EFFECTS OF TORREFACTION AND DENSIFICATION ON DEVOLATILIZATION KINETICS AND GASIFICATION PERFORMANCE OF SWITCHGRASS

By

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“UNLESS EXPRESSED, GRATITUDE IS INCOMPLETE”

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Abstract:

The overall goal of this research was to investigate effects of pretreatments (torrefaction at 230 and 270°C, densification, and combined torrefaction and densification) on biomass properties, devolatilization kinetics and gasification performance of switchgrass. Devolatilization kinetics was determined at three heating rates (10, 30 and 50°C min^{-1}) in inert (nitrogen) and oxidizing (air) atmospheres using a thermogravimetric analyzer. Gasification performance were evaluated at three gasification temperatures (700, 800 and 900°C) using an externally-heated fixed-bed reactor with air at an equivalence ratio (ER) of 0.3. Devolatilization study showed that switchgrass torrefied at 270°C had the highest carbon (C) and the lowest hydrogen (H) and oxygen (O) contents (59.16, 4.67, and 34.53% d.b., respectively). This resulted in the lowest atomic O/C (0.44) and H/C (0.95) ratios and the highest higher heating value (27.11 MJ kg^{-1}, d.b.). Combined torrefaction and densification of switchgrass resulted in the least volatile and the highest ash and fixed carbon contents (62.63, 5.91, and 31.45% d.b., respectively). Combined torrefied and densified switchgrass had the highest rate of devolatilization in both atmospheres as evidenced by the largest rate of weight loss peaks (34 and 44 mg min^{-1} in inert and oxidizing atmospheres, respectively), the lowest start and end temperatures of the rate of weight loss peak (250-300 and 230-310°C in inert and oxidizing atmospheres, respectively). Gasification study showed that bulk density of combined torrefied and densified switchgrass was the highest (598.17 kg m^{-3}, d.b.) requiring less space to store and transport. Pretreatments of switchgrass and gasification temperatures had significant effects on gasification performance. Among all pretreatments, gasification of combined torrefied and densified switchgrass resulted in the highest yields of H_2 (0.03 kg/kg biomass) and CO (0.72 kg/kg biomass), highest syngas LHV (5.08 MJ Nm^{-3}), CCE (92.53%), and CGE (68.40%) at the gasification temperature of 900°C, which show that combined torrefaction and densification significantly improved gasification performance of switchgrass.

Keywords: Torrefaction, densification, switchgrass, devolatilization, heating rates, kinetics, gasification, gasification temperature, gas yields, gasifier efficiencies

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INTRODUCTION

Gasification and pyrolysis are two major thermochemical processes for converting biomass into fuels (syngas) and chemicals (ethanol, methanol). Gasification, through partial oxidation, converts carbonaceous compounds such as biomass into a gas mixture called syngas whereas pyrolysis, in an inert atmosphere, results in primarily a liquid product, called bio-oil. Uncontrolled variation in moisture, fibrous structure, non-uniform particle size and low bulk density of biomass adversely affects the transportation logistics, storage and handling. Pretreatment of biomass by torrefaction (roasting process at temperatures ranging between 200-300°C in an inert atmosphere) results in a hydrophobic product with higher carbon content and calorific value, whereas pretreatment by densification (drying and pressing of biomass under high pressure to produce cylindrical pellets) results in more uniform product with higher bulk density. Combining torrefaction and densification has potential to make biomass uniform and hydrophobic with low oxygen and high carbon contents, and high bulk and energy densities that might increase the heating value and yield of syngas and decrease the cost of transportation, storage and handling of biomass.

Switchgrass has been identified as one of the biomass energy feedstocks in the US, to reduce our dependency on fossil fuels. It is a perennial grass grown in North America and has a high yield of 4-7 tons/acre (Ragan and Kenkel, 2007). Thermochemical biomass gasification involves moisture removal through drying followed by formation of volatiles through devolatilization (or pyrolysis) and formations of final syngas, char and tars through several multiphase reactions. During devolatilization, biomass breaks down into volatile matter in an inert atmosphere. The study of devolatilization kinetics of the pyrolysis and gasification reactions is essential to predict chemical transformation of solid feedstocks into gaseous products and optimize overall process efficiency. Devolatilization kinetics of switchgrass with five pretreatments (raw, torrefied at 230 and 270°C, densified, combined torrefied and densified) were investigated using a thermogravimetric analyzer in inert (nitrogen) and oxidizing (air) atmospheres (Chapter II). The effects of pretreatments and heating rates on the weight loss and rate of weight loss with respect to temperature were evaluated. The parameters of the devolatilization reaction kinetics such as pre exponential factor (A), activation energy (E), the order of the reaction (n) and the rate constant (k) were determined based on the Arrhenius equation. The effects of biomass pretreatments and heating rate on proximate and ultimate analyses and energy content were also evaluated. The goal of chapter III was to evaluate the effect of pretreatments on the performance parameters of gasification such as syngas yield, higher heating value of dry gas, and the gasifier efficiencies. Switchgrass with five pretreatments (raw, torrefied, densified, torrefied and densified) were gasified at three temperatures of 700, 800 and 900°C with air as the oxidizing agent.

The overall goal of this research was to investigate how advanced pretreatments of switchgrass affect its properties and gasification performance. The specific objectives were to:

1. Investigate the effects of pretreatments (torrefaction and densification) on thermal devolatilization characteristics of switchgrass in inert (nitrogen) and oxidizing (air) atmospheres,
2. Investigate the effect of heating rates on the devolatilization reaction kinetics, and
3. Investigate the effects of pretreatments (torrefaction and densification) and reactor temperatures on gasification performance of switchgrass.

CHAPTER II

DEVOLATILIZATION KINETICS OF SWITCHGRASS PRETREATED WITH TORREFACTION AND DENSIFICATION

Abstract

Pretreatment of switchgrass by torrefaction or densification can improve its physical and chemical characteristics by making it hydrophobic, increasing the bulk density and energy content and improving ability to store and transport. The goal of this study was to investigate the effects of four pretreatments (torrefaction at 230, torrefaction at 270°C, densification, and combined torrefaction and densification) and heating rates on the thermal devolatilization characteristics of switchgrass and its reaction kinetics in both inert and oxidizing atmospheres. The thermal devolatilization characteristics of biomass were determined using a thermogravimetric analyzer. Torrefaction of switchgrass increased its carbon content and higher heating value but decreased hydrogen and oxygen contents. These effects increased with increase in torrefaction temperature from 230 to 270°C. However, the rate of devolatilization of switchgrass torrefied at 230°C was higher than that of switchgrass torrefied at 270°C in both inert and oxidizing atmospheres. The weight loss of switchgrass occurred in three stages in both inert and oxidizing atmospheres. In both atmospheres at a heating rate of 50°C min^{-1}, switchgrass pretreated with combined torrefaction and densification showed the highest rate of weight loss peak (34 and 44 mg min^{-1} in inert and oxidizing atmospheres, respectively), the lowest start and end temperatures of the rate of weight loss peak (250-300 and 230-310°C in inert and oxidizing atmospheres, respectively). Overall, in both inert and oxidizing atmospheres, switchgrass pretreated with combined torrefaction and densification had the highest rates of devolatilization followed by switchgrass pretreated with densification, switchgrass with torrefaction at 230°C, switchgrass with torrefaction at 270°C, and raw switchgrass. Heating rate also had significant effects on the weight loss and rate of weight loss of switchgrass but did not have any significant effect on the start and end temperatures of the rate of weight loss peaks.

Keywords. Pretreatment, switchgrass, torrefaction, densification, reaction kinetics, thermogravimetric analyzer

1. Introduction

Combustion of fossil fuels such as coal, petroleum and natural gas results in carbon dioxide (CO_2) emissions into the atmosphere, leading to global warming (Jeguirim et al., 2010). Unlike fossil fuels, biomass is a renewable energy source because carbon dioxide released during use, is recycled through photosynthesis for biomass production in short duration (Biagini et al., 2006; Biswas, 2011; Chen et al., 2012). Switchgrass, a perennial grass native to the prairies of North America, has emerged as an ideal biomass to produce biofuels because of its high yields of about 15 Mg ha^{-1} (Sokhansanj et al., 2009), environmental benefits such as a 95% reduction in soil erosion and 90% reduction in pesticide and fertilizer usage (Kasi David, 2010). Switchgrass can grow on degraded soil and has the ability to accumulate carbon in the soil and restore the soil fertility (Mead, 2011; Scott, 2010). However, similar to other biomass, properties of switchgrass such as low energy and bulk densities, and high moisture content create challenges for storage, transportation and conversion into final fuels, chemicals and power (Karunanithy et al., 2012).

Pretreatments such as torrefaction and densification can be used to improve properties of switchgrass because pretreatments can break down the biomass lignin structure and disrupt the cellulose structure rendering the biomass more accessible to be pyrolyzed (Yang et al., 2010). Torrefaction, a roasting of biomass at temperatures between 230 and 300°C in an inert atmosphere, improves its physical and chemical properties by making the biomass hydrophobic (Chen and Kuo, 2011b) and increasing energy density (Prins et al., 2006b), which makes the biomass more suitable to store for longer duration and transport (Chen and Kuo, 2011a). Densification converts loose biomass into pellets having more uniformity and higher bulk density that can possibly solve challenges in storing and transporting biomass (Karunanithy et al., 2012). The pellets formed have more uniform shape and size, and high bulk density that require less space for storing and transporting (Karunanithy et al., 2012). Hence, biomass pretreatments can reduce the cost of biomass storage and transportation logistics. A combination of torrefaction and densification may provide additional benefits by increasing both the bulk and energy densities while making biomass hydrophobic.

Gasification and pyrolysis are two major thermochemical processes for converting biomass into fuels and chemicals. Gasification converts carbonaceous feedstocks such as biomass into primarily a gaseous product, called syngas or producer gas, in a partial oxidizing atmosphere at a high temperature ranging from 500°C to 1400°C and at a pressure ranging from atmospheric pressure to 33 bar (Morrin et al., 2012; Ruiz et al., 2013). Pyrolysis results in primarily a liquid product, called bio-oil, in an inert atmosphere at high temperature ranging from 700°C to 1500°C and at a pressure ranging from atmospheric pressure to 150 bar (Biswas, 2011; Cai et al., 1996). To understand the chemical transformation of solid feedstocks into gaseous and liquid products, understanding the kinetics of biomass devolatilization reactions is critical (Damartzis et al., 2011).

Thermogravimetric analysis is one of the most commonly used techniques to determine the thermal degradation of biomass. The analysis provides information about the gasification and pyrolysis decomposition profile of the biomass and the associated reaction kinetics. The weight loss of sample is recorded with respect to temperature and time under controlled heating rates and defined gas atmospheres (inert or oxidizing). The occurrence of thermal degradation of biomass is due to a pyrolysis or combustion process depending on the atmosphere (inert or oxidizing) in which it occurs. The derivative thermo gravimetric (DTG) curves or rate of weight loss curves are derived from the weight loss (TG) curves and are used to determine the kinetic parameters such as the order of the reaction, pre exponential factor and the activation energy. The TG analysis has been used to determine the thermal characteristics of Miscanthus Straw under inert atmosphere (Jeguirim et al., 2010) and to determine the reaction kinetics of corn stover in inert and oxidizing atmospheres at different heating rates (Kumar et al., 2008). An insight into the isothermal kinetics of torrefied biomass was provided by Chen et al. (2011a) who developed a model to predict the thermal decomposition of the hemicellulose (from Aspergillus niger), cellulose, lignin and xylan (from Beechwood). Carter et al. (2012) analyzed the pyrolysis and combustion characteristics of raw and torrefied pine, sweetgum and switchgrass and concluded that the torrefaction increased the rate of weight loss indicated by increased height of the DTG peak. The pyrolysis of secondary refuse fuel briquettes and biomass materials was modeled and characterized by Liu et al. (2012). However, there is no literature available on the kinetics of switchgrass pretreated with torrefaction and densification.

The specific objectives of this study were to investigate the effects of torrefaction and densification pretreatments on thermal devolatilization characteristics of switchgrass in inert (nitrogen) and oxidizing (air) atmospheres, and to investigate the effect of heating rate on the devolatilization reaction kinetics.

2. Materials and methods

2.1 Materials

2.1.1 Biomass feedstock

Kanlow Switchgrass (*Panicum Virgatum)* grown at the Plant and Soil Sciences department at Oklahoma State University was used as the biomass. Bales of Kanlow switchgrass were chopped using a Haybuster tub grinder (H1000, Duratech Industries International Inc. Jamestown, N.D) with a screen size of 25 mm. The chopped switchgrass was then ground using a hammer mill (Bliss Industries, Ponca City, Oklahoma) with a mesh size of 4 mm and sent to INL (Idaho National Laboratory, Idaho Falls) for torrefaction and densification.

2.2 Methods

2.2.1 Torrefaction

A moving-bed gravity-fed atmospheric pressure thermal treatment system was used to torrefy switchgrass (Fig. 1). It consisted of horizontal auger-driven sections to feed material into and out of a vertical, central reactor with diameter and height of 0.305 and 1.68 m, respectively. The details and schematic of the torrefaction unit can be found elsewhere (Westover et al., 2013). The ground switchgrass was weighed and manually loaded into the feeder hopper. Biomass was then metered into the torrefaction reactor through a rotary airlock and a horizontal auger rotating at 0.4 RPM. The exterior of the reactor was heated using band heater and the biomass temperature was monitored at six different points along the reactor section. A stirrer was provided in the reactor to help prevent bridging of particles. Biomass samples were torrefied for 30 min at temperatures of 230 and 270°C. Torrefied biomass exited at the reactor bottom and was removed via a horizontal auger that cooled the material to about 50°C before it exited through the twin knife-blade air locks. The residence time of the material in the torrefaction reactor can be controlled between 15 min to 1 hr by adjusting the speed of the out-feed auger. An inert environment was maintained in the reactor by injecting clean nitrogen gas (heated to the desired torrefaction temperature of 230 and 270°C) into the sides and bottom of the vertical thermal section. The inert gas, combined with process off-gas exited from the thermal unit at the upper end in a counter flow configuration. The gas was then passed through a heated cyclone separator to remove the particulates and then to a thermal oxidizer to burn the combustibles. After exiting the thermal oxidizer, the gas stream passed through an enlarged knockout vessel that provided velocity reduction and slight cooling to allow condensable constituents to drop out of the steam for separate collection. The gas was then reheated prior to recycling into the reactor. The cooled torrefied material collected was stored in air tight barrels.

