



Experimental study of torrefied pine as a gasification fuel using a bubbling fluidized bed gasifier



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ABSTRACT

Torrefied biomass has higher C/O ratio, resulting in improved heating value and reduced hygroscopic nature of the biomass, thus enabling longer storage times. In the southeastern United States, pine is has been identified as a potential feedstock for energy production. The objective of this study was to understand the performance of torrefied pine as a gasification fuel in a bench-scale bubbling fluidized bed gasifier. The gasification of torrefied pine was carried out at 790, 935 and 1000 °C and three equivalence ratios (ERs: 0.20, 0.25 and 0.30). The effect of process variables were studied based on i) products yield, ii) syngas composition iii) syngas energy content, and iv) contaminants. The mean concentration of CO increased with an increase in temperature, but was not statistically significant. On the other hand, H₂ concentration increased whereas CH₄ concentration decreased significantly with an increase in temperature from 790 to 935 °C. Further, with an increase in ER from 0.20 to 0.30, only CO₂ concentrations increased in the syngas. Results from torrefied pine were compared with raw pine gasification, and it was observed that torrefied pine gasification led to much higher char yield (more than twice) than pine; however, it produced less than half as much tar.

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1. Introduction

The energy production from coal has drastically decreased with recent increase in natural gas production [1]. Along with increase in natural gas production, the improved emission standards have forced several coal power plants in the United States to use it. One alternative to its usage is to explore coal-biomass co-feeding scenarios that can help meet the emissions standard. In the south-eastern U.S., the abundant forest resources provide the opportunity for co-feeding biomass with coal to help meet the emission goals [2–4]. However, several issues such as low energy density, high moisture content, low bulk density, higher transportation cost and low grindability associated with the raw biomass impede coal-biomass co-feeding [5–7]. Therefore, biomass pretreatment has been suggested to improve its properties and enable co-feeding in existing coal plants [8,9]. Torrefaction is one such pretreatment

method. During this process hemicellulose is decomposed and increases grindability of biomass, improves energy and carbon content, and bulk density while reducing the hygroscopic nature, and thus making biomass handling easier [8–13]. One of the key benefits of this process is increase in biomass energy and carbon content closer to that of coal. This makes torrefied biomass an excellent choice for co-feeding with coal for power generation purposes.

A handful of studies have been performed on understanding the characteristics of torrefied biomass and its effect on syngas composition from gasification [14–19]. Some studies have conducted bench-scale studies to understand effect of densification along with torrefaction [16], while others have performed simulations [15] to understand performance of torrefied biomass. A few pilot scale studies have also been reported [14,17]. However, only a few of these studies have reported the contaminants released along with the primary syngas composition [14]. Couple of studies with torrefied biomass have been conducted using downdraft gasifiers [14,16]. The torrefaction or pretreatment of biomass affects the

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syngas production and composition. Kuo et al. [15] studied performance of torrefied bamboo using thermodynamic simulation and observed that torrefied bamboo produced lower hydrogen concentration and higher CO production. While Strandberg et al. [18] observed a reduction in methane production from torrefied saw dust when compared with raw saw dust in a pilot-scale entrained flow gasifier. Gasification of torrefied biomass in a downdraft gasifier [14,17] produced syngas with comparable syngas composition and energy content with raw biomass samples. However, Dudyński et al. [14] reported unstable temperature inside gasifier during torrefied biomass gasification. Sarkar et al. [16] suggested that when torrefaction was accompanied by densification, the syngas composition and carbon conversion increased. A study on torrefied *Miscanthus x giganteus* by Xue et al. [19] on a TGA suggested that torrefied biomass favored gasification at higher temperatures (above 850 °C).

It is clear based on the information available in the open literature that there is no study on torrefied biomass in a fluidized bed gasifier. If a large scale application is desired then it is important to understand the performance of torrefied biomass as a feedstock in a fluidized bed gasifier. The availability of pine in the Southeast and growing interest in torrefaction as a pretreatment process encouraged a comprehensive study of torrefied pine as a gasification fuel in a bubbling fluidized bed gasifier. The objective of this study was to experimentally investigate the performance of torrefied pine at three temperatures and equivalence ratios (ERs) based on the syngas composition (CO, CO₂, CH₄, H₂, C₂H₂, C₂H₄), syngas energy, cold gas efficiency and the contaminants (HCl, HF, NH₃, HCN, SO₂, COS and tar) produced when gasified using a bench-scale bubbling fluidized bed with sand as the bed material. A comparison was made between torrefied and raw pine gasification to better understand the effect of torrefaction on the performance of pine.

2. Materials and methodology

2.1. Materials

Southern pine was used for this gasification. Torrefied pine was obtained in the pelletized form whereas raw pine biomass (same biomass that was used for torrefaction) was received in chips from

carbohydrates and lignin in biomass" [20].

