethyl-	0.4	
Dodecane, 2,6,10-trimethyl-	3.5	
Cyclotetradecane	1.3	
Cyclododecane	0.3	
Dodecane, 4,6-dimethyl-	1.8	
Tridecane, 2-methyl-	0.5	
Decane, 1-bromo-2-methyl-	0.3	
Hexane, 2-phenyl-3-propyl-	0.2	

Hexadecane	8.5	
Octadecane	0.3	
Heptadecane	2.6	36.2

Table 4

Phenolic compounds detected in switchgrass pyrolysis oil.

Compound	%	Total %
Phenol, 2-ethyl-	1.5	
Phenol, 4-ethyl-	3.3	
Phenol, 3,5-dimethyl-	1.4	
2-methoxy-5-methylphenol	0.4	
Phenol, 2-1-methylethyl- acetate	1.2	
Phenol, 2,4,5-trimethyl-	1.3	
Phenol, 4-propyl-	0.6	
Phenol, 4-ethyl-2-methoxy-	6.4	
Phenol, 5-methyl-2- acetate	1.1	
Phenol, 2,6-dimethoxy-	0.9	
Phenol, 2-methoxy-4-methyl-	2.3	20.5

Table 5

Aromatics; indene, naphthalene, and toluene detected in switchgrass pyrolysis oil.

Compound	Group	%	Total %
1h-indene, 2,3-dihydro-4,7-dimethyl-		0.3	
1h-indene, 2,3-dihydro-1,1,5,6-tetramethyl-		0.4	
1-tetradecene		3.1	
3-octadecene, (e)-		0.4	
1-heptadecene		0.8	
9-eicosene, (e)-	Aromatics	0.3	
2-hexadecene, 3,7,11,15-tetramethyl		0.2	
1-decene, 3,3,4-trimethyl-		0.5	
2,4-diphenyl-4-methyl-1-pentene		0.2	
5,8-dimethylenebicyclo[2.2.2]oct-2-ene		0.7	
1,4-dihydronaphthalene		0.5	
5-octadecene, (e)-		1.2	8.8
Naphthalene, 2-methyl-		0.7	
Naphthalene, 1,2,3,4-tetrahydro-5,6,7,8-tetramethyl-	Napthalene	0.4	
Naphthalene, 1,5-dimethyl-		0.6	1.7
Toluene, 4-(1,1-dimethyl-2-propynyloxy)-		0.3	
1,1'-bicyclohexyl	Toluene	0.6	
Fluorene, 2,4a-dihydro-		0.5	1.4

Benzene, 1-ethyl-3-methyl-		1.1	
Benzene, 1,1'-[3-(3-cyclopentylpropyl)-1,5-pentanediy]bis-	Benzene	0.3	
Benzene, nonyl-		0.3	
Benzene, 1,2,3-trimethyl-		0.5	2.2

Table 6

Furans, ketones, acids, alcohols, ester and amide detected in switchgrass pyrolysis oil.

Compound	Group	%	Total %
Furfural		0.8	
2-hexanoylfuran	Furan	1.3	
Benzofuran, 4,7-dimethyl-		1.7	
Benzofuran, 2-methyl-		0.5	4.2
Cyclopentanone, 2-methyl-		1.8	
1-(3h-imidazol-4-yl)-ethanone		0.6	
Ethanone, 1-[4-(1-methylethenyl)phenyl]-		1.1	
Cyclohexanone, 4-(benzoyloxy)-	Ketone	0.3	
2-tridecanone		0.7	
2-pentadecanone, 6,10,14-trimethyl-		0.4	
Cyclopentanone, 2-ethyl-		0.2	5.1
Benzoic acid, 4-isopropenylcyclohexenylmethyl ester		0.9	
9-hexadecenoic acid, methyl ester, (z)-		0.4	
Pentadecanoic acid, 14-methyl-, methyl ester		1.1	
Pentadecanoic acid		0.6	
Oxalic acid, 2-isopropylphenyl pentyl ester	Fame/acid	2.0	
Oxalic acid, isobutyl 2-isopropylphenyl ester		1.7	
Oxalic acid, 6-ethyloct-3-yl ethyl ester		1.2	
Dodecanoic acid, methyl ester		0.5	
Acetic acid, trichloro-, nonyl ester		0.3	8.7
Mequinol		0.4	
Thymol		1.0	
Benzenepropanol, 2-methoxy-		0.8	
1-dodecanol, 3,7,11-trimethyl-	Alcohol	2.9	
3,7,11,15-tetramethyl-2-hexadecen-1-ol		0.3	
1h-benzimidazole, 5,6-dimethyl-		0.8	
Benzeneethanol, .alpha.-methyl-		0.7	
3-buten-2-ol, 4-phenyl-		0.5	7.4
Isodecyl methacrylate	Ester	1.9	
Methyl n-isopropyl-3-phenylpropanimidate		0.6	2.4
Acetamide, 2-(1-naphthyl)-n-(3,4-methylendioxybenzyl)-	Amide	1.5	1.5

Table 7

Compounds detected in aqueous phase of bio-oil from switchgrass pyrolysis.