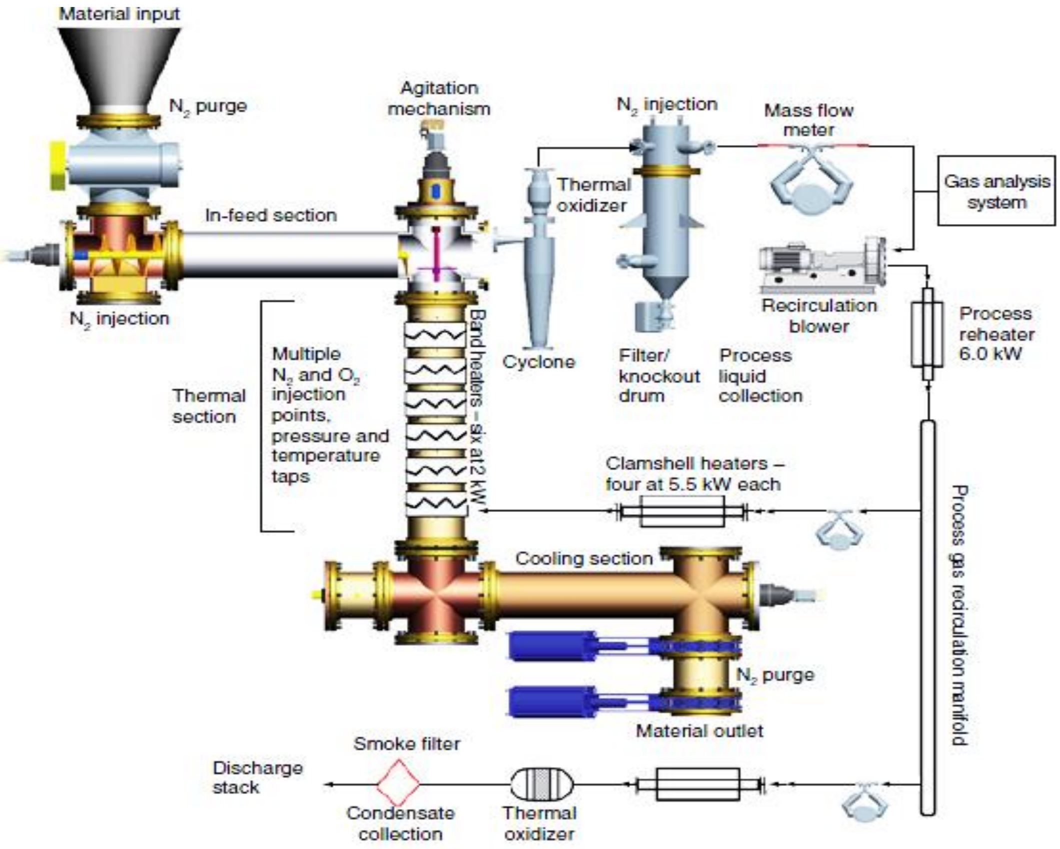

Figure 1. Torrefaction system (adopted from Westover et al., 2013)

2.2.2 Densification

A laboratory-scale flat-die pellet mill (model ECO-10, Colorado Mill Equipment) with a 10 HP, 460-volt, 3-phase motor was used for the pelletization (densification). This machine has been designed for research and development applications for testing the pelletability of variety of raw and pretreated biomass. The rated output of this pellet mill was 30–50 kg/hr. The pellet mill was equipped with a hopper to hold the biomass and a screw feeder to uniformly feed biomass into the pellet mill. A flexible rectangular heater (Silicon Rubber Heater, Branom Instrument, WA) and a flexible tape heater (Briskheat Xtremeflex grounded heavy-insulated heating) with J-type thermocouples and controllers (Model 96A-FDAA-00RG, Watlow, USA) were used to maintain a constant temperature of 70°C in the hopper and feeder, respectively. A variable frequency drive (model Altivar 71, variable-frequency AC motor driver) was used to control the rotational speed of the pellet mill die maintained at 110°C. Further details of the mill can be found in Tumuluru et al., (2011a).

For pelletization of raw chopped switchgrass, moisture was added to the biomass to make it 26% (w.b.) moisture content and commercial corn starch was added as a binder with quantity of 2% by weight of the original sample. The biomass, moisture and binder were mixed for 30 min in a ribbon blender (RB 500, Colorado Mill Equipment, Cañon City, CO). The mixed biomass was stored in cold storage, at about 4°C. For pelleting torrefied biomass, commercial corn starch with quantity of 5% by weight of the original biomass and a biobased lubricant (product number CGL8000 with 99% soyseed oil and 1% molybdenum, Green Cold Lubricants LLC, Colorado Springs, CO) with quantity of 2% by weight of the original biomass were used. Moisture was added to increase the original biomass moisture content to 26% (w.b.). The feeding was carried out uniformly at about 10–12 kg/hr to ensure that there were no flow irregularities inside the pelletizer. Following the cooling step, pellets were further dried in a mechanical oven at 60–65°C for about 3–4 hours to reduce the moisture to safe storage levels of about 5-7% (w.b.).

2.2.3 Proximate and ultimate analyses

Proximate analysis (contents of moisture, volatile, ash and fixed carbon) of biomass sample was determined using a furnace (model 3-550A, Dentsply Prosthetics, PA). The moisture, volatile and ash contents were determined following ASAE standard S358.2 (ASABE Standards, 2006), ASTM D3175 and ASTM E1755-01 respectively. The fixed carbon content was determined by subtracting the volatile and ash contents from the total biomass on dry basis. The ultimate analysis of biomass was measured using an elemental analyzer (PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, Shelton, CT) at Kansas State University.

The Higher Heating Value (HHV) of biomass was measured using an adiabatic Parr 6200 Bomb Calorimeter (model A1290DDEB, Parr Instrument Co., Moline, Ill). Biomass sample (0.5 g) was pelletized using a pellet press and the pellet was kept in a nickel crucible and burned inside a bomb calorimeter surrounded by a water jacket. The sample was ignited by a 10 cm length aluminum wire in the presence of oxygen. The wire was placed in such a way that only the tip touched the pellet. Upon ignition, the released heat transferred to the water jacket causing temperature to rise. The increase in temperature was used to calculate HHV of the sample. The HHV measurements were done three times and the average value was reported.

3. Experimental design and statistical analyses

A full factorial experimental design was used with two factors: switchgrass pretreatment and heating rate of devolatilization. Five levels of switchgrass pretreatment were (i) no pretreatment (raw switchgrass), (ii) torrefaction at 230°C, (iii) torrefaction at 270°C, (iv) densification and (v) combined torrefaction and densification (torrefaction at 270°C followed by densification). Three levels of heating rates were 10, 30 and 50°C min^{-1}. All experiments were replicated three times.

The effects of pretreatment and heating rate on the weight loss profiles during thermal devolatilization, and the effect of pretreatment on the proximate and ultimate analyses and HHV of switchgrass were analyzed using SAS by analysis of variance (ANOVA) and Duncan multiple range tests at the level of statistical significance, alpha, equal to 0.05.

4. Thermogravimetric analysis and determination of kinetic parameters

The devolatilization of biomass with temperature was performed in a thermogravimetric analyzer (model: Versa Therm, ThermoFischer Scientific, USA). The samples for TGA were prepared according to ASTM D2013-86. Approximately 20 mg of sample was placed in a platinum crucible. Small sample size was preferred to increase uniformity of sample temperature, and diminish mass and heat transfer limitations (Ghaly and Ergudenler, 1991; Jeguirim et al., 2010). The biomass samples were heated from ambient temperature to 1000°C at the three heating rates. Nitrogen and air were used for inert and oxidizing atmospheres, respectively, at a flow rate of 60 ml min^{-1}. Weight loss (g), the percentage of the weight loss (%) and rate of change in weight with respect to time (dw/dt) and temperature (dw/dT) were obtained. All experiments were replicated.

The parameters of the devolatization reaction kinetics such as pre – exponential factor, A (s^{-1}), activation energy, E (KJ mol^{-1}), and the order of the reaction, n, were determined using procedures similar to the those used by Kumar et al. (2008) for corn stover, Jeguirim et al. (2009) for arundo donax, Munir et al. (2009) for cotton stalk, sugarcane bagasse and Shea meal, and Pasangulapati et al. (2012) for switchgrass, cellulose, hemicellulose, and lignin. The region with highest peak of rate of weight loss was considered as the devolatization region. Then the start and end temperatures of the devolatilization region (peak) were determined as the temperatures when derivative of rate of weight loss curve started to deviate from zero baseline.

Global kinetics of devolatilization reaction can be written as:

$$\frac{-dw}{dt} = kw^n \tag{1}$$

where,

x = sample weight (g),

k = rate constant (min^{-1}),

n = order of the reaction, and

t = time (min).

The rate constant, k, can be expressed using the Arrhenius equation as

$$k = Ae^{-E/RT} \tag{2}$$

where,

A = pre – exponential factor (s^{-1}),

E = activation energy (KJ mol^{-1}),

R = universal gas constant ($\text{KJ K}^{-1}\text{mol}^{-1}$), and

T = temperature (K).

Equations (1) and (2) can be simplified in a linear form as:

$$\ln\frac{-(\frac{dw}{dt})}{w_f - w_i} = \ln A - \frac{E}{RT} + n\ln\frac{w - w_f}{w_i - w_f} \tag{3}$$

where,

w = weight of sample (g) at time t,

w_f = final weight of the sample in the specific weight loss stage (g),

w_i = initial weight of the sample in the specific weight loss stage (g), and

dw/dt = ratio of change in weight to change in time.

The equation (3) is in the form:

$$y = B + Cx + Dz \tag{4}$$

where,

$B = \ln(A)$, $C = \frac{-E}{R}$, and $D = n$.

$x = \frac{1}{T}$, $y = \ln \frac{dw/dt}{w_f - w_i}$, and $z = \ln \frac{w - w_f}{w_i - w_f}$.

The variables (B, C and D) for the devolatilization stage were calculated using multi regression method in Excel™. The devolatilization kinetic parameters were then calculated.

5. Results and discussions

5.1 Effects of pretreatments on proximate and ultimate analyses and higher heating value

Samples of the raw and pretreated switchgrass used in this study are shown in Fig. 2. Table 1 shows the effects of pretreatment on proximate analysis, and the higher heating value (HHV) of switchgrass. As expected, moisture contents of switchgrass torrefied at 230 and 270 °C were lower than that of raw switchgrass because torrefaction, a thermal treatment, results in removal of water and increase in hydrophobicity of biomass. However, moisture content of pellets (switchgrass with densification and combined pretreatments) were not analyzed because pellets were dried after densification to safely store pellets. The switchgrass volatile content significantly decreased with the torrefaction and with the increase in torrefaction temperature from 230°C to 270°C (Table 1). This was expected because torrefaction partially decomposes biomass polymers (cellulose, hemicellulose and lignin) and releases lighter volatiles (Tumuluru et al., 2011b). Higher torrefaction temperature leads to release of even more volatiles.

However, no significant difference was observed between the volatile contents of raw and densified switchgrass (Table 1) because densification of switchgrass did not release volatiles. Densification, however, appears to partially destruct the polymer structure, hence, when torrefaction was followed by densification, the resulted switchgrass had the least volatile content (62.63 wt.%). Ash content of switchgrass was affected significantly only by the torrefaction at 270°C and combined torrefaction and densification pretreatments. Due to the low volatile contents of switchgrass pretreated with torrefaction at 270°C and combined torrefaction and densification, the ash contents were higher. No significant difference was observed between the ash contents of switchgrass torrefied at 230°C, densified and raw switchgrass (Table 1). Fixed carbon content was significantly affected by all pretreatments except densification. The fixed carbon content was the highest for switchgrass pretreated with combined torrefaction and densification (31.45 wt.%) followed by that for switchgrass pretreated with torrefaction at 270 and 230°C.

(a) (b) (c) (d) (e)

Figure 2. Samples of raw and pretreated switchgrass: (a) raw switchgrass, (b) switchgrass torrefied at 230°C, (c) switchgrass torrefied at 270°C, (d) densified switchgrass, (e) combined torrefied and densified switchgrass

Table 1. Effects of pretreatment on proximate analysis and HHV on dry basis (d.b.)

Pretreatment	Moisture (wt.%)	Volatile (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	HHV (MJ kg^{-1})
No pretreatment	9.80^{A} $(0.65)^{\#}$	80.63^{A*} (0.18)	3.50^{C*} (0.44)	15.87^{D*} (0.42)	20.60^{D} (0.69)
Torrefaction at 230°C	2.39^{B*} (0.61)	78.99^{B} (0.54)	3.63^{C*} (0.15)	17.38^{C} (0.45)	23.53^{B} (0.19)
Torrefaction at 270°C	2.05^{B*} (1.04)	67.52^{C} (0.93)	4.98^{B} (0.50)	27.51^{B} (1.38)	27.11^{A} (0.27)
Densification	5.05 (0.78)	80.23^{A*} (0.54)	3.62^{C*} (0.14)	16.15^{D*} (0.67)	19.14^{E} (0.25)
Combined torrefaction and densification	7.44 (0.15)	62.63^{D} (0.23)	5.91^{A} (0.16)	31.45^{A} (0.38)	22.27^{C} (0.32)

*Means with the same letters in the same column are not significantly different at 5% level

$^{\#}$Number in parentheses are standard deviation (n=3)

The HHV of switchgrass was significantly affected by all pretreatments (Table 1). The HHV was the highest for switchgrass pretreated with torrefaction at 270°C (27.11 MJ kg^{-1}) followed by that for switchgrass pretreated with torrefaction at 230°C and combined torrefaction and densification pretreatments. The increase in HHV could be due to low oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios in the switchgrass pretreated with torrefaction. Switchgrass torrefied at 270°C had the lowest O/C ratio of 0.58 and H/C ratio of 0.08.