2.2. Experimental setup

The experiments were carried out using a bench-scale bubbling fluidized bed gasification rig. A detailed description of this set up has been presented elsewhere [21]. Briefly, the set-up consisted of a hopper, an auger feeder, a fluidized bed gasifier, a high temperature filter unit (HTF), a pair of condensers, an electrostatic precipitator and a tar analysis impinger train. The bubbling fluidized bed gasifier had a diameter of two inches (0.0508 m) and a freeboard with diameter of four inches (0.1016 m). The overall height of the gasifier was 30 inches (0.762 m), while the freeboard was 6 inches (0.1524 m) high. The biomass was stored in the hopper and fed into the gasifier with the help of the auger feeder. Oxygen and nitrogen were used for gasification as the oxidizing and the fluidizing agent, respectively. The flow rate of the nitrogen supplied for fluidization was kept constant at 15 l/min and the corresponding superficial velocity was 0.12 m/s with Reynolds number of 1.11 at NTP. The flow rate of oxygen supplied was varied to achieve the target ER. ER was defined as the ratio of the actual amount of oxygen supplied to the gasifier to the amount of oxygen required for complete combustion of a given quantity of biomass [21].

2.3. Data sampling and analysis

Char and liquid condensate yields were gravimetrically calculated and the char was further analyzed using Perkin Elmer elemental analyzer for elemental composition. Tar collection method has been described in details in published document [21]. This tar collected was later analyzed using an Agilent GC-FID. The GC inlet and FID detector temperature were both maintained at 250 °C and the oven ramped at 5 °C/min from 40 °C to 250 °C. Gas components (CO, CO₂, CH₄, H₂, C₂H₂, and C₂H₄) and contaminants (HCl, HF, NH₃, HCN, SO₂, COS) were collected as discussed in details by Abdoulmoumine et al. [21]. The cold gas efficiency was calculated from syngas composition as shown in Eq. (1). It is defined as the ratio of the sum of the heating values (LHV) of the primary syngas components to that of the LHV (which was calculated from HHV) of the biomass. This efficiency showed how much energy in the biomass was converted to useful syngas components.

$$\text{Cold gas efficiency} = 100 \times \frac{\sum \text{Heating value of syngas component } i \times \text{volumetric flow rate of syngas } i}{\text{LHV of biomass} \times \text{biomass feed rate}} \quad (1)$$

New Biomass Energy, LLC (Quintman, Mississippi). The pellets were ground and sieved through a 850 μm sieve before feeding into the gasifier. In the case of raw pine chips, they were first air-dried, ground, and also sieved through the same screen prior to gasification. The elemental analysis of biomass was performed using CHNS/O analyzer (Perkin Elmer, model 2400, Waltham, MA) and the higher heating value was obtained using bomb calorimeter (IKA Bomb Calorimeter, Model C-200, Wilmington, NC). The ash content, volatile matter and moisture content were performed according to ASTM D1102, BS EN 15148:2009, and ASTM E871, respectively. Structural carbohydrates and lignin were measured using an NREL (National Renewable Energy Laboratory) Laboratory Analytical Procedure (LAP) entitled "Determination of structural

2.4. Experimental design and statistical analysis

Several studies [14,16,21] have reported gasification with an ER ranging from 0.2 to 0.4 and a temperature range of 600–900 °C. In this study, the experiments were carried out at an ER of 0.25 at 790, 935, and 1000 °C and ER of 0.20, 0.25, and 0.30 at 935 °C to study the effect of the temperature and the ER on the gasification products, respectively. A limited number of raw pine gasification experiments were performed at feed rate of approximately 9 g/min to compare the results with the torrefied pine under similar conditions (ER 0.25, temperature 935 °C and feed rate ~9 g/min). The data presented in Section 3 are the average of three runs for every ER and temperature unless otherwise noted. Statistical analysis was carried out using 1-

Table 1
Proximate and ultimate analyses of raw and torrefied pine.

Sample	Proximate analysis, db			Ultimate analysis, daf					Moisture, % ^a
	Ash	VM	FC	C	H	N	S	O	
Raw pine	0.53 ± 0.21	84.94 ± 3.16	14.53 ± 3.03	51.13 ± 0.03	7.15 ± 0.02	0.44 ± 0.02	0.32 ± 0.01	40.96 ± 0.25	7.94 ± 0.16
Torrefied pine	1.17 ± 0.11	75.74 ± 0.22	23.10 ± 0.32	58.61 ± 0.40	6.27 ± 0.27	0.35 ± 0.01	0.31 ± 0.04	34.46 ± 0.17	6.73 ± 0.26

VM: volatile mater, FC: fixed carbon, daf: dry ash free basis, db: dry basis.

^a Wet basis, as received.

way ANOVA with an alpha of 5% (95% confidence interval) to determine the significance of ER and temperature on syngas products, and the analysis was performed using Minitab®. It is important to note that only one tar datum point was collected for each condition.

3. Results and discussion

In this section, effect of temperature and ER on product yield, syngas composition, syngas energy, cold gas efficiency and contaminants have been discussed thoroughly. The biomass characterization and the syngas profile obtained for various process conditions have also been discussed.