Compounds	Group	%
2-propanone	Ketone	13
Acetic acid, methyl ester	Ester	8.1
2,3-butanedione	Ketone	2.8
2-butanone	Ketone	17
Furan, tetrahydro-	Furan	4.5
2-pentanone	Ketone	3
Acetic acid	Acid	28
2-propanone, 1-hydroxy-	Ketone	1
Pyridine	-	0.8
Cyclopentanone	Ketone	2.6
2-furancarboxaldehyde	Aldehyde	6.6
Cyclopentanone, 2-methyl-	Ketone	1.5
2-cyclopenten-1-one, 2-methyl-	Ketone	1.6
5-decene	Alkene	1.1
Cyclopentane, 1,1,3-trimethyl-	Alkane	1.3
4-nonene, 5-methyl-	Alkene	1.0
1-decene	Alkene	1.1
Phenol, 2-methyl-	Phenol	1.5
Phenol, 2-methoxy-	Phenol	3.2

Bio-oil from switchgrass is composed of a complex mixture of alcohols, esters, ketones, lignin-derived phenols, long-chain alkanes, aldehydes, fatty acid methyl esters, furans, naphthalene, amides, and various aromatics (Tables 3, 4, 5, 6). The GC-MS analysis of the switchgrass bio-oil from this research shows that its composition is similar to switchgrass bio-oil analyzed by Wang and Guo [69,70]. Many of the components identified are phenols and long chain hydrocarbons, and most functional groups show presence of oxygen. Analyses of bio-oil and the aqueous phase are grouped into various hydrocarbon groups to clarify chemical properties and to upgrade products for future research. The results show: 36% branched and long-chains alkanes (Table 3); 20% methyl, methoxy and propenyl attached phenols (Table 4); 14.1% aromatics (indene, methyl-indene, benzene, toluene, methyl-naphthalene, Table 5); 8.7% mixed acids and methyl ester fatty acids (Table 6); 7.4% methyl, methoxy attached alcohols (Table 6); and the rest mostly are furans, and ketones. The complex mixture of switchgrass bio-oil from this research is comparable to that of Peng's study of bio-oil [71].

Table 7 shows the distribution of some detected compounds in the aqueous phase of the bio-oil from switchgrass pyrolysis. This aqueous phase is comprised mainly of acetic acid (28.2%) and various branched ketones (42%), small amounts methyl and methoxy phenols (4.7%), and minor aromatic hydrocarbons. Presence of abundant aldehydes and ketones (Table 7) make this aqueous phase of the oil hydrophilic [56] and highly hydrated, which makes it difficult to eliminate water from the bio-oil.

3.4. Syn-gas characterization

Total produced syn-gas increased from 8% at pyrolysis temperature of 400 °C to 26% at pyrolysis temperature of 600 °C (Figure 1). Syn-gas composition varied with pyrolysis temperature (Table 8). With an increase in temperature, CO₂, CO, C₂H₄ and C₂H₆ contents increased, whereas H₂ and CH₄ contents decreased. Similar trends for CO and CO₂ were shown in the Baker et al. study [72], where the increase in CO and CO₂ was explained by the oxidation of the carbonized bio-char at higher temperatures of pyrolysis [10,72]. In their study, other components of the syn-gas had no significant variations in abundance with increasing pyrolysis temperature [72].

Table 8

Syn-gas composition as a function of pyrolysis temperature, determined by GC.