Table 2 shows the effects of pretreatment on the ultimate analysis. Torrefaction significantly affected carbon, hydrogen and oxygen contents of switchgrass showing an increase in carbon content and decreases in hydrogen and oxygen contents (Table 2). This trend can be attributed to the removal of hydroxyl (OH) groups in biomass in the form of light volatiles containing high oxygen and hydrogen such as water (H_2O) and carbon dioxide (CO_2). Increase in torrefaction temperature from 230°C to 270°C further increased carbon content and decreased hydrogen and oxygen contents. Among all pretreatments, torrefaction at 270°C resulted in the highest carbon content (59.16 wt.%) and the lowest hydrogen (4.67 wt.%) and oxygen (34.53 wt.%) contents. The effects of densification were significant on hydrogen and oxygen contents but not significant on the carbon content. However, similar to the effects of other thermal treatment (torrefaction), combined torrefaction and densification significantly increased carbon content but decreased hydrogen and oxygen contents.

Table 2. Effect of pretreatments on ultimate analysis (wt.% on d.b.)

Pretreatment	Carbon	Hydrogen	Oxygen	Nitrogen	Sulphur
No Pretreatment	47.37^{C} $(0.03)^{\#}$	6.61^{A} (0.18)	43.97^{A} (0.35)	0.62^{A} (0.01)	1.43^{B} (0.13)
Torrefaction at 230°C	52.79^{B*} (0.16)	5.77^{B} (0.27)	39.58^{C} (0.59)	0.32^{B} (0.08)	1.54^{A} (0.08)
Torrefaction at 270°C	59.16^{A} (0.45)	4.67^{C} (0.28)	34.53^{D} (1.00)	0.44^{B} (0.18)	1.20^{C} (0.08)
Densification	47.11^{C} (0.29)	5.93^{B} (0.12)	45.44^{A} (0.37)	0.29^{B} (0.01)	1.24^{C} (0.04)
Combined torrefaction and densification	52.09^{B*} (0.34)	5.13^{C} (0.11)	41.34^{B} (0.15)	0.39^{B} (0.01)	1.05^{C} (0.06)

*Means with the same letters in the same column are not significantly different at 5% level

Number in parentheses are standard deviation (n=3)

5.2 Devolatilization in inert (nitrogen) atmosphere

The weight loss of raw and pretreated biomass samples showed a typical three stage weight loss profile (Fig. 3) similar to those reported by Kumar et al., (2008) for corn stover. The first stage, called the drying stage, ranged from ambient temperature to 160°C and released moisture and possibly some light volatiles such as acetic acid, methanol, formic acid, lactic acid, CO, CH_4 and H_2O (Bates and Ghoniem, 2012; Bridgewater, 1996; Duncan et al., 2013; Kitani, 1989; Pasangulapati, 2012) from biomass. Following the first stage, there was negligible weight loss (<0.05%) in the temperature range of 160 to 220°C. The second stage, called the active pyrolysis stage, showed a significant weight loss between 220 and 420°C. The third stage, called the passive pyrolysis stage, ranged from 580 to 1000°C and the weight loss in this stage was not as high as the weight loss in the active pyrolysis stage.

The effects of pretreatments were evaluated based on the weight loss profile, DTG peaks (Fig. 3) and the start and end temperatures of the dominant DTG peaks (Table 3) of switchgrass devolatilization in inert atmosphere. Pretreatments significantly affected ($p<0.05$) the weight loss, the DTG peak and the start and end temperatures of the dominant DTG peaks.

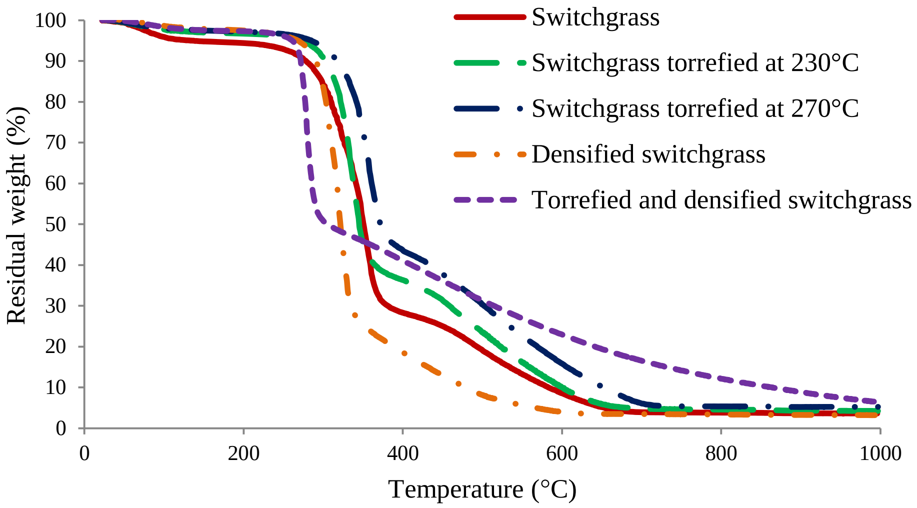

Figure 3. Weight loss profile at a heating rate of 50°C min^{-1} in inert (nitrogen) atmosphere

5.2.1 Effect of torrefaction and torrefaction temperature

In the active pyrolysis region, the weight loss and the rate of weight loss of raw switchgrass were significantly different from those of torrefied switchgrass (Table 3). The weight loss was also affected by the torrefaction temperature (230 and 270°C). However, no significant difference was observed between the rates of weight loss of switchgrass torrefied at 230 and of switchgrass torrefied at 270°C (Table 3, denoted by same alphabet).

Table 3. Effects of pretreatment on the weight loss and rate of weight loss during active pyrolysis stage in inert atmosphere

Pretreatment	Total weight loss (%)	Average rate of weight loss (mg min^{-1})
No Pretreatment	46.39^{E}	1.94^{C}
Torrefaction at 230°C	75.91^{B}	1.66^{D*}
Torrefaction at 270°C	83.43^{A}	1.23^{D*}
Densification	73.68^{D}	3.46^{B}
Combined torrefaction and densification	78.13^{C}	6.48^{A}

*Means with the same letters in the same column are not significantly different at 5% level

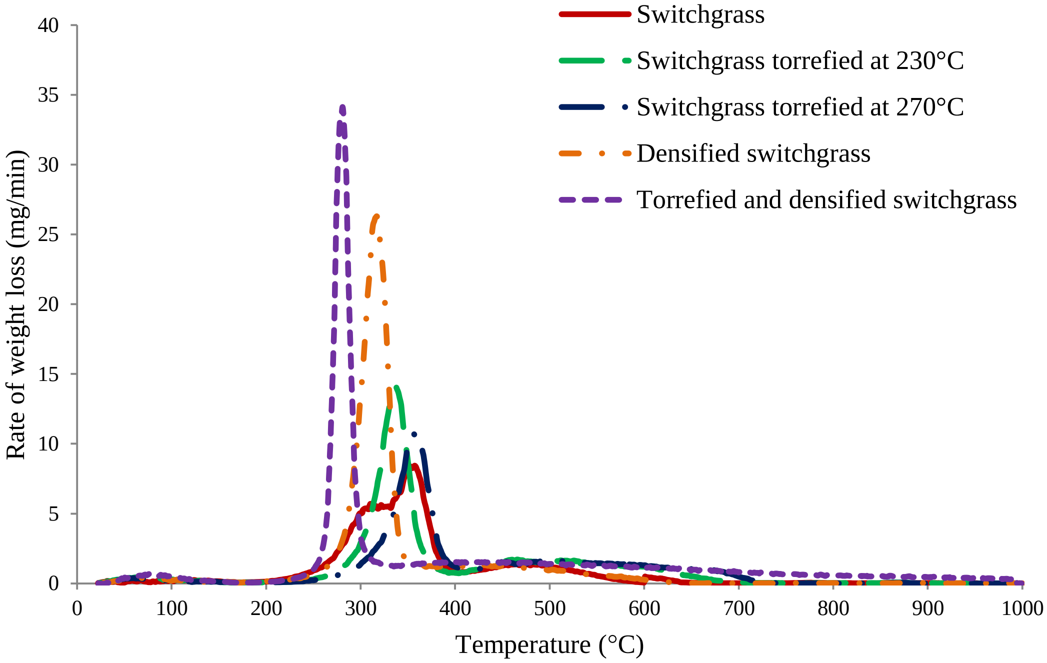

Figure 4. Rate of weight loss profile at a heating rate of 50°C min^{-1} in inert (nitrogen) atmosphere

A small DTG peak in the drying stage (first stage between 25 to 100°C) was observed at both torrefaction temperatures (Fig. 4). Between 100 and 260°C, the weight loss (<0.05%) was negligible with no DTG peak observed at both torrefaction temperatures. In the active pyrolysis stage, unlike raw switchgrass that had two DTG peaks corresponding to devolatilization of hemicellulose and cellulose (Pasangulapati, 2012), only one DTG peak was observed for torrefied switchgrass (Fig. 4). This suggests that torrefaction resulted in loss of hemicellulose and only one peak, corresponding to cellulose, was found in the rate of weight loss profile of torrefied switchgrass. A similar observation was made by Chen et al. (2011a) who studied thermal devolatilization of torrefied biomass at five temperatures and observed the disappearance of the hemicellulose shoulder from the DTG profile of the torrefied biomass. During the active pyrolysis stage, the dominant DTG peak for switchgrass torrefied at 230°C was taller (Fig. 4 and Table 4) than that for switchgrass torrefied at 270°C, which suggests that switchgrass torrefied at 230°C had a higher rate of devolatilization than switchgrass torrefied at 270°C. However, the difference between average rates of weight loss during the active pyrolysis stage was not significant (Table 3). These observations imply that the DTG peak of switchgrass torrefied at 230°C was taller and narrower than that of switchgrass torrefied at 270°C.

Table 4. Effects of pretreatment and heating rate on temperature range and height of the dominant DTG peak during active pyrolysis stage in inert (nitrogen) atmosphere

Pretreatment	10°C min^{-1}		30°C min^{-1}		50°C min^{-1}	
	Temperature range (°C)	H_m[b] (mg min^{-1})	Temperature range (°C)	H_m[b] (mg min^{-1})	Temperature range (°C)	H_m[b] (mg min^{-1})
No pretreatment[a]	350-400	1.6	340-400	4.0	340-400	8.5
Torrefaction at 230°C	280-400	2.2	280-400	8.0	260-400	14.0
Torrefaction at 270°C	280-400	1.8	280-360	6.5	260-400	10.5
Densification	260-320	5.0	250-390	19.5	250-350	25.0
Combined torrefaction and densification	260-310	13.6	220-360	26.0	250-300	34.0

[a] Data obtained from Pasangulapati et al. (2012)

[b] Height of the dominant DTG peak

The dominant DTG peaks for switchgrass torrefied at 230 and 270°C occurred in similar temperature ranges (Table 4 and Fig. 4). The start and end temperatures of the dominant DTG peaks for torrefied switchgrass were lower than those for raw switchgrass (Table 4 and Fig. 4). This suggests that torrefaction of switchgrass improved its devolatilization characteristics because low peak temperature is indicative of better devolatilization characteristics and vice-versa (Vamvuka et al., 2006). In the third stage, weight loss of torrefied switchgrass (primarily of devolatilization of lignin and fixed carbon) was lower (<0.5 wt. %) than that of raw switchgrass (Fig. 4).

5.2.2 Effect of densification

In the second stage of active pyrolysis, the weight loss and the rate of weight loss of densified switchgrass was significantly larger than those of raw switchgrass (Table 3). The dominant DTG peak in this stage was significantly larger than those of raw and torrefied switchgrass. The start and end temperatures of the dominant DTG peak for densified switchgrass also shifted to lower temperatures at all heating rates (Fig. 4 and Table 4). The high weight loss, tall DTG peak and low DTG peak temperatures suggest that densified switchgrass had a higher rate of devolatilization than the raw switchgrass probably because densification disrupts the weak branched structures of hemicellulose enabling faster devolatilization. In the third stage, weight loss of densified switchgrass was lower (0.14%) and occurred over a wider temperature range of 540 and 1000°C as compared to those of raw and torrefied switchgrass (Fig. 4).

5.2.3 Effect of combined torrefaction and densification

In the active pyrolysis (second) stage, the weight loss and rate of weight loss of switchgrass with combined torrefaction and densification were significantly different from those of the raw switchgrass (Table 3). At all heating rates, rate of weight loss peaks for switchgrass pretreated with combined torrefaction and densification were the largest

(Fig. 4 and Table 4). The start and end temperatures of the dominant DTG peak also shifted to the lowest temperatures. These trends indicate that switchgrass with the combined pretreatment had the highest rate of devolatilization due to the most severe pretreatment of the switchgrass. In the third stage, switchgrass with combined torrefaction and densification had the least weight loss (0.13%) with the widest temperature range of 520 to 1000°C (Fig. 4).

Overall, based on the height of the dominant DTG peak in the active pyrolysis stage (shown in Table 4), the rate of devolatilization of raw and pretreated switchgrass considered in this study can be arranged in the following order: combined torrefied and densified switchgrass > densified switchgrass > switchgrass torrefied at 230°C > switchgrass torrefied at 270°C > raw switchgrass.

5.2.4 Effect of heating rate

Heating rates had significant effects ($p<0.05$) on the weight loss and the rate of weight loss but did not have a significant effect ($p=0.6984$) on the start and end temperatures of the dominant DTG peak in the active pyrolysis (second) stage. An increase in the heating rate significantly increased height of the dominant DTG peak, (Fig. 5 and Table 5) and the DTG peak temperatures (Fig. 5). This can be attributed to increased thermal lag at the higher heating rates (Damartzis et al., 2011) as suggested by the kinetic study of Arundo donax (Jeguirim, 2009) and thermo gravimetric study of corn stover (Kumar et al., 2008).