3.1. Biomass characterization

Table 1 summarizes the properties of torrefied and raw pine used in this study. Due to torrefaction, the fixed carbon increased in the sample. An increase in carbon by percent weight was also observed in ultimate analysis of torrefied pine. The proximate and ultimate analyses of this feedstock are consistent with the typical values reported for torrefied biomass [16,18,22]. Also, the heating value of 23.60 ± 0.13 MJ/kg (dry basis) is in agreement with those reported for the torrefied pine by other studies [9,15,17,23]. The bulk and particle density of the torrefied pine were found to be 1474.46 ± 10.48 kg/m³ and 489.91 ± 3.88 kg/m³, respectively. The average particle size (d_{50}) obtained was 0.289 ± 0.01 mm. Similarly, the bulk and particle density of the raw pine were 1469.27 ± 2.41 kg/m³ and 224 ± 0.54 kg/m³, respectively. The average particle size (d_{50}) of raw pine used in this study was 0.468 ± 0.044 mm.

Biomass composition analysis of two samples are presented in Table 2. The total hemicellulose and cellulose contents decreased from 16.39% to 10.35% and from 50.83% to 39.51%, respectively. This decrease was due to decomposition of cellulose and hemicellulose around 300 °C [9,16,17]. The high content of Klason lignin was due to decomposition of polysaccharides and more condensation reactions of biopolymers as a result of torrefaction process [24]. Biomass composition reported in Table 2 agreed well with the literature [9] [24].

3.2. Syngas profile

Syngas was analyzed continuously for its composition. The syngas profile obtained for each run were similar to those reported by Abdoulmoumine et al. [21] for raw pine. It was observed that the steady state was reached faster with an increase in temperature, while no such effect was observed with an increase in ER. Steady

state was obtained around 20–30 min into the run, and the experiments were run for at least 120 min. Only the steady state data were used for the calculations, which agreed well with those reported in some of the previous studies [25] [21].

3.3. Effect of temperature and equivalence ratio

Table 3 summarizes the product yield, gas composition, gas energy, carbon conversion, cold gas efficiency and energy content of the syngas as obtained in this study. Subsequent sections will further discuss these responses as well as the selected contaminants measured in details.

3.3.1. Product yield

Char, condensate liquid and gas yields were depended on the operating conditions. The char yield decreased with an increase in temperature due to increase in char reactivity (Table 3). This resulted in increase in gas yield with an increase in temperature. The liquid condensate yield also reduced with an increase in temperature. This was due to increase in steam reforming of char and syngas with an increase in temperature. The change was significant when the temperature was increased from 790 to 935 °C. Similar trends were observed with pine gasification [21]. An increase in gas yield with increase in temperature was also reported by Narvaez et al. [26] for saw dust and for four different biomass samples by Carpenter et al. [25]. Thus, torrefied pine followed similar trend to the raw biomass samples.

As the ER is increased, higher oxygen availability influenced the oxidation reactions, resulting in increase in oxidation products in syngas. Table 3 shows that the reduction in char yield and increase in liquid yield with increase in ER are not statistically significant in the range of ER under study. Similarly, an increase in gas yield was not significant. Few other studies have observed trends similar to those observed in this study for the char yield as the ER increased [21,27]. The increase in the gas yield was also observed for pine gasification [21] and also agreed with simulation results for fluidized bed gasifier [21,27].

The performance of torrefied pine was compared with raw pine under the same gasification conditions (935 °C, ER = 0.25, feeding rate ~ 9 g/min) and shown in Table 4. It was observed that even though the gas yields were similar for both samples, the char yield was higher for torrefied pine, this was due to lower char reactivity of the torrefied pine [28]. On the other hand, higher liquid yield from the raw pine could also due to slightly higher moisture content (7.94 ± 0.16) in it as compared to the torrefied pine (6.73 ± 0.26).

Table 2
Component analysis of biomass samples.^a

Biomass sample	Cellulose % Glucan	Hemicellulose %					Klason lignin %
		Xylan	Galactan	Arabinan	Mannan	Total	
Pine	50.83 ± 0.15	4.23 ± 0.05	1.69 ± 0.01	1.79 ± 0.01	8.68 ± 0.06	16.39 ± 0.14	29.75 ± 0.89
Torrefied pine	39.51 ± 6.97	2.02 ± 0.31	1.00 ± 0.09	2.52 ± 2.15	4.82 ± 2.94	10.35 ± 6.11	45.00 ± 0.02

^a Cellulose, hemicellulose and lignin are calculated on extractive free basis.