Pyrolysis T (°C)	H ₂ (%)	CO (%)	CH ₄ (%)	CO ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)
400	28.0	21.7	39.2	9.1	1.2	0.8
500	25.4	21.5	39.4	9.4	2.3	1.9
600	9.7	27.7	17.6	33.2	4.3	7.0

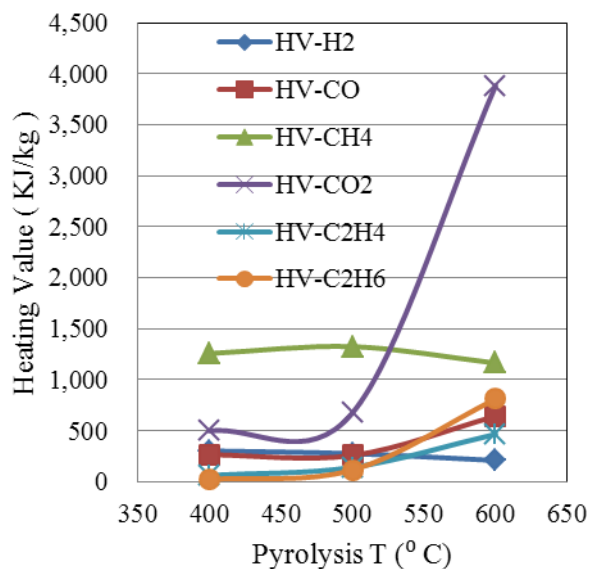


Fig. 3. Heating value of syn-gas as a function of pyrolysis temperature.

Syn-gas heating values were analyzed based on the standard heating values from combustion of common fuel gases reported in the Engineering Handbook (http://www.engineeringtoolbox.com/heating-values-fuel-gases-d_823.html). Heating values of our gas samples varied with gas compositions that, in turn, resulted from different pyrolysis temperatures. Heating values of gases increased as the contents of C_2H_6 , CO, and C_2H_4 increased (Figure 3). There was a decrease in CH_4 and H_2 production with increasing pyrolysis temperature (Table 8), causing decrease in the heating values from these gases. At the higher temperature of 600 °C, more C and CO were oxidized to CO_2 , causing the C to CO_2 conversion heating value to increase relative to the lower temperatures of 400 and 500 °C. This is shown by higher CO_2 production at 600 °C compared to 400 and 500 °C (Table 8).

3.5. Bio-char characterization

Bio-char yield from switchgrass pyrolysis decreased from 48% to 43% from samples pyrolyzed at 400 and 500 °C, respectively; the bio-char yield decreased markedly from 43% to 25% between samples pyrolyzed at 500 and 600 °C, respectively (Figure 1). Proximate analyses of bio-chars from different pyrolysis temperatures are characterized in Figure 4, and ultimate analyses of bio-char are presented in Table 9. The volatile content of bio-char decreases from 20% to 17.8% for samples pyrolyzed at 400 and

500 °C, respectively; volatile content further decreases to 8.2% for samples pyrolyzed at 600 °C. Fixed carbon content is approximately 70% for samples pyrolyzed at 400 and 500 °C, but it increases to 79% for samples pyrolyzed at 600 °C. Ash content increases slightly with increasing pyrolysis temperature (Figure 4). This can be explained by higher pyrolysis temperature removing greater percentages of volatiles.

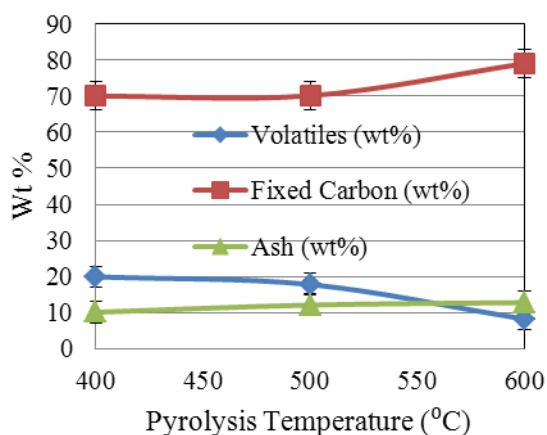


Fig. 4. Proximate analyses of bio-char at various pyrolysis temperatures.

Char elemental analysis shows that carbon content increased, whereas oxygen and hydrogen contents decreased with increasing pyrolysis temperature (Table 9). A similar trend was reported by Onay [58]. Losses in hydrogen and oxygen are explained by breaking of weaker bonds within bio-char's structure and the bio-char becoming highly carbonaceous at higher pyrolysis temperatures [58,73]. The heating values of bio-char increased slightly with an increase in pyrolysis temperature (Table 9). This may be due to the slight increase in the carbon content in bio-char with increased temperature.

Table 9

Elemental composition, heating value, surface area and total pore volume of bio-char.