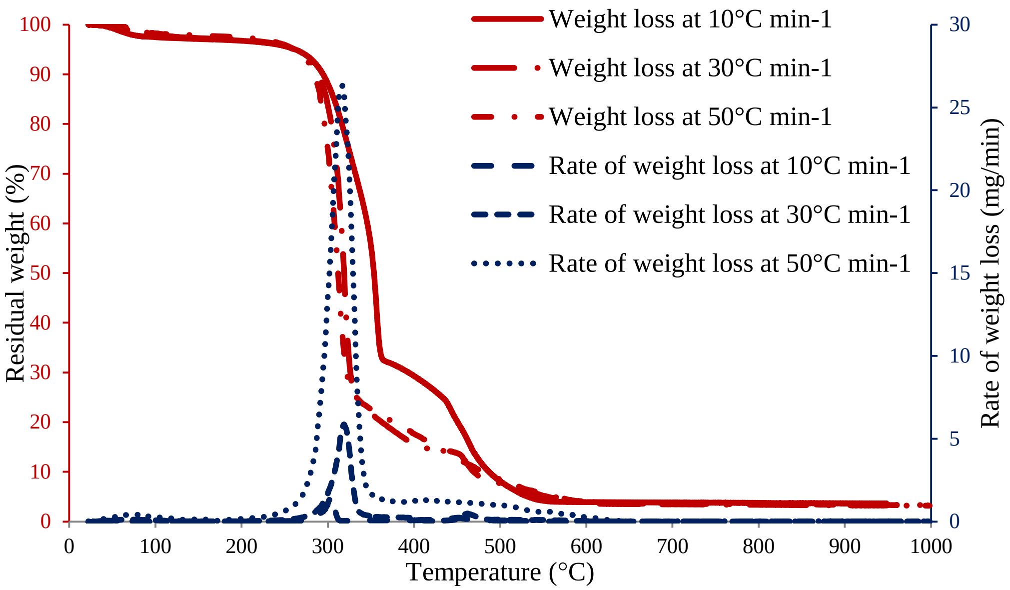

Figure 5. Weight loss and rate of weight loss profiles of densified switchgrass at three heating rates in inert (nitrogen) atmosphere

Table 5. Effect of heating rates on the weight loss and rate of weight loss of the active pyrolysis stage in inert atmosphere

Heating rate (°C min^{-1})	Total weight loss (%)	Average rate of weight loss (mg min^{-1})
10	78.64^{A}	1.29^{C}
30	69.44^{C}	3.32^{B}
50	71.17^{B}	5.47^{A}

5.2.5 Reaction kinetics parameters of devolatilization during active pyrolysis stage

The kinetic parameters of the devolatilization reaction for the active pyrolysis (second) stage in inert atmosphere were determined for all samples and are shown in Table 6. The activation energy (E) was the maximum for switchgrass pretreated with combined torrefaction and densification. However, the rate of devolatilization cannot be judged by directly analyzing only the activation energies of all biomass because their orders of reaction were different. The order of devolatilization reaction ranged from 0.02 (zero order reaction) to 1.14 (close to first order reaction) for all pretreatments with a regression coefficient (R^2) greater than 0.93.

Table 6. Effects of pretreatment on weight loss kinetic parameters during active pyrolysis stage in inert (nitrogen) atmosphere

Pretreatment	Heating rate (°C min^{-1})	Temperature range (°C)	A (s^{-1})	E (KJ mol^{-1})	n	R^2
No pretreatment	10	350 - 400	$1.54*10^{7}$	93.86	0.92	0.92
	30	340 - 400	$7.78*10^{7}$	95.41	0.77	0.96
	50	340 - 400	$9.48*10^{7}$	93.55	0.94	0.90
Torrefaction at 230°C	10	280 - 400	$1.15*10^{8}$	104.95	0.33	0.99
	30	280 - 400	$5.59*10^{14}$	163.68	0.13	0.97
	50	260 - 400	$2.45*10^{13}$	152.90	0.57	0.99
Torrefaction at 270°C	10	280 - 400	$1.36*10^{10}$	126.02	0.74	0.93
	30	280 - 360	$1.39*10^{7}$	90.13	0.02	0.99
	50	260 - 400	$2.06*10^{9}$	111.03	0.38	0.99
Densification	10	260 - 320	$1.15*10^{5}$	91.85	0.01	0.97
	30	250 - 390	$1.87*10^{14}$	160.04	0.17	0.99
	50	250 - 350	$2.78*10^{15}$	171.40	0.55	0.99
Combined torrefaction and densification	10	260 - 310	$9.37*10^{28}$	315.67	0.28	0.95
	30	220 - 360	$3.85*10^{14}$	161.46	0.55	0.97
	50	250 - 300	$2.64*10^{37}$	391.37	1.14	0.93

5.3 Devolatilization in oxidizing (air) atmosphere

The weight loss profile of raw and pretreated biomass samples in oxidizing atmosphere showed a three-stage weight loss profile (Fig. 6). The first stage, ranging from 25 to 120°C, was the drying stage, where the release of the biomass moisture occurred. The second stage, from 240 to 360°C, was the combustion stage, where combustion of the volatiles took place and the third stage, from 520 to 1000°C, was the residual combustion stage, which was mostly due to combustion of lignin and fixed carbon. The effect of switchgrass pretreatment on the thermal devolatilization of switchgrass was analyzed based on the weight loss profile (Fig. 6), the rate of weight loss (DTG) peaks (Fig. 7), and the start and end temperatures of the dominant DTG peaks (Table 8). Similar to observations with an inert atmosphere, pretreatments significantly affected ($p<0.05$) the weight loss, the rate of weight loss of switchgrass and the start and end temperatures of the dominant DTG peaks.

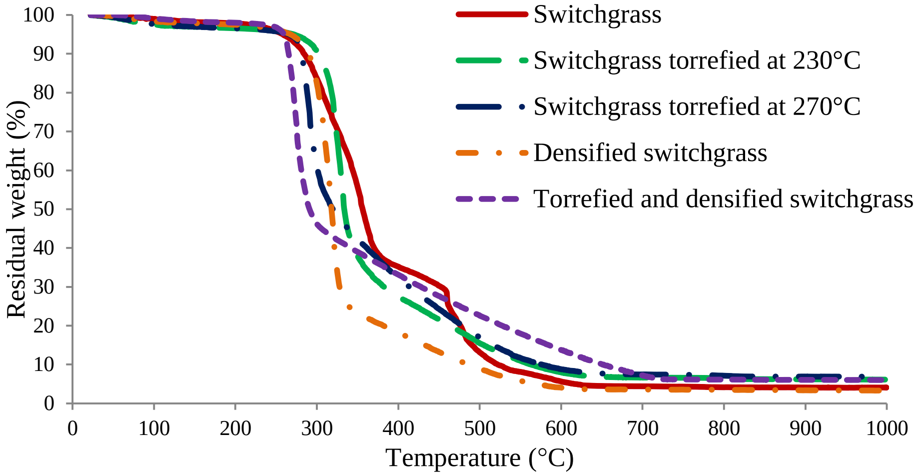

Figure 6. Weight loss profiles at a heating rate of 50°C min^{-1} in oxidizing (air) atmosphere

5.3.1 Effect of torrefaction and torrefaction temperature

Torrefaction increased weight loss and height of the dominant DTG peak of switchgrass during the volatile combustion stage in an oxidizing atmosphere (Tables 7 and 8). The start and end temperatures of the dominant DTG peak also decreased with torrefaction (Table 8 and Fig. 7). Similar to observations in the inert atmosphere, weight loss and rate of weight loss of torrefied switchgrass (at 230 and 270°C) was significantly different than those of raw switchgrass (Table 7). However, no significant difference was observed between the average rates of weight loss of switchgrass torrefied at 230 and 270°C (Table 7). These observations suggest that torrefied biomass had a higher rate of devolatilization than the raw switchgrass, which can be attributed to partial decomposition of switchgrass, especially hemicellulose component, during torrefaction.

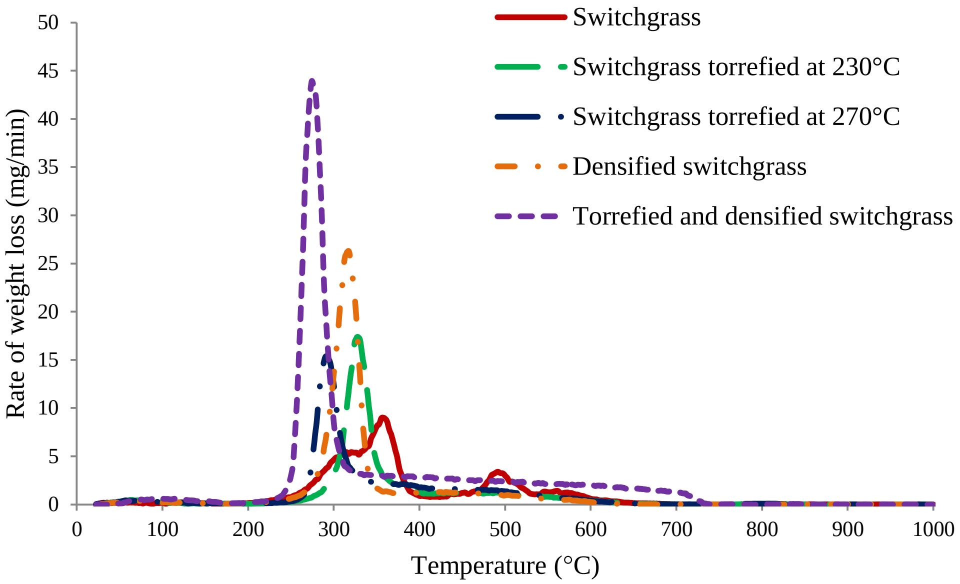

Figure 7. Rate of weight loss profiles at a heating rate of 50°C min^{-1} in oxidizing (air) atmosphere

In the volatile combustion (second) stage, DTG peak heights for switchgrass torrefied at 230°C were larger (Fig. 7 and Table 8) than those for switchgrass torrefied at 270°C. Similar to the observations in inert atmosphere, taller DTG peaks (Fig. 7) at the light torrefaction (at temperature of 230°C) suggests that torrefaction at 230°C had a higher rate of devolatilization than switchgrass torrefied at 270°C. Also, similar to observations in inert atmosphere, unlike raw switchgrass that had two DTG peaks, torrefied switchgrass showed only one large DTG peak between 260 and 400°C implying disappearance of hemicellulose during torrefaction. This was consistent with observations of Chen et al. (2011a). This suggests that the hemicellulose structure was severely affected when the switchgrass was subjected to torrefaction. Also, as expected, the height of the dominant DTG peaks in the oxidizing atmosphere was higher (Fig. 7) than those in an inert atmosphere (Fig. 7) because the oxidizing atmosphere provides a much more reactive environment than the inert atmosphere.

Table 7. Effect of pretreatment on weight loss and rate of weight loss during volatile combustion stage in oxidizing atmosphere

Pretreatment	Total weight loss (%)	Average rate of weight loss (mg min^{-1})
No pretreatment	50.69^{E}	2.72^{C}
Torrefaction at 230°C	77.99^{A}	2.51^{D*}
Torrefaction at 270°C	63.61^{D}	2.24^{D*}
Densification	70.35^{C}	4.18^{B}
Combined torrefaction and densification	73.27^{B}	12.02^{A}

*Means with the same letters in the same column are not significantly different at 5% level

Table 8. Effects of pretreatment and heating rate on temperature range and height of the dominant DTG peak during volatile combustion stage in oxidizing (air) atmosphere

Pretreatment	10°C min^{-1}		30°C min^{-1}		50°C min^{-1}	
	Temperature range (°C)	H_m[b] (mg min^{-1})	Temperature range (°C)	H_m[b] (mg min^{-1})	Temperature range (°C)	H_m[b] (mg min^{-1})
No pretreatment[a]	320-360	2.0	320-400	5.0	320-400	9.0
Torrefaction at 230°C	270-320	6.0	280-390	12.5	250-280	16.5
Torrefaction at 270°C	270-340	4.5	280-400	11.5	250-320	15.5
Densification	270-310	15.0	230-360	19.0	250-350	26.0
Combined torrefaction and densification	240-270	35.0	240-300	37.5	230-310	44.0

[a] Data obtained from Pasangulapati et al. (2012)

[b] Height of the dominant DTG peak

Similar to the observations in inert atmosphere, in the oxidizing atmosphere the dominant DTG peaks of switchgrass torrefied at 230 and 270°C occurred at similar temperatures (Fig. 7), but the start and end temperatures of the dominant DTG peak in the oxidizing atmosphere were lower than corresponding temperatures in the inert atmosphere (Table 4 and 9). The temperature range of the dominant DTG peak of torrefied switchgrass was also lower (Fig. 7 and Table 8) than that of raw switchgrass which suggested that torrefaction improved the rate of devolatilization of switchgrass. A similar trend was seen by Carter et al. (2012) and Chen et al. (2011) by conducting a thermogravimetric analysis of different biomass in an oxidizing atmosphere. As expected, the weight loss in the third stage of torrefied switchgrass was lower (<0.3%) in the oxidizing atmosphere than that in the inert atmosphere because most of the biomass combusted and devolatilized during the second stage in oxidizing atmosphere (Fig. 7).

5.3.2 Effect of densification

During the volatile combustion stage, the weight loss and DTG peak of densified switchgrass were significantly different from that of raw switchgrass (Table 7 and Fig. 7). The start and end temperatures of the dominant DTG peak of densified switchgrass shifted to lower temperatures (Fig. 7 and Table 8), probably because densification disrupted the weak branched structures of hemicellulose. These observations suggest that densified switchgrass had a higher rate of devolatilization than the raw switchgrass in the oxidizing atmosphere. As expected, the weight loss and height of DTG peak of densified switchgrass in the oxidizing atmosphere (Fig. 7) were higher than those in the inert atmosphere (Fig. 7) because the oxidizing atmosphere provides a more reactive environment than the inert atmosphere. During the third stage, slow lignin decomposition (~0.15 wt.%) occurred that spread over a wider temperature range of 520 and 1000°C for of densified switchgrass as compared to that for torrefied and raw switchgrass (Fig. 7).