Table 3Gasification products obtained as a function of temperature (with ER 0.25) and ER (at temperature 935 °C) with sand as bed material.^a

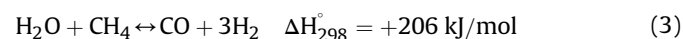
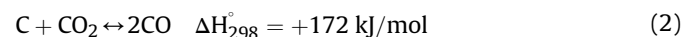
	Temperature, °C			ER		
	790	935	1000	0.20	0.25	0.30
Product yield, %						
Gas	69.21 ± 0.85 ^B	79.62 ± 5.17 ^A	80.56 ± 2.57 ^A	77.89 ± 3.46 ^X	79.62 ± 5.17 ^X	79.31 ± 2.54 ^X
Char	12.98 ± 0.80 ^A	7.33 ± 3.12 ^B	6.99 ± 1.19 ^B	9.33 ± 3.38 ^X	7.33 ± 3.12 ^X	5.43 ± 1.43 ^X
Liquid	17.82 ± 0.91 ^A	13.04 ± 2.10 ^{A,B}	12.44 ± 1.57 ^B	12.77 ± 3.38 ^X	13.04 ± 2.10 ^X	15.04 ± 1.12 ^X
Composition, vol %						
CO	9.32 ± 0.85 ^A	11.78 ± 2.31 ^A	12.26 ± 1.03 ^A	11.27 ± 0.99 ^X	11.78 ± 2.31 ^X	12.85 ± 1.86 ^X
CO ₂	10.97 ± 0.53 ^A	10.09 ± 0.16 ^B	9.39 ± 0.95 ^B	8.39 ± 0.54 ^Z	10.09 ± 0.16 ^Y	11.59 ± 0.39 ^X
CH ₄	11.15 ± 0.90 ^A	5.39 ± 0.91 ^B	4.62 ± 0.11 ^B	5.76 ± 0.84 ^X	5.39 ± 0.91 ^X	4.89 ± 0.89 ^X
H ₂	3.54 ± 1.03 ^B	6.91 ± 0.76 ^A	7.61 ± 0.31 ^A	7.28 ± 0.05 ^X	6.91 ± 0.76 ^X	6.74 ± 0.99 ^X
C ₂ H ₂	0.05 ± 0.001 ^A	0.11 ± 0.03 ^A	0.10 ± 0.02 ^A	0.11 ± 0.001 ^X	0.11 ± 0.03 ^X	0.11 ± 0.01 ^X
C ₂ H ₄	0.84 ± 0.17 ^C	1.16 ± 0.07 ^A	0.41 ± 0.01 ^B	0.48 ± 0.01 ^Y	1.16 ± 0.07 ^X	0.95 ± 0.2 ^X
Efficiency, %						
Cold gas	73.50 ± 11.47 ^A	52.12 ± 12.64 ^{A,B}	49.67 ± 4.82 ^B	52.55 ± 8.35 ^X	52.13 ± 12.64 ^X	54.14 ± 5.05 ^X
Syngas energy						
Energy content, MJ/Nm ³	6.29 ± 0.23 ^A	4.51 ± 0.69 ^B	4.3 ± 0.13 ^B	4.64 ± 0.45 ^X	4.51 ± 0.69 ^X	4.43 ± 0.37 ^X
Contaminant concentration (ppm Volume)						
Ammonia	459.82 ± 22.64 ^A	637.23 ± 25.07 ^A	529.75 ± 20.10 ^A	564.77 ± 45.65 ^X	637.23 ± 25.07 ^X	622.79 ± 12.04 ^X
Hydrogen cyanide	89.47 ± 4.21 ^B	175.95 ± 13.24 ^A	165.50 ± 19.43 ^A	183.63 ± 30.82 ^X	175.95 ± 13.25 ^X	162.82 ± 19.14 ^X
Hydrogen chloride	2.29 ± 1.09 ^A	0.90 ± 0.15 ^A	0.33 ± 0.03 ^A	1.28 ± 0.07 ^X	0.90 ± 0.15 ^X	1.16 ± 0.25 ^X
Hydrogen fluoride	0.15 ± 0.01 ^A	0.27 ± 0.06 ^A	0.27 ± 0.08 ^A	0.28 ± 0.08 ^X	0.27 ± 0.06 ^X	0.28 ± 0.04 ^X
Carbonyl sulfide	16.41 ± 0.90 ^A	11.48 ± 4.25 ^{A,B}	5.38 ± 3.24 ^B	6.41 ± 3.72 ^X	11.48 ± 4.25 ^X	11.97 ± 3.9 ^X
Sulfur dioxide	86.29 ± 3.38 ^A	105.44 ± 21.58 ^A	82.09 ± 4.85 ^A	109.29 ± 4.27 ^X	105.44 ± 21.58 ^X	93.13 ± 9.90 ^X

^a Effect of temperature (superscript A, B and C) and ER (superscript X, Y and Z) were analyzed independently and interaction between them was not studied. Means with same superscripts are not statistically different (P-value > 0.05) based on a one-way ANOVA test.

3.3.2. Syngas composition

Volumetric syngas composition as a function of temperature and ER are shown in Table 3, whereas Fig. 1 illustrates the variation of component yield (g/kg dry biomass) as a function of the temperature and ER.