Pyrolysis T (°C)	C (%)	H (%)	N (%)	O (%)	S (%)	HV (MJ/kg)	Surface area (m ² /g)	Pore volume (cm ³ /g)
400	75.2	4.9	1.9	17.7	0.3	28.9	0.1	0.6
500	78.3	3.6	1.3	16.5	0.3	29.0	0.9	0.7
600	82	2.4	1.2	14.1	0.3	29.4	1.0	0.7

The reactivity and combustion behavior of bio-char are strongly affected by surface area [58]. With an increasing pyrolysis temperature from 400 to 600 °C, the surface area of the char increases from 0.1 to 1.0 m²/g (Table 9). Higher pyrolysis temperature causes higher devolatilization, resulting in more pore volume in the samples and, in turn, greater surface area for reaction or adsorption activities [58,74]. The total pore volume per gram of sample also increases with temperature (Table 9). These trends of increased porosity and surface area with increased temperature of pyrolysis are consistent with results reported in other studies [74–76].

3.6. Pyrolysis products mass balance and energy distribution

Product distributions differ with pyrolysis temperatures (Figure 5). Product recovery increases with (loss is least) with increasing temperature: 88% at 600 °C; 80% at 500 °C; and 78% at 400 °C. The mass loss may have been from the non-condensable gases or from incomplete bio-oil recovery during collection. The percentages of produced bio-oil and syn-gas increase with higher pyrolysis temperature, at the expense of bio-char (Figure 5). Agblevor et al. [27] showed 7.4% mass loss for fluidized bed pyrolysis of switchgrass, and Mullen et al.[44] reported 19 to 26% mass loss, where the loss was mostly unused biomass remaining in the tubing and piping of the pyrolyzer. In comparison, in this study mass loss varied from 12% - 22%. Lee [10] further explained low heating rate (10 °C/min) close to the heating rate of this research (6 °C/min) resulted in lower mass loss versus higher heating rates of more than 10 °C/min.

Figure 6 shows the energy distribution of the pyrolysis products and energy losses in the system at different pyrolysis temperatures. Energy loss was the lowest at the highest temperature (600 °C), which may be due to the higher energy value from the greater amount of bio-oil and syn-gas production in comparison to the pyrolysis at lower temperatures (400 and 500 °C). The energy value of the produced syn-gas increases from 11% to 13% and finally to 28% with increasing pyrolysis temperature (Figure 6). Since bio-oil production increases significantly with pyrolysis temperature, the energy content of bio-oil at 600 °C is significantly higher (47%) in comparison to energy content for oils from switchgrass pyrolyzed at 400 and 500 °C (33% and 39%, respectively). Mullen et al. [44] showed an energy loss of

25%, which was explained as reactor heat loss and energy lost from the condenser, while Boateng et al. [45] reported 18% energy loss from heat losses from the input energy.

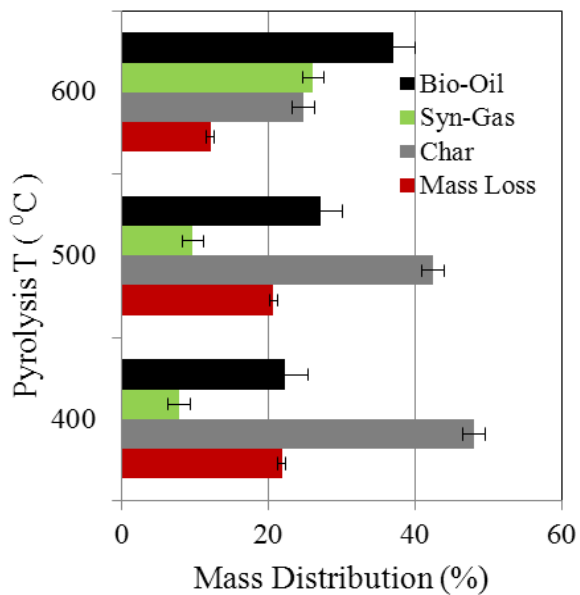


Fig. 5. Product distribution for different pyrolysis temperatures.