5.3.3 Effect of combined torrefaction and densification

During the volatile combustion stage, the weight loss and DTG peak height of switchgrass pretreated with combined torrefaction and densification differed significantly from that of raw switchgrass (Table 7). Start and end temperatures of the dominant DTG also shifted to lower temperatures. The highest average rate of weight loss, largest dominant DTG peaks (Fig. 7) and the lowest start and end temperatures of the dominant DTG peaks (Table 8) clearly suggest that the switchgrass pretreated with combined torrefaction and densification had the highest rate of devolatilization in the oxidizing condition. This conclusion was similar to the conclusion made in inert conditions. However, as expected, heights of the dominant DTG peaks were higher and the temperatures of the dominant DTG peak in the oxidizing atmosphere were lower than those in the inert atmosphere. The third stage of combined torrefied and densified switchgrass showed the lowest weight loss of 0.14%, which spread over on even wider temperature range of 400 and 1000°C (Fig. 7).

Overall, similar to the observations in the inert atmosphere, based on the height of the dominant DTG peak in the volatile combustion stage in the oxidizing atmosphere (shown in Table 8), the rate of devolatilization of raw and pretreated switchgrass considered in this study can be arranged in the following order: switchgrass with combined torrefied and densified switchgrass > densified switchgrass > switchgrass torrefied at 230°C > switchgrass torrefied at 270°C > raw switchgrass. These observations in both inert and oxidizing atmospheres confirm the order of the rate of devolatilization of raw and pretreated switchgrass.

5.3.4 Effect of heating rate

During the volatile combustion stage, heating rate had significant effects on the weight loss and the dominant DTG peaks of raw as well as pretreated switchgrass, but did not have significant effects ($p=0.1174$) on the start and end temperatures of the dominant DTG peak. Similar to the trends in the inert atmosphere, increase in heating rate from 10 to 50°C min^{-1} increased the height of the dominant DTG peaks (Table 9 and Fig. 8) shifting the DTG peaks towards higher temperatures possibly due to a thermal lag. The dominant DTG peak was the tallest for switchgrass pretreated with combined torrefaction and densification (44 mg min^{-1}) at a heating rate of 50°C min^{-1} in the oxidizing atmosphere.

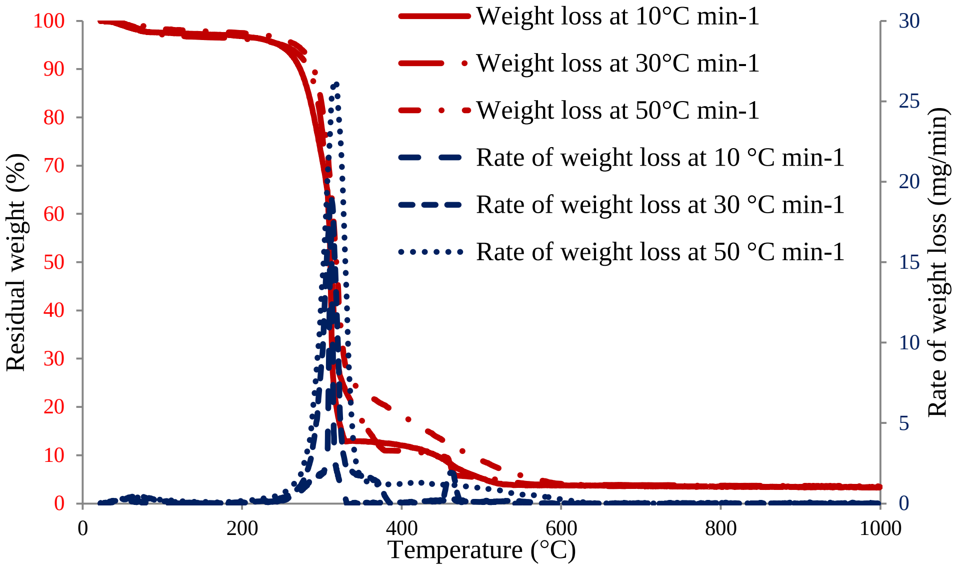

Figure 8. Weight loss and rate of weight loss profiles of densified switchgrass at the three heating rates in oxidizing (air) atmosphere

Table 9. Effects of heating rate on the weight loss and rate of weight loss during volatile combustion stage in oxidizing atmosphere

Heating rate (°C min^{-1})	Total weight loss (%)	Average rate of weight loss (mg min^{-1})
10	72.93^{A}	2.27^{C}
30	57.85^{C}	4.35^{B}
50	65.74^{B}	8.93^{A}

5.3.5 Reaction kinetics parameters of devolatilization during combustion stage

Similar to the observations in inert atmosphere, kinetic parameters of the devolatilization reaction were determined during the volatile combustion (second) stage where the maximum weight loss occurred. The activation energy, E, was the maximum for switchgrass pretreated with combined torrefaction and densification (711.89 KJ mol^{-1} at a heating rate of 50°C min^{-1}) followed by that for switchgrass pretreated with torrefaction and densification, respectively (Table 10). However, as stated earlier, the rate of devolatilization cannot be directly judged by analyzing only the activation energies of all biomass because their orders of reaction were different. The order of the devolatilization reaction of all pretreatments ranged from 0.19 (zero order reaction) to 1.18 (close to first order reaction) with a regression coefficient, R^2, greater than 0.87.

Table 10. Effects of pretreatments on weight loss kinetic parameters of switchgrass in oxidizing atmosphere during the volatile combustion stage

Pretreatment	Heating rate (°C min^{-1})	Temperature range (°C)	A (s^{-1})	E (KJ mol^{-1})	n	R^2
No pretreatment	10	320 - 360	$5.76*10^{7}$	95.88	0.20	0.95
	30	320 - 400	$5.86*10^{10}$	123.84	0.68	0.96
	50	320 - 400	$4.11*10^{9}$	109.92	1.18	0.88
Torrefaction at 230°C	10	270 - 320	$2.05*10^{11}$	135.96	0.19	0.95
	30	280 - 390	$2.37*10^{15}$	176.17	0.86	0.92
	50	250 - 280	$2.25*10^{14}$	162.39	0.20	0.98
Torrefaction at 270°C	10	270 - 340	$6.94*10^{14}$	170.06	0.29	0.94
	30	280 - 400	$1.01*10^{25}$	261.94	0.42	0.94
	50	250 - 320	$5.11*10^{30}$	324.87	0.62	0.98
Densification	10	270 - 310	$7.37*10^{11}$	137.98	0.49	0.87
	30	230 - 360	$2.45*10^{14}$	160.74	0.06	0.98
	50	250 - 350	$4.09*10^{16}$	183.47	0.42	0.99
Combined torrefaction and densification	10	240 - 270	$3.52*10^{19}$	200.33	0.93	0.90
	30	240 - 300	$2.67*10^{37}$	384.45	0.75	0.98
	50	230 - 310	$3.15*10^{70}$	711.89	0.41	0.93

6. Conclusions

The effects of four pretreatments (torrefaction at 230°C, torrefaction at 270°C, densification, and combined torrefaction and torrefaction) of switchgrass on its thermal devolatilization characteristics at heating rates of 10, 30 and 50°C min^{-1} in inert and oxidizing atmospheres were investigated. Torrefaction of switchgrass increased its carbon content and HHV but decreased hydrogen and oxygen contents. These effects increased with increase in torrefaction temperature from 230 to 270°C. However, based on the larger DTG peak of switchgrass torrefied at 230°C, its rate of devolatilization appears to be higher than that of switchgrass torrefied at 270°C in both inert and oxidizing atmospheres. In both atmospheres, switchgrass pretreated with combined torrefaction and densification showed the highest dominant DTG peaks (34 and 44 mg min^{-1} in inert and oxidizing atmospheres, respectively), the lowest start and end temperatures of the dominant DTG peaks and the highest activation energies (391.37 and 711.90 KJ mol^{-1} in inert and oxidizing atmospheres, respectively) at a heating rate of 50°C min^{-1}. Overall, in both inert and oxidizing atmospheres, switchgrass pretreated with combined torrefaction and densification had the highest rate of devolatilization followed by switchgrass pretreated with densification, switchgrass with torrefaction at 230°C, switchgrass with torrefaction at 270°C, and raw switchgrass. Heating rate also had significant effects on the weight loss and rate of weight loss of switchgrass but did not have a significant effect on the start and end temperatures of the dominant DTG peaks.

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CHAPTER III

GASIFICATION PERFORMANCE OF SWITCHGRASS PRETREATED WITH TORREFACTION AND DENSIFICATION

Abstract

The purpose of this study was to investigate gasification performance of four switchgrass pretreatments (torrefaction at 230 and 270°C, densification, and combined torrefaction and densification) and three gasification temperatures (700, 800 and 900°C). Gasification was performed in a fixed-bed externally heated reactor with air as an oxidizing agent. Among all pretreatments, bulk density of switchgrass with combined torrefaction and densification pretreatment was the highest (598.17 kg m^{-3}) followed by those of densified switchgrass (498.63 kg m^{-3}), switchgrass torrefied at 270°C (186.78 kg m^{-3}), switchgrass torrefied at 230°C (166.79 kg m^{-3}) and raw switchgrass (138.33 kg m^{-3}). Switchgrass pretreatment and gasification temperature also had significant effects on its gasification performance such as gas yields, syngas lower heating value (LHV), and carbon conversion and cold gas efficiencies. With an increase in the gasification temperature, yields of H_2 and CO, syngas LHV, and gasifier efficiencies increased whereas CH_4, CO_2 and N_2 yields decreased. Among all switchgrass pretreatments, gasification of combined torrefied and densified switchgrass resulted in the highest yields of H_2 (0.03 kg/kg biomass) and CO (0.72 kg/kg biomass), highest syngas LHV (5.08 MJ Nm^{-3}), CCE

(92.53%), and CGE (68.40%) at the gasification temperature of 900°C. Results show that combined torrefaction and densification significantly improved gasification performance of switchgrass.

Keywords: torrefaction; densification; gasification; efficiency; switchgrass; biofuels

1. Introduction

The increase in the world population to 7 billion and further projected increase to 10 billion has increased awareness about need of more resource to supply the need of energy, food and other consumable products (Shaw, 2008). Currently, a huge proportion of the demand for energy and chemicals are met by fossil fuels which are non-renewable, increases greenhouse gas (GHG) emissions and make many countries heavily dependent on import. The fossil fuels can be replaced with second generation biofuels, derived from lignocellulosic feedstocks, agricultural residues and their byproducts (Damartzis and Zabaniotou, 2011; Naik et al., 2010). Biomass, an organic plant-based material, converts solar energy and carbon dioxide into chemical energy through photosynthesis. Since sunlight is a sustainable resource, biomass can be generated through photosynthesis on a sustainable basis, which makes the biomass a renewable resource that can be utilized worldwide.

Switchgrass (*Panicum virgatum L.*), a native North American perennial lignocellulosic grass grown in the central USA is one of the ideal biomass feedstocks due to its high crop yield (10-12 t/ha/annum) (Goel et al., 2000), adaptation to soil and climatic conditions and minimal requirement of fertilizers to grow the biomass (Boylan et al., 2000; Matts et al., 2010). However, certain properties of switchgrass (similar to the properties of other biomass feedstocks) such as high moisture content, low bulk density, low calorific value, high volatile and oxygen contents and tenacious and fibrous nature of the biomass, create challenges to store the biomass for long hours, to transport and convert efficiently into fuels and other products (Bibens, 2010; Tumuluru et al., 2011b). Pretreatments such as torrefaction and densification have potential to improve the properties of biomass such as switchgrass making it a better feedstocks for conversion into fuels and chemicals (Pach et al., 2002). Torrefaction, a thermochemical process, taking place at temperatures ranging between 200 and 300°C in an inert atmosphere, produces a hydrophobic product which prevents the biomass from getting decomposed when exposed to the atmosphere (Arias et al., 2008; Chen and Kuo, 2011b; Couhert et al., 2009; Phanphanich and Mani, 2011; Sadaka and Negi, 2009). The product obtained also has higher heating value (HHV) and a high energy density (Prins et al., 2006b). Densification converts loose biomass into pellets having more uniformity and higher bulk density that can possibly solve challenges in storing and transporting biomass (Tumuluru et al., 2011). Pellets are also more uniform and create fewer fines (Kallis et al., 2012). A combination of torrefaction and densification of biomass may provide even further improvements in biomass properties as it will lead to a uniform hydrophobic product with high energy and bulk densities ultimately resulting in less storage and transportation costs (Bergman and Kiel, 2005; Tumuluru et al., 2012; Tumuluru et al., 2011b).

The second generation biofuels are produced through two distinct conversion processes namely the biochemical and thermochemical conversions. The biochemical conversion consists of enzymatic transformation of cellulose and hemicellulose to sugars and further fermentation into ethanol and higher alcohols (Damartzis and Zabaniotou, 2011; Naik et al., 2010), whereas, the thermochemical conversion uses heat and catalysts to convert biomass into intermediate products syngas and bio-oil through gasification and pyrolysis, respectively (Chen et al., 2003; Heiskanen, 2011; Kumar et al., 2009b; Kumar et al., 2008; Ruiz et al., 2013). The syngas (gasification intermediate) is composed of carbon monoxide, carbon dioxide, hydrogen, nitrogen (if air is used as oxidizing agent), and small quantities of hydrocarbons such as methane, ethane etc. The syngas can be further synthesize into useful fuels (gasoline and diesel), chemicals (methanol and ethanol) through catalytic and microbial processes (Bacovsky et al., 2013; Heiskanen, 2011). The gasification can take place in a variety of gasifiers such as fixed bed (updraft, downdraft and cross draft, batch) and fluidized bed (bubbling and circulating) gasifiers (Basu, 2010; Sadaka, 2012). Fixed bed gasifiers are advantageous over fluidized bed gasifiers especially for small scale applications as the design of fixed bed gasifiers is simple, less expensive and are suitable for biomass combustion, biomass gasification, small scale power generation and industrial heating applications (Di Blasi et al., 1999; Guangul et al., 2012; Hsi et al., 2008; Rahardjo, 2013; Reed, 1988). Fluidized bed gasifiers (FBG) are more suitable for large scale applications because of their higher mass and heat transfer efficiencies but FBG are also more complex in design and operation as compared to fixed bed gasifiers (Maniatis, 1986; Salam et al., 2010; Xu and Antal, 1998). This paper reports study on a fixed-bed gasifier.