3.3.2.1. Effect of temperature. As seen in the Table 3 and Fig. 1a, the average concentration and yield of CO and H₂ increased with an increase in temperature. However, the concentration of CO was statistically not significant but H₂ concentration was increased when the temperature was increased from 790 to 935 °C. On the other hand, CO₂ and CH₄ reduced significantly with an increase in temperature from 790 to 935 °C. The reduction in CO₂ and the corresponding increase in CO (even though it was statistically not significant but the mean values were increasing) could be explained by Boudouard reaction as shown in Eq. (2). Furthermore, the steam reforming of methane into H₂ and CO, explained by Eq. (3), at higher temperature was responsible for its reduction.



The increase in the concentration of CO and H₂ agrees with that reported in the literature for switchgrass and other biomass feedstocks [16,21,25,26]. Although an increase in C₂H₂ was noticed, it was not statistically significant with an increase in temperature. The C₂H₄ yields on the other hand showed a peak at 935 °C. The increase in the acetylene and the ethylene production could be due to the reaction of carbon and hydrogen present in the char, which increases with an increase in temperature from 790 to 935 °C. At 1000 °C steam reforming of these compounds resulted in reduction of the yield and concentrations. The values reported agreed well with those reported previously [21,25,29]. Thus, increase in temperature had similar effect on performance of torrefied pine and raw biomass samples.

3.3.2.2. Effect of ER. Table 3 and Fig. 1b show the variation in the yields of syngas components as a function ER with CO₂

significantly increasing as ER increased. This was due to higher oxidation of char, which was also responsible for slight increase in CO, though this was not statistically significant. The increase in oxygen reduced methane and hydrogen concentration, though not significantly in the range of ER studied. C₂H₂ was not affected with an increase in ER, whereas C₂H₄ showed an increase with an increase in the ER. Pine gasification study reported a decrease in the CO, CH₄ and H₂ concentrations, and a significant increase in CO₂ in the range of 0.15–0.35 ER [21]. The presence of higher amount of hemicellulose in raw biomass makes the resulting char more reactive as compared to the torrefied pine where hemicellulose is comparatively much lower [28]. The CO and H₂ yields agreed well with those reported for torrefied switchgrass gasification using a TGA [16]. However, the methane yields were almost twice of those reported in the same study probably due to the difference in TGA and bench scale setup.

Furthermore, a comparison with raw pine was made under similar operating conditions as shown in Table 5. The volumetric syngas compositions were slightly better with raw pine than torrefied samples. Energy content and cold gas efficiency were higher in the case of raw pine than with torrefied samples. Thus, it can be concluded that the change in biomass composition due to torrefaction did not improve syngas composition and energy value. When compared with torrefied pellets gasified in downdraft gasifiers [14,23] with much higher feed rate (almost 30 to 60 times that of bench-scale fluidized bed gasifier), significantly higher concentrations of CO and H₂, but much lower CH₄ were observed. This was probably due to the downdraft gasifier design which helped thermally decompose the hydrocarbons resulting in reduction of CH₄.

Table 4

Product yield for raw pine and torrefied pine at 935 °C, ER 0.25 and feed rate ~9 g/min.

Biomass sample	Product yield		
	Gas yield, %	Char yield, %	Liquid yield, %
Pine	78.10 ± 1.25	3.45 ± 0.85	18.44 ± 1.44
Torrefied pine	79.62 ± 5.17	7.33 ± 3.12	13.04 ± 2.10

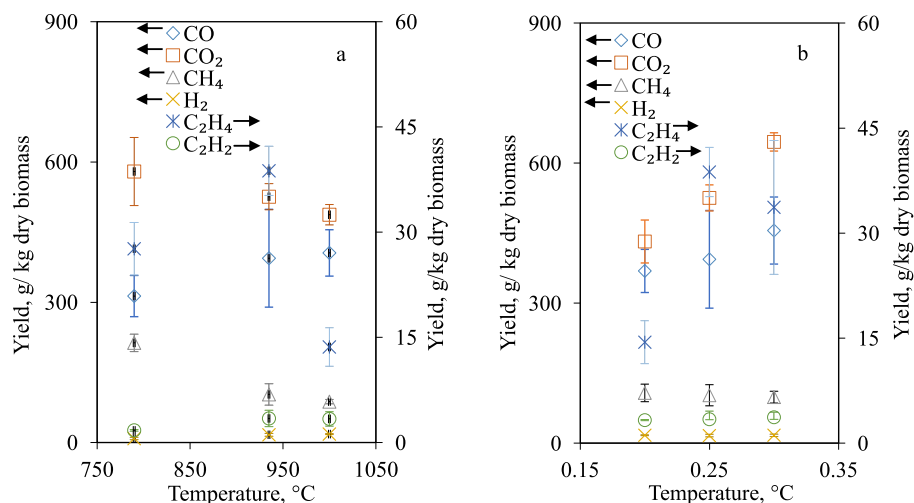


Fig. 1. Effect of (a) temperature at 0.24 ER and (b) ER at 935 °C, on syngas composition.