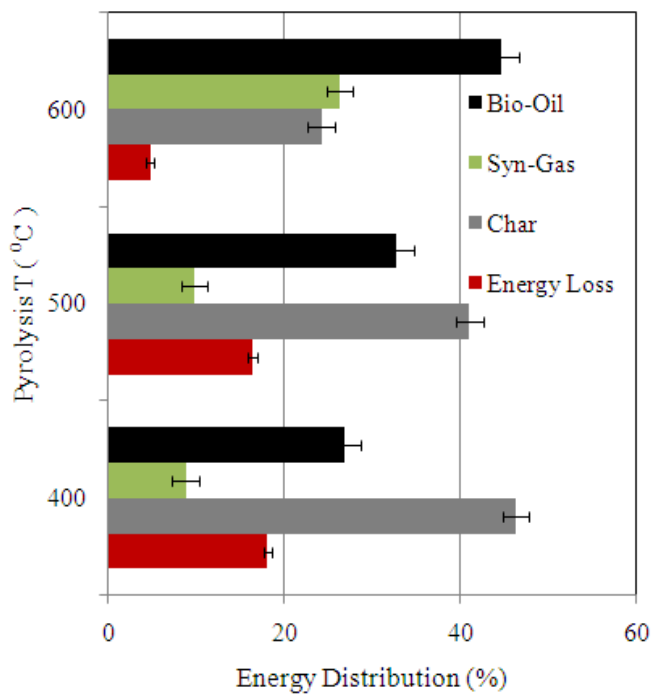


Fig. 6. Energy distribution for different pyrolysis temperatures.

4. Conclusions

Bio-oil and syn-gas yields increase, whereas bio-char yield decreases with increasing temperature of pyrolysis. From pyrolysis at 600 °C, product yield was 37% bio-oil, 26% syn-gas and 25% bio-char. However, at 400 °C pyrolysis, product yield was 22% bio-oil, 8% syn-gas and 56% bio-char. Efficiency of pyrolysis improved with the pyrolysis temperature; product yield increased from 78% at 400 °C to 88% at 600 °C.

The bio-oil was highly oxygenated (37%). It had a heating value of 36.3 MJ/kg. Viscosity of the bio-oil was 10 cST, which is comparatively higher than viscosities of gasoline (0.12) or diesel (2.1). The oil phase is a complex mixture of hydrocarbons; alkanes, phenols, aromatics, acids, alcohols, and ketones, and the aqueous phase is comprised mainly of branched ketones and acetic acid. For syn-gas, heating values of CO, C₂H₄, C₂H₆, and C to CO₂ conversion increase, whereas heating values of H₂ and CH₄ decrease at higher temperature, owing to decrease in the volumes of the latter products produced at higher temperatures. This is due to the compositional variations of the syn-gas components; CH₄, and H₂ production decreases whereas CO, CO₂, C₂H₄ and C₂H₆ production increases with pyrolysis temperature. The fixed carbon increased and volatile matter content of bio-char decreased with increasing temperature of pyrolysis. Bio-char surface area increased from 0.1 m²/g at 400 °C to 1.0 m²/g at 600 °C pyrolysis.

From pyrolysis at 400 °C, energy distribution was 33% from bio-oil, 11% from syngas and 56% from bio-char; energy distribution from pyrolysis at 600 °C was 47% from bio-oil, 28% from syn-gas, and 25% from bio-char. Because bio-oil and syn-gas yields are significantly greater from switchgrass pyrolysis at high temperature, we will pyrolyze samples at 600 °C in future research to optimize production of bio-oil and to upgrading pyrolysis processes.

This research advances understanding of products and mass balance from pyrolysis of switchgrass, a renewable energy source that is readily available globally. Bio-oil, syn-gas, and bio-char are important products of pyrolysis in terms of energy supply and the environment concerns. Biomass may be considered a viable, renewable energy source when used in an integrated process where all three pyrolysis products are marketed to maintain sustainable development and improve project economics.

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Highlights

1. Bio-oil and syn-gas yields increase, whereas bio-char yield decreases with increasing temperature of pyrolysis. From pyrolysis at 600 °C, product yield was 37% bio-oil, 26% syn-gas and 25% bio-char. However, at 400 °C pyrolysis, product yield was 22% bio-oil, 8% syn-gas and 56% bio-char.
2. Efficiency of pyrolysis improved with the pyrolysis temperature; product yield increased from 78% at 400 °C to 88% at 600 °C.
3. The bio-oil was highly oxygenated (37%). It had a heating value of 36.3 MJ/kg. Viscosity of the bio-oil was 10 cST, which is comparatively higher than viscosities of gasoline (0.12) or diesel (2.1).
4. The oil phase is a complex mixture of hydrocarbons; alkanes, phenols, aromatics, acids, alcohols, and ketones, and the aqueous phase is comprised mainly of branched ketones and acetic acid.
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6. From pyrolysis at 400 °C, energy distribution was 33% from bio-oil, 11% from syngas and 56% from bio-char; energy distribution from pyrolysis at 600 °C was 47% from bio-oil, 28% from syn-gas, and 25% from bio-char.