The gasification performance of raw and pretreated biomass can be evaluated based on the composition and yield of syngas, and energy and carbon conversion efficiencies. Gasification performances of several types of raw biomass feedstocks and gasifiers have been extensively reported in literature (Ahmed and Gupta, 2009; Ahmed and Gupta, 2012; Baggio et al., 2009; Di Blasi et al., 1999; Karmakar and Datta, 2011; Konda et al., 2012; Kumar et al., 2009a; Lv et al., 2004; Narvaez et al., 1996; Patel, 2013). Limited studies have also been reported on pretreated biomass other than switchgrass (Bibens, 2010; Lucas et al., 2004; Prins et al., 2005). Bibens et al. (2010) investigated the downdraft gasification performance of pine chips torrefied at 250, 275 and 300°C for 30 and 60 min and concluded that at a gasifier temperature of 800°C and an equivalence ratio (ER) of 0.25, with an increase in the torrefaction temperature and time, the syngas HHV, and syngas yield and net energy output per unit of material increased. By fluidized-bed air gasification of raw and torrefied wood at 250 and 300°C at a gasifier temperature of 950°C, Prins et al. (2005) observed that the overall exergetic efficiency of torrefied wood was lower than of raw wood because the part of biomass energy was lost in the released volatiles during torrefaction. With high-temperature air/steam gasification of densified wood pellets in an updraft gasifier using preheated air and steam, Lucas et al. (2004) observed that an increase in the gasifier temperature from 350 to 900°C increased the gas yield and HHV and reduced production of tars, soot and char. However, to our knowledge, there is no literature available on gasification of switchgrass pretreated with torrefaction and densification.

The goal of this study was to investigate the effects of four pretreatment (torrefaction at 230 and 270°C for 30 min residence time, pelletization and combined torrefaction and pelletization) and three gasification temperature (700, 800 and 900°C) on the gasification performance of switchgrass.

2. Materials and methods

2.1 Materials

2.1.1 Biomass feedstock

Kanlow Switchgrass (Panicum Virgatum) grown at the Plant and Soil Sciences department at Oklahoma State University was used as the biomass. Bales of Kanlow switchgrass were chopped using a Haybuster tub grinder (H1000, Duratech Industries International Inc. Jamestown, N.D) with a screen size of 25 mm. The chopped switchgrass was then ground using a hammer mill (Bliss Industries, Ponca City, Oklahoma) with a mesh size of 4 mm and sent to Idaho National Laboratory (INL, Idaho

Falls) for torrefaction at 230°C and 270°C for 30 min residence time, pelletization of switchgrass ground to particle size less than 4 mm and combined torrefaction and pelletization of switchgrass (torrefaction at 270°C for 30 min followed by densification).

2.2 Methods

2.2.1 Torrefaction

A moving-bed gravity-fed atmospheric pressure thermal treatment system was used to torrefy switchgrass (Fig. 1). It consisted of horizontal auger-driven sections to feed material into and out of a vertical, central reactor with diameter and height of 0.305 and 1.68 m, respectively. The details and schematic of the torrefaction unit can be found elsewhere (Westover et al., 2013). The ground switchgrass was weighed and manually loaded into the feeder hopper. Biomass was then metered into the torrefaction reactor through a rotary airlock and a horizontal auger rotating at 0.4 RPM. The exterior of the reactor was heated using band heater and the biomass temperature was monitored at six different points along the reactor section. A stirrer was provided in the reactor to help prevent bridging of particles. Biomass samples were torrefied for 30 min at temperatures of 230 and 270°C. Torrefied biomass exited at the reactor bottom and was removed via a horizontal auger that cooled the material to about 50°C before it exited through the twin knife-blade air locks. The residence time of the material in the torrefaction reactor can be controlled between 15 min to 1 hr by adjusting the speed of the out-feed auger. An inert environment was maintained in the reactor by injecting clean nitrogen gas (heated to the desired torrefaction temperature of 230 and 270°C) into the sides and bottom of the vertical thermal section. The inert gas, combined with process off-gas exited from the thermal unit at the upper end in a counter flow configuration. The gas was then passed through a heated cyclone separator to remove the particulates and then to a thermal oxidizer to burn the combustibles. After exiting the thermal oxidizer, the gas stream passed through an enlarged knockout vessel that provided velocity reduction and slight cooling to allow condensable constituents to drop out of the steam for separate collection. The gas was then reheated prior to recycling into the reactor. The cooled torrefied material collected was stored in air tight barrels.

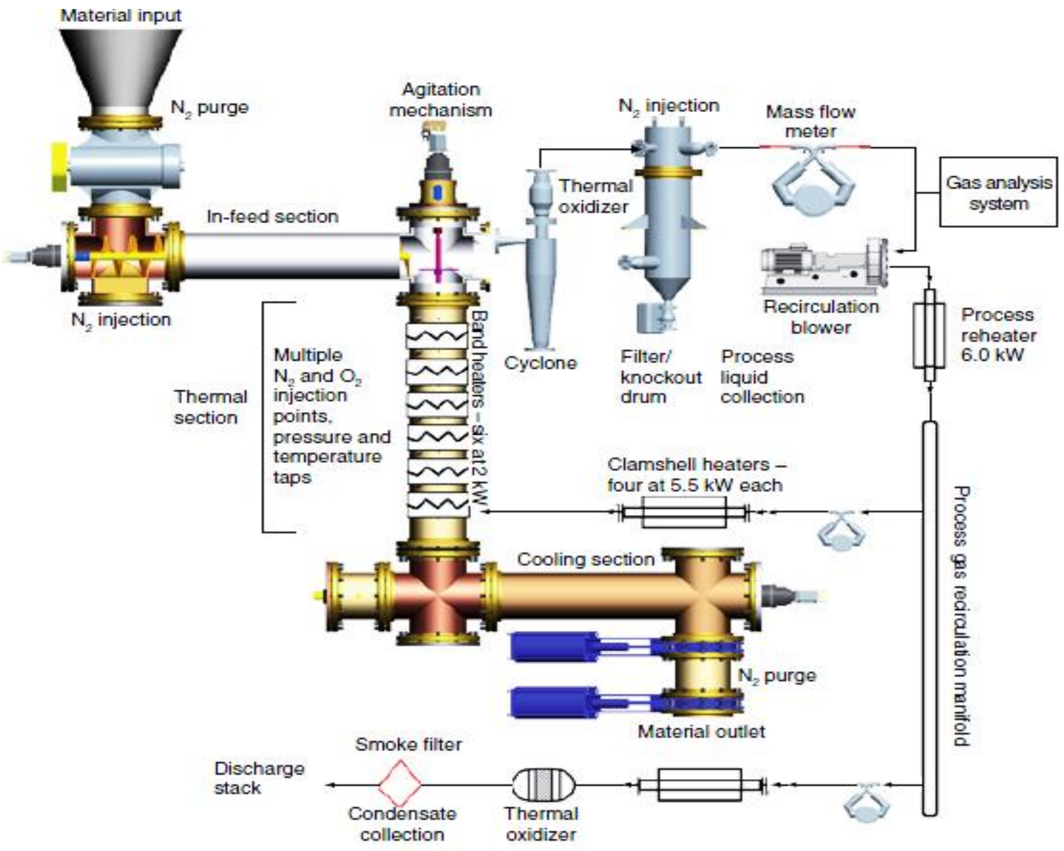


Fig. 1. Torrefaction system (adopted from Westover et al. (2013))

2.2.2 Densification

A laboratory-scale flat-die pellet mill (model ECO-10, Colorado Mill Equipment) with a 10 HP, 460-volt, 3-phase motor was used for the pelletization (densification). This machine has been designed for research and development applications for testing the pelletability of variety of raw and pretreated biomass. The rated output of this pellet mill was 30–50 kg/h. The pellet mill was equipped with a hopper to hold the biomass and a screw feeder to uniformly feed biomass into the pellet mill. A flexible rectangular heater (Silicon Rubber Heater, Branom Instrument, WA) and a flexible tape heater (Briskheat Xtremeflex grounded heavy-insulated heating) with J-type thermocouples and controllers (Model 96A-FDAA-00RG, Watlow, USA) were used to maintain a constant temperature of 70°C in the hopper and feeder, respectively. A variable frequency drive (model Altivar 71, variable-frequency AC motor driver) was used to control the rotational speed of the pellet mill die maintained at 110°C. Further details of the mill can be found in Tumuluru et al. (2011).

For pelletization of raw chopped switchgrass, moisture was added to the biomass to make it 26% (w.b.) moisture content and commercial corn starch was added as a binder with quantity of 2% by weight of the original sample. The biomass, moisture and binder were mixed for 30 min in a ribbon blender (RB 500, Colorado Mill Equipment, Cañon City, CO). The mixed biomass was stored in cold storage, at about 4°C. For pelleting torrefied biomass, commercial corn starch and a biobased lubricant (product number CGL8000 with 99% soyseed oil and 1% molybdenum, Green Cold Lubricants LLC, Colorado Springs, CO) were used with quantity of 5 and 2%, respectively, by weight of the original biomass. Moisture was added to increase the original biomass moisture content to 26% (w.b.). The feeding was carried out uniformly at about 10–12 kg/h to ensure that there were no flow irregularities inside the pelletizer. Following the cooling step, pellets were further dried in a mechanical oven at 60–65°C for about 3–4 hours to reduce the moisture to safe storage levels of about 5-7% (w.b.).

2.2.3 Proximate and ultimate analyses, lower heating value, bulk density and scanning electron microscopy (SEM) images

Using a furnace (model 3-550A, Dentsply Prosthetics, PA), moisture, volatile and ash contents were determined following ASAE standard S358.2 (ASABE Standards, 2006), ASTM D3175 and ASTM E1755-01 respectively. The fixed carbon content was determined by subtracting the volatile and ash contents from the total biomass on dry basis. The ultimate analysis of biomass was measured using an elemental analyzer (PerkinElmer 2400 Series II CHNS/O Elemental Analyzer, Shelton, CT) at Kansas State University (Manhattan, KS).

The lower heating value ($LHV_{biomass}$, d.b.) of raw and pretreated switchgrass was determined using equation 1 (Núñez-Regueira et al., 2001; Suarez et al., 2000) and the higher heating value (HHV) of biomass was measured using an adiabatic Parr 6200 Bomb Calorimeter (model A1290DDEB, Parr Instrument Co., Moline, Ill).

$$LHV_{biomass} = HHV_{biomass} - 2.44\ (9H) \qquad (1)$$

where HHV is the higher heating value, MJ kg^{-1} (d.b.), and H is the amount of hydrogen in the biomass determined through ultimate analysis (%, d.b.).

The bulk density was measured by packing the biomass tightly in a beaker of known weight and volume. The initial and final weights of the beaker were measured and the bulk density was determined by the ratio of the weight of the biomass to the volume of the beaker similar to the procedure described earlier in Sharma et al. (2011).

The SEM images of raw and pretreated switchgrass were obtained using a Scanning Electron Microscopy (Quanta 600, FEI, NJ). The dry ground biomass sample was sprinkled on a stub (with a carbon paper attached to it) and the excess sample removed with a brush. Since, the SEM detects only conductive samples, the biomass sample was bombarded with an ionized gas (Argon) forming a gold colored coating on the top. After sputtering of the biomass sample, it was introduced into a vacuum chamber of the SEM and the images were obtained by adjusting the voltage, magnification and the aperture. The quality of the images was improved by adjusting the sharpness and the brightness (Acharya, 2013; Stelte et al., 2011).

2.2.4 Experimental design

A full factorial experimental design was used with two factors: switchgrass pretreatment and gasification temperatures. Five levels of switchgrass pretreatment were no pretreatment (raw switchgrass), torrefaction at 230°C and 270°C for 30 min, densification, and combined torrefaction and densification (torrefaction at 270°C for 30 min followed by densification) and three levels of gasification temperatures were 700, 800 and 900°C. The experiments were repeated two times.

2.2.5 Gasification

The gasification experiments were performed in a fixed stainless steel gasifier tube with a diameter of 0.0254 m (1 inch) and a length of 0.9 m as shown in Fig. 1. The tube was housed inside a vertical split-hinge tube furnace (model TVS 12/600, Carbolite Inc., WI, USA). A square metal mesh of diameter 0.0254m (1 inch) was weld inside the gasifier tube, 0.125m from the bottom, to hold the biomass inside the gasifier for gasification. Two inlets were available at distances of 0.015 and 0.025 m from the gasifier top for injecting nitrogen (to maintain inert atmosphere before gasification) and air (gasification agent) into the gasifier tube. The nitrogen and air flow rates were adjusted using calibrated rotameters (Airgas, Tulsa, OK).

An air tight cylindrical biomass hopper with diameter of 0.0508 m and length of 0.15 m with a tapered bottom was used to store the biomass. A ball valve (McMaster-

Carr, Atlanta, GA) below the hopper was used to control the biomass flow into the gasifier. A char box, a thermocouple (K-type) and a gas outlet were connected at the bottom of gasifier. The producer gas was collected in gas bags (Tedlar, VWR International, Radnor, PA) at the gas outlet. The gasification temperature was monitored and recorded from the control panel display of the vertical tube furnace and the exit gas temperature was recorded using a Lab VIEW system (National Instruments, Austin, TX). The gases obtained were analyzed using a gas chromatograph (model CP3800, Varian Inc., CA) with a packed column (HayeSep DB-100/120, Alltech Associates, Inc., Deefield, Ill.) and a thermal conductivity detector (TCD).