3.3.3. Syngas energy

Syngas heating value or the energy content of syngas was in the range of 4.3–6.3 MJ/Nm³ as seen in Table 3 and these values agreed well with that reported in literature [16,23,25,26,30]. CH₄ is an important component in syngas, with an increase in temperature resulting in a reduction in CH₄. This led to decreased in syngas energy with an increase in temperature, even though CO and H₂ increased. The torrefied pine produced much higher methane at lower temperature, which is advantageous if syngas is used for power application. ER did not significantly affect the energy content of syngas. Since the ER did not have any significant effect on CO, CH₄ and H₂, the effect on energy content was justified. For pine studies, an increase in ER resulted in a decrease in energy content. The gasification experiments carried out for torrefied pine using downdraft gasifiers reported syngas HHV around 5.6 MJ/Nm³ at temperature around 800 °C [14,17]. This value is slightly lower than what was obtained at 790 °C (Table 3).

3.3.4. Cold gas efficiency

The cold gas efficiency decreased with an increase in the temperature; this was mostly the result of decrease in methane concentration in the syngas with an increase in temperature as shown in Table 3. The cold gas efficiency for downdraft gasifier was around 65–70% [16,17]. The range of the cold gas efficiency (30–70%) also agreed well with the values reported for fluidized bed gasifiers in the literature [14,16,17,29].

During the gasification of torrefied pine in a 25 KW_{th} downdraft

gasifier, the carbon conversion and cold gas efficiency were reported to be around 79% and 63%, respectively at 800 °C [17]. Yet another study reported carbon conversion and cold gas efficiency around 87% and 75%, respectively [14]. A small-scale study on torrefied switchgrass gasified in a small bench scale downdraft gasifier reported increased carbon conversion at 75–80% and cold gas efficiency at 50–55%, with increase in temperature [16]. When torrefied pine was compared with raw pine at a similar feed rate (~9 g/min), temperature (935 °C) and ER (0.25) as shown in Table 4, it was noticed that pine gasification resulted in higher conversion of biomass into syngas. Also, raw pine produced syngas with higher cold gas efficiency. The lower carbon conversion efficiency in torrefied pine was due to high Klason lignin content in torrefied pine.

3.3.5. Contaminants

Fig. 2 and Fig. 3 show the contaminants yield obtained as a function of temperature and ER. It can be seen that ammonia was the main contaminant obtained during gasification followed by hydrogen cyanide and sulfur dioxide.

3.3.5.1. Nitrogen contaminants (NH₃ and HCN). The yield and concentrations of nitrogen contaminants (i.e., HCN and NH₃) were directly proportional to the amount of nitrogen present in the biomass samples.

Fig. 2a and Table 3 show that with an increase in temperature average yields and concentrations of both NH₃ and HCN increased even though they are not statistically significant except between

Table 5
Comparison of syngas gas composition obtained from torrefied and raw pine.

	Torrefied pine	Raw pine	Torrefied pine pellets [17]	Torrefied Pellets [14]
Temperature, °C	935	935	800	800
ER	0.25	0.25	0.28	0.28
Mean Feed rate	9.3 g/min	9.8 g/min	383.5 g/min	583.3 g/min
Composition, vol %				
CO, %	11.78 ± 2.31	13.89 ± 0.60	24.51 ± 0.62	29
CO ₂ , %	10.09 ± 0.16	9.24 ± 0.14	7.88 ± 1.33	6.7
CH ₄ , %	5.39 ± 0.91	6.81 ± 0.30	1.49 ± 0.54	1.6
H ₂ , %	6.91 ± 0.76	6.03 ± 0.21	15.13 ± 0.25	10.3
C ₂ H ₄ , %	1.16 ± 0.07	1.25 ± 0.34	n.r.	0.2
C ₂ H ₂ , %	0.11 ± 0.03	0.12 ± 0.02	n.r.	n.r.
Energy content (MJ/Nm ³)	4.51 ± 0.69	5.24 ± 0.2	5.61 ± 0.06	5.79
Cold gas efficiency, %	52.12 ± 12.64	66.46 ± 3.10	63.00 ± 1.0	75

n.r. not reported.

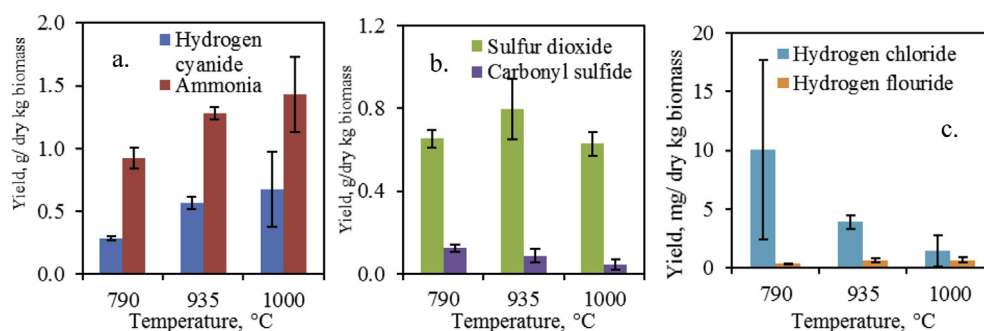


Fig. 2. Effect of temperature on (a) HCN and NH_3 yield, (b) SO_2 and COS and (c) HCl and HF.

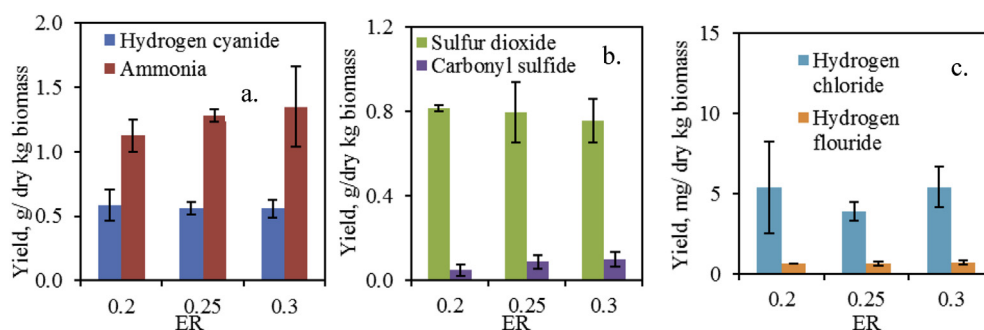


Fig. 3. Effect of ER on (a) HCN and NH_3 yield, (b) SO_2 and COS and (c) HCl and HF.

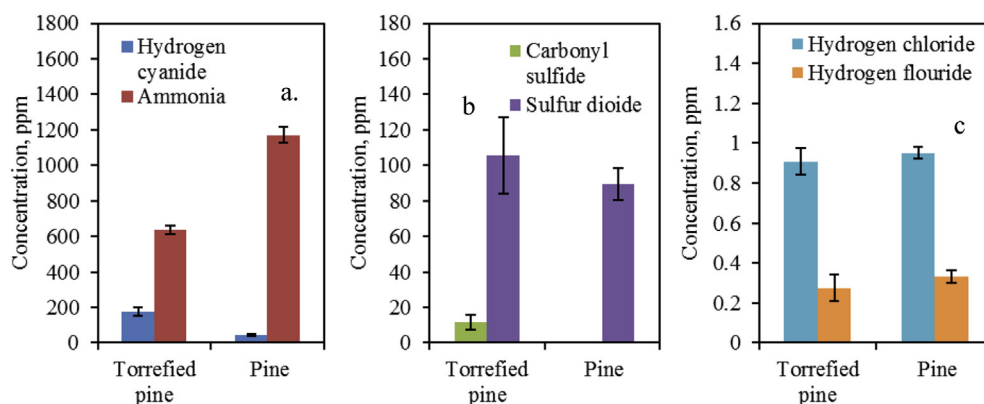


Fig. 4. Concentrations of contaminants NH_3 and HCN (a), COS and SO_2 (b), and HCl and HF (c) at ER of 0.25 and temperature of 935 °C with feed rate of approximately 9 g/min.

790 and 935 °C in the case of HCN. The NH_3 and HCN yields are result of release of fuel-bound nitrogen. The increase in concentrations of NH_3 and HCN with temperature could be due to increase in release of nitrogen release with an increase in temperature. Since N_2 was also used as a fluidizing agent thus increase in release of nitrogen with an increase in temperature could not be confirmed. This trend agreed well with that reported in the literature [29,31]; however, it was opposite of the trend reported for ammonia release from raw pine [21].

With an increase in ER, the NH_3 and HCN concentration and yield, however, remained statistically no different over the range of study as seen in Table 3 and Fig. 3a. This trend was slightly different than that observed for pine, where much higher concentrations (660–1000 ppm) of ammonia were reported even at lower feeding rate [21]. When the NH_3 and HCN values obtained for all raw and torrefied pine samples under similar gasification conditions were compared, it was noted that the raw biomass pine produce twice as

much NH_3 and one third as much of HCN compared to torrefied biomass (Fig. 4a) although raw and torrefied pine had almost same N content.

3.3.5.2. Sulfur contaminants (COS and SO_2). The effects of temperature and ER on the concentration and yield of sulfur contaminants are illustrated in Table 3 and Figs. 2b and 3b. It was observed that with an increase in the temperature, the yield of COS and SO_2 was remained unaffected. Similarly, with an increase in the ER the yield of COS and SO_2 were not affected either. It is important to note that though the concentrations of SO_2 were reported to be around 100 ppm; this was much lower than that reported for coal and biomass co-feeding in a fluidized bed combustor [32]. A study to understand distribution of sulfur species in gasification, reported SO_2 values around 2–4 ppm and COS around 30 ppm at ER 0.26 and S/B ratio of 1.3 at around 1000 °C for corn stover in a bench-scale downdraft gasifier [33]. When the concentrations of COS and SO_2