Two grams of biomass was loaded into the gasifier hopper. Biomass was fed after gasifier temperature stabilized at the set point temperature. Purging gas was switched from nitrogen to air at the flow rate of 2 L/min. Gas samples were collected for 2min. The 2 min was selected based on preliminary experiments that showed that CO concentration reached below 0.1 %.

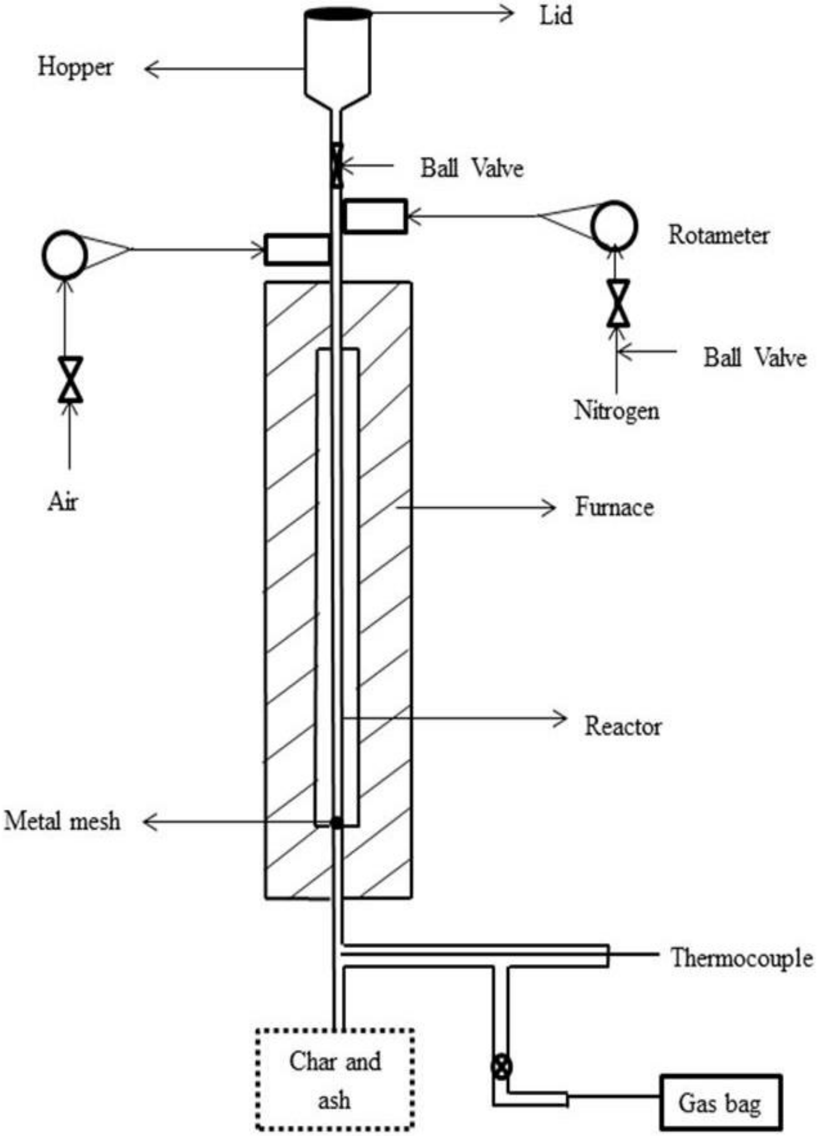


Fig. 2. Schematic of the fixed-bed reactor

3. Measurements and calculations

The gasification performance was evaluated based on yield and LHV of syngas, and gasifier efficiencies such as carbon conversion and cold gas efficiencies. The yield of each component of the syngas was calculated from the product of concentrations and density of each component of the syngas, and the total syngas yield.

The total yield of syngas was calculated using equation 2 (Guangul et al., 2012; Ju et al., 2010; Sharma et al., 2011).

$$Y_{syngas} = (Q_{air} * 79)/(N_2 * m_b) \tag{2}$$

where, Y_{syngas} is the yield of syngas per kg of biomass, $Nm^3\ kg^{-1}$ (d.b.), Q_{air} is the flow rate of air, $Nm^3\ hr^{-1}$, N_2 is the concentration of nitrogen in the syngas, %V/V, and m_b is biomass used per unit time, $kg\ h^{-1}$.

The lower heating value, LHV, of the dry syngas was calculated using equation 3 (Lv et al., 2004; Yin et al., 2012).

$$LHV_{syngas} = ((25.7 * H_2) + (30 * CO) + (85.4 * CH_4) + \big(151.3 * (C_2\,H_2 + C_2\,H_4 + C_2H_6)\big) * (\frac{4.2}{1000}) \tag{3}$$

where, LHV_{syngas} is the lower heating value of syngas, $MJ\ Nm^{-3}$, and H_2, CO, CH_4, C_2H_2, C_2H_4 and C_2H_6 are the concentrations (%V/V) of H_2, CO, CH_4, C_2H_2, C_2H_4, C_2H_6, respectively, in the syngas.

Carbon conversion efficiency (CCE) (%) was the ratio of amount of carbon present in the syngas and the carbon in biomass (Chen et al., 2010; Patel, 2013). Cold gas efficiency (CGE) was calculated using equations 4 (Guangul et al., 2012).

$$CGE = \frac{LHV_{syngas} * Y_{syngas}}{LHV_{biomass}} * 100 \tag{4}$$

where, $LHV_{biomass}$ is the lower heating value of biomass, $MJ\ kg^{-1}$.

SAS analysis of variance (ANOVA) and Duncan multiple range tests were used at the 0.05 level of statistical significance (alpha) to analyze the effects of pretreatment and gasification temperature on the individual and total gas yields, syngas LHV, gasifier efficiencies, and bulk density of switchgrass.

4. Results and discussions

The effects of pretreatment were significant on all feedstock characteristics i.e. proximate and ultimate analyses, higher heating value and bulk density. Effects of pretreatment and gasifier temperature were also significant on the gasifier performance. However interaction between effects of pretreatment and gasification temperature on gasifier performance was not significant. The details are explained below.

4.1 Effects of pretreatment on properties of switchgrass

Table 1 shows the effects of pretreatment on proximate analysis, and the higher heating value (HHV) of switchgrass. As expected, moisture contents of switchgrass torrefied at 230 and 270 °C were lower than that of raw switchgrass because torrefaction, a thermal treatment, results in removal of water and hydroxyl (OH) groups from biomass. However, moisture content of pellets (switchgrass with densification and combined pretreatments) were not analyzed because pellets were dried after densification to safely store pellets. The switchgrass volatile content significantly decreased with the torrefaction and with the increase in torrefaction temperature from 230°C to 270°C due to the partial decomposition of biomass polymers (cellulose, hemicellulose and lignin) and release of lighter volatiles (Tumuluru et al., 2011b). Higher torrefaction temperature leads to release of even more volatiles. But densification of switchgrass did not release volatiles. Densification, however, appears to partially destruct the polymer structure, hence, when torrefaction was followed by densification, the resulted switchgrass had the least volatile content (62.63 wt.%). Ash content of switchgrass was affected significantly only by the torrefaction at 270°C and combined torrefaction and densification pretreatments. Due to the low volatile contents of switchgrass pretreated with torrefaction at 270°C and combined torrefaction and densification, the ash contents were higher. No significant difference was observed between the ash contents of switchgrass torrefied at 230°C, densified and raw switchgrass. Fixed carbon content was significantly affected by all pretreatments except densification. The fixed carbon content was the highest for switchgrass pretreated with combined torrefaction and densification (31.45 wt.%) followed by that for switchgrass pretreated with torrefaction at 270 and 230°C.

Table 1. Effects of pretreatment on proximate analysis and HHV on dry basis (d.b.)

Pretreatment	Moisture (wt.%)	Volatile (wt.%)	Ash (wt.%)	Fixed carbon (wt.%)	HHV (MJ kg^{-1})
No pretreatment	9.80^{A} (0.65)$^{\#}$	80.63^{A*} (0.18)	3.50^{C*} (0.44)	15.87^{D*} (0.42)	20.60^{D} (0.69)
Torrefaction at 230°C	2.39^{B*} (0.61)	78.99^{B} (0.54)	3.63^{C*} (0.15)	17.38^{C} (0.45)	23.53^{B} (0.19)
Torrefaction at 270°C	2.05^{B*} (1.04)	67.52^{C} (0.93)	4.98^{B} (0.50)	27.51^{B} (1.38)	27.11^{A} (0.27)
Densification	5.05 (0.78)	80.23^{A*} (0.54)	3.62^{C*} (0.14)	16.15^{D*} (0.67)	19.14^{E} (0.25)
Combined torrefaction and densification	7.44 (0.15)	62.63^{D} (0.23)	5.91^{A} (0.16)	31.45^{A} (0.38)	22.27^{C} (0.32)

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

#Numbers in parentheses are standard deviation (n=3)

The HHV of switchgrass was significantly affected by all pretreatments. The HHV was the highest for switchgrass pretreated with torrefaction at 270°C (27.11 MJ kg^{-1}) followed by that for switchgrass pretreated with torrefaction at 230°C and combined torrefaction and densification pretreatments (Table 1). The increase in HHV could be due to low oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratios in the switchgrass pretreated with torrefaction. Switchgrass torrefied at 270°C had the lowest O/C ratio of 0.58 and H/C ratio of 0.08 (Fig. 3).

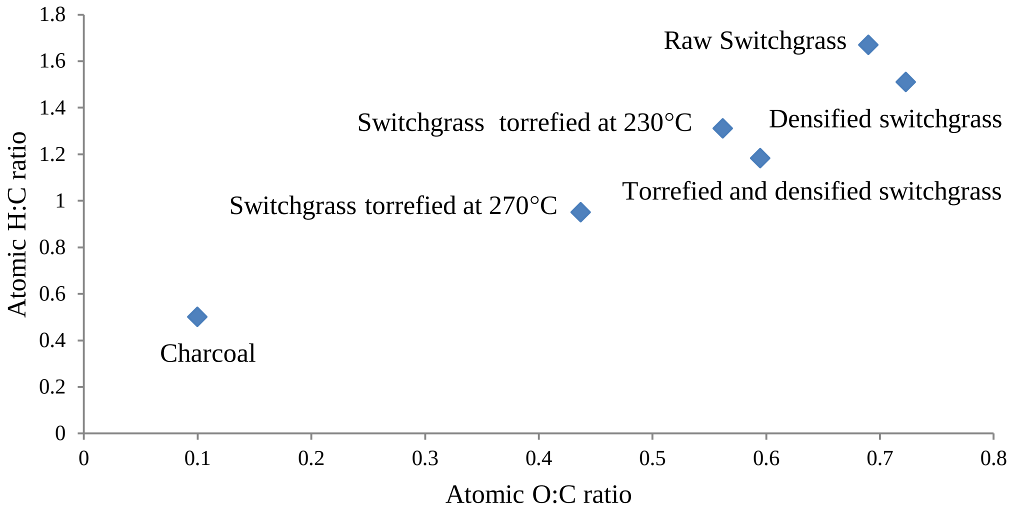
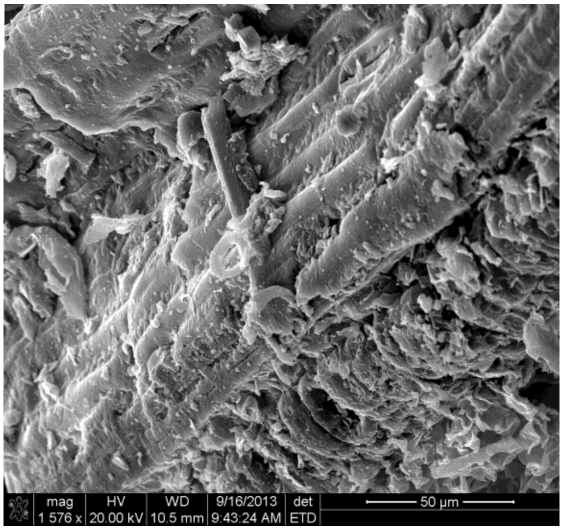


Fig. 3. Van Krevelen diagram comparing charcoal (Tumuluru et al., 2011b) with raw and pretreated switchgrass

The bulk density of switchgrass was significantly affected ($p<0.05$) by all pretreatments: the highest being for the switchgrass pretreated with combined torrefaction and densification (598.17 ±3.09 kg m^{-3}) followed by those for densified switchgrass (498.63 ±6.76 kg m^{-3}), switchgrass torrefied at 270°C (186.78 ±16.45 kg m^{-3}), switchgrass torrefied at 230°C (166.79 ±16.79 kg m^{-3}) and raw switchgrass (138.33 ±4.93 kg m^{-3}). Bergman et al. (2005) also reported that bulk density of wood pellets pretreated with combined torrefaction and densification was the highest (850 kg m^{-3}) followed by those pretreated with densification (650 kg m^{-3}) and torrefaction (230 kg m^{-3}). Higher bulk density of combined torrefied and densified switchgrass would make the biomass easier to store and transport as compared to densified, torrefied and raw switchgrass. However, these bulk densities for densified, and combined torrefied and densified switchgrass were lower as compared to those reported in Bergman et al. (2005) because higher moisture content biomass (26%, w.b.) was used for pelletization tests in this study. Also Bergman et al. (2005) pelletized the hot torrefied biomass whereas in our studies the torrefied biomass was cooled before pelletization.

Unlike raw and densified switchgrass that showed no openings or pores in its structure (Fig. 4a), torrefaction of switchgrass resulted in development of pores, cracks and fissures in the switchgrass (Fig. 4b, c). With an increase in the torrefaction temperature from 230 to 270°C, number of openings or pores increased (Fig. 4b, c). SEM images obtained for torrefied biomass were similar to the ones obtained by Cheng et al. (2009), Ibrahim et al. (2012) and Phanphanich et al. (2010). Densification, however, did not result in development of pores (Fig. 4d). Similar SEM images were obtained by Kaliyan et al. (2010) and Stelte et al. (2011b). Unlike raw switchgrass that showed prominent fibrous structures, switchgrass with the combined pretreatments of torrefaction and densification showed severely disintegrated fibrous structure due to severe pretreatment first by torrefaction at 270°C and then by densification with binder (corn starch and a bio-based lubricant) (Fig. 4e). Similar SEM images of effects of combined torrefaction and densification on pine were reported by Reza et al. (2012).

(a)



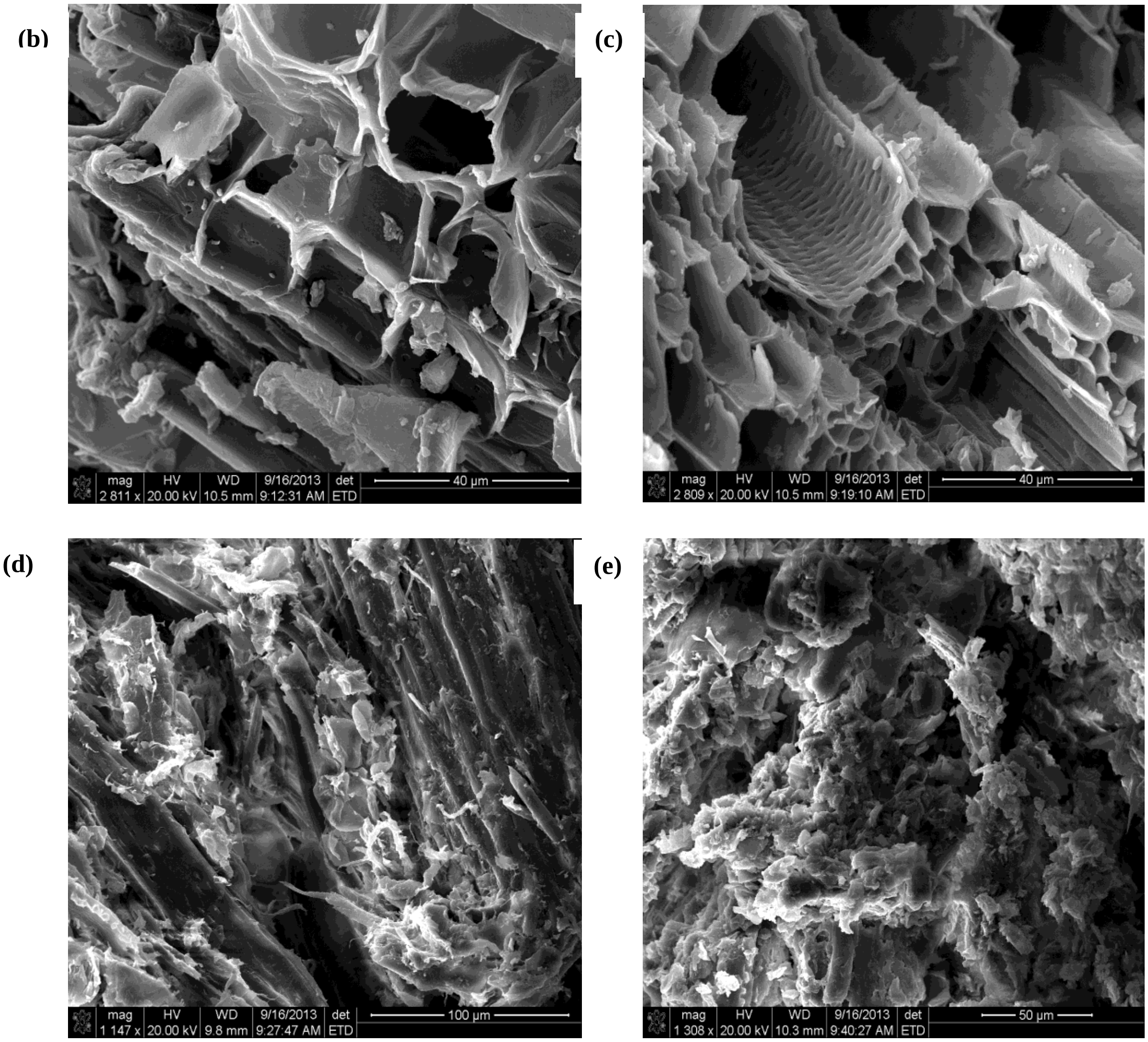


Fig. 4. Scanning Electron Microscopy (SEM) images of (a) raw switchgrass, (b) switchgrass torrefied at 230°C, (c) switchgrass torrefied at 270°C, (d) densified switchgrass, (e) combined torrefied and densified switchgrass

4.2 Effects of pretreatment and gasification temperature on H_2 and CO yields

Pretreatment and gasification temperature significantly affected ($p<0.05$) H_2 and CO yields. Among all pretreatments, gasification of combined torrefied and densified switchgrass resulted in the highest H_2 (0.03 kg/kg biomass) and CO (0.72 kg/kg biomass) yields at the gasification temperature of 900°C and switchgrass torrefied at 270°C resulted in the lowest H_2 (0.005 kg/kg biomass) and CO (0.09 kg/kg biomass) yields at the gasification temperature of 700°C. At all gasification temperatures, the H_2 and CO yields were observed in the following order: combined torrefied and densified switchgrass > densified switchgrass > raw switchgrass > switchgrass torrefied at 230°C > switchgrass torrefied at 270°C (Table 2). However, as expected, the H_2 and CO yields also increased with an increase in gasification temperature from 700 to 900°C for all switchgrass (Table 3). The trend of increasing H_2 and CO yields with increasing gasification temperature was consistent with results reported by Mom et al. (2013), Gao et al. (2008), Patel et al. (2013) and Umeki et al. (2009) for various types of biomass other than pretreated switchgrass. The H_2 and CO yields from all torrefied (only) switchgrass were lower than those from raw switchgrass (Table 2) because oxygen-containing volatiles such as CO and CO_2 are released during torrefaction (Bridgeman T.G., 2008; Couhert et al., 2009; Prins et al., 2006a; Prins et al., 2005; Van der Stelt et al., 2011). Also, H_2 and CO yields from switchgrass torrefied at 270°C was lower (0.22 kg/kg biomass) than those from switchgrass torrefied at 230°C (0.3 kg/kg biomass) possibly due to release of more volatiles during torrefaction at higher (270°C) temperature. In spite of the lowest volatile content (Table 2) of combined torrefied and densified switchgrass, gasification of this biomass resulted in the highest CO yield (Table 3). This implies that densification at 110°C with binder and moisture might have significantly improved biomass properties.

Table 2. Effects of pretreatments on average H_2, CO, CH_4 yields, CCE and CGE

Pretreatment	H_2 yield (kg/kg biomass)	CO yield (kg/kg biomass)	CH_4 yield (kg/kg biomass)	LHV (MJ Nm^{-3})	CCE (%)	CGE (%)
No pretreatment	0.013^{C}	0.41^{C}	0.10^{C}	4.46^{B*}	87.61^{C}	58.28^{C}
Torrefaction at 230°C	0.01^{D}	0.23^{D}	0.11^{D*}	4.06^{C}	66.86^{D}	42.65^{D}
Torrefaction at 270°C	0.007^{E}	0.16^{E}	0.12^{D*}	3.89^{D}	58.12^{E}	34.12^{E}

Densification	0.02^{B}	0.49^{B}	0.08^{B}	4.48^{B*}	89.58^{B}	63.98^{B}
Torrefaction and densification	0.03^{A}	0.62^{A}	0.07^{A}	4.98^{A}	90.69^{A}	64.76^{A}

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

For all switchgrass, increases in H_2 and CO yields with increase in gasification temperatures were expected because high temperatures (>800°C) favor the H_2-producing endothermic water gas and methane reforming reactions, and CO-producing endothermic water gas, Boudouard and methane reforming reactions (Table 3).

Table 3. Effects of gasification temperatures on H_2, CO, CH_4 yields, CCE and CGE

Gasification temperature (°C)	H_2 yield (kg/kg biomass)	CO yield (kg/kg biomass)	CH_4 yield (kg/kg biomass)	LHV (MJ Nm^{-3})	CCE (%)	CGE (%)
700	0.01^{C}	0.31^{C}	0.11^{A}	4.29^{C}	76.72^{C}	50.28^{C}
800	0.015^{B}	0.37^{B}	0.098^{B}	4.37^{B}	78.69^{B}	52.66^{B}
900	0.02^{A}	0.46^{A}	0.083^{C}	4.47^{A}	80.31^{A}	55.33^{A}

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

Table 4. Prominent reactions occurring inside the gasifier

Reaction name	Reactions	Heat of reaction (ΔH)
Water gas	$C + H_2O \Leftrightarrow CO + H_2$	+131KJ $kmol^{-1}$
Boudouard	$C + CO_2 \Leftrightarrow 2CO$	+173KJ $kmol^{-1}$
Methane reforming	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	+206 KJ $kmol^{-1}$

4.3 Effects of pretreatment and gasification temperature on CH_4 yield

Effects of pretreatment and gasification temperature on CH_4 yield were significant ($p<0.05$). Switchgrass torrefied at 270°C resulted in the highest CH_4 yield (0.12 kg/kg biomass) at the lowest gasification temperature of 700°C, whereas combined torrefied and densified switchgrass resulted in the lowest CH_4 yield (0.05 kg/kg biomass) at the highest gasifier temperature of 900°C. This trend was contrary to the trend of CO and H_2 yields. At all gasification temperatures, CH_4 yield can be arranged in the following order: combined torrefied and densified switchgrass < densified switchgrass < raw switchgrass

< switchgrass torrefied at 230°C < switchgrass torrefied at 270°C (Table 2). CH_4 yield decreased with an increase in gasification temperature, for all switchgrass (Table 3) similar to the trends reported by Mom et al. (2013) for oil palm fronds and by Chen et al. (2010) for municipal waste. Since high (>800°C) temperature provides more favorable conditions for thermal cracking and steam reforming (Table 1), decrease in CH_4 yield with increase in gasification temperature for all switchgrass was expected.

4.4 Effects of pretreatment and gasification temperature on syngas LHV

Pretreatment and gasification temperature had significant effect ($p<0.05$) on syngas LHV. The syngas LHV was the highest for combined torrefied and densified switchgrass (4.92, 4.93 and 5.08 MJ Nm^{-3} at gasification temperatures of 700, 800 and 900°C respectively) followed by those for densified switchgrass (4.35, 4.49 and 4.56 MJ Nm^{-3} at gasification temperatures of 700, 800 and 900°C respectively), raw switchgrass (4.39, 4.49 and 4.57 MJ Nm^{-3} at gasification temperatures of 700, 800 and 900°C respectively), switchgrass torrefied at 230°C (4.05, 4.06 and 4.07 MJ Nm^{-3} at gasification temperatures of 700, 800 and 900°C respectively), and switchgrass torrefied at 270°C (3.71, 3.89 and 4.07 MJ Nm^{-3} at gasification temperatures of 700, 800 and 900°C respectively). At all gasification temperatures, syngas LHV can be arranged in the following order: combined torrefied and densified switchgrass > densified switchgrass > raw switchgrass > switchgrass torrefied at 230°C > switchgrass torrefied at 270°C. As can be seen, an increase in the gasification temperature also increased the syngas LHV for all switchgrass similar to the trends reported by Mom et al. (2013) and Lucas et al. (2004). The highest H_2 (0.03 kg/kg biomass) and CO (0.72 kg/kg biomass) (main combustible components of syngas) yields of combined torrefied and densified switchgrass resulted in the highest LHV of the syngas gas at the gasification temperature of 900°C. Similarly, the lowest H_2 (0.005 kg/kg biomass) and CO (0.09 kg/kg biomass) yields of switchgrass torrefied at 270°C resulted in the lowest LHV of syngas at the gasification temperature of 700°C.

4.5 Effects of pretreatment and gasification temperature on gasifier efficiencies (carbon conversion efficiency, CCE, and cold gas efficiency, CGE)

CCE and CGE was significantly affected ($p<0.05$) by pretreatment and gasification temperature. Among all switchgrass pretreatments, combined torrefaction and densification resulted in the highest CCE (92.53%) and CGE (68.40%) at the gasification temperature of 900°C due to its highest H_2 and CO yields, whereas, torrefaction of switchgrass at 270°C resulted in the lowest CCE (56.06%) and CGE (31.79%) at the gasification temperature of 700°C due to its lowest H_2 and CO yields. The low gasification efficiencies (CCE and CGE) of torrefied switchgrass can be attributed to the loss of volatiles released during torrefaction. At all gasification temperatures, CCE and CGE can be arranged in the following order: combined torrefied and densified switchgrass > densified switchgrass > raw switchgrass > switchgrass torrefied at 230°C > switchgrass torrefied at 270°C (Table 2). CCE and CGE also increased for all switchgrass with an increase in the gasification temperature (Table 3) as reported by others (Chen et al., 2010; Mom and Sulaiman, 2013; Patel, 2013).

5. Conclusions

The effects of switchgrass pretreatment and gasification temperature on the gasification performance were evaluated. Among all pretreatments, combined torrefaction and densification of switchgrass increased its bulk density the most to 598.17 kg m^{-3}. Gasification temperature and pretreatment had significant effects on gas yields, syngas LHV and gasifier efficiencies (CCE and CGE). With an increase in the gasification temperature from 700 to 900°C, the H_2 and CO yields, syngas LHV, and gasifier efficiencies increased but the CH_4, CO_2 and N_2 yields decreased for all switchgrass. Among all switchgrass pretreatments, gasification of combined torrefied and densified switchgrass resulted in the highest yields of H_2 (0.03 kg/kg biomass) and CO (0.72 kg/kg biomass), highest syngas LHV (5.08 MJ Nm^{-3}), CCE (92.53%), and CGE (68.40%) at the gasification temperature of 900°C. Gasification of switchgrass torrefied at 270°C resulted in the lowest yields of H_2 (0.005 kg/kg biomass) and CO (0.09 kg/kg biomass), lowest syngas LHV (3.71 MJ Nm^{-3}), CCE (56.06%), and CGE (31.79%) at the gasification temperature of 700°C. Hence, switchgrass with combined torrefaction and densification showed the best gasification performance.

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