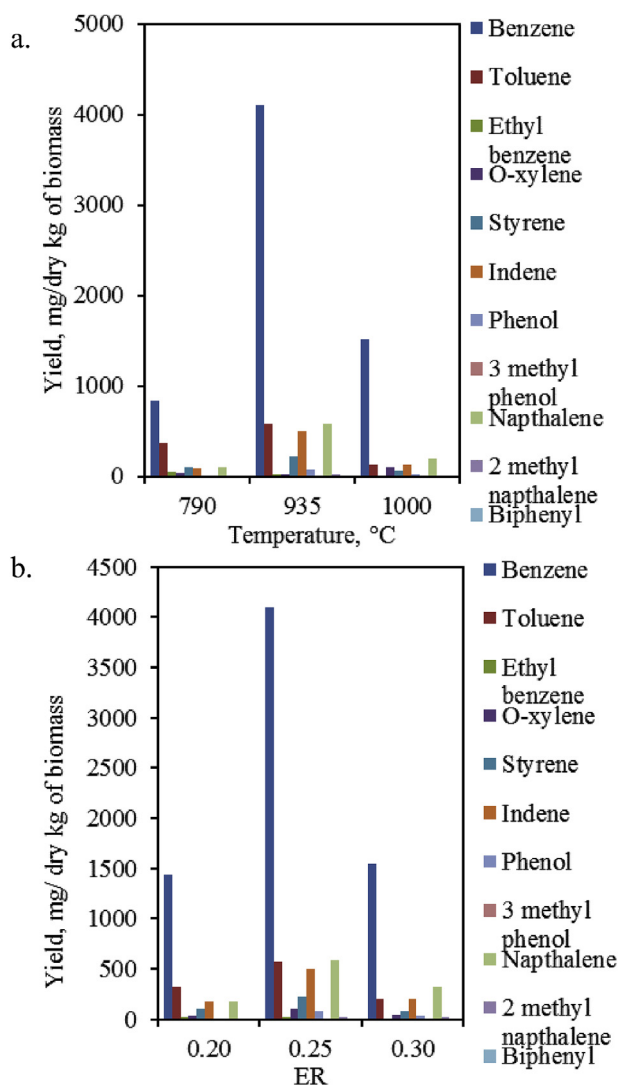


Fig. 5. Effect of temperature (a) and ER (b) on the tar component yield.

obtained from torrefied pine were compared with those obtained for pine under similar conditions, as shown in Fig. 4b, it was observed that the COS concentrations were around 11.47 ppm for torrefied pine and below detection level for raw biomass samples. This indicated that torrefied biomass favored COS production as compared to the raw biomass. H_2S is the other major contaminant in the syngas; it was measured to be around 70 ppm at temperature 790 °C (at feed rate 9 g/min), which compared well with pine gasification (21.70 ppm at similar temperature and biomass feed rate of ~3 g/min) reported in Abdoulmoumine et al. [21].

3.3.5.3. Halides (HCl and HF). Biomass consists of various amounts of chlorine and fluorine. The halides present in the biomass reacted with the hydrogen to produce HCl and HF, which are highly reactive acids causing corrosion for downstream processes. The concentrations of HCl and HF have been reported in Table 3, and Figs. 2c and 3c show the yield in g/kg biomass on dry basis as a function of temperature and ER, respectively. It can be seen that with an increase in temperature, the mean concentration of HCl decreased, while that of HF increased but they are statistically insignificant. Overall, the concentrations are less than 2.5 ppm. On the other hand, the ER range under study does not seem to have any effect on the halide concentration. During the gasification of raw pine, as reported in by Abdoulmoumine et al. (2014), it was observed that the HCl concentration decreased with an increase in temperature [21], and this trend agreed with that for torrefied biomass. Also, the concentrations of halides for pine and torrefied pine were in a rather similar range. The HCl concentrations for coal have been reported to be around 600 ppm; this corresponds to the higher chlorine content (up to 0.60%) in coal [34,35]. When the hydrogen halides concentrations were compared for pine, and torrefied pine under similar conditions, as shown in Fig. 4c, it was observed that the torrefied pine and raw pine produced approximately the same amount of hydrogen halides. The torrefaction process did not affect the halides present in the raw biomass and hence the similarity in hydrogen halides yields.

3.3.5.4. Tar. The collected tar was analyzed for benzene, toluene, ethyl benzene, o-xylene, styrene, indene, phenol, 3-methyl phenol, naphthalene, 2-methyl naphthalene, and bi-phenyl. Fig. 5 shows the yield of each of the above mentioned compounds as a function of temperature and ER, while Fig. 6 shows the total tar yield as a function of temperature and ER. It is important to note that the data shown in these figures were obtained from single runs and hence, a clear trend was difficult to predict with an increase in temperature and ER. It was seen that with an increase in temperature, the tar yield increased from 1.56 g/kg biomass at 790 °C to 3.87 g/kg biomass at 935 °C and with further increase in temperature it reduced to 2.08 g/kg biomass at 1000 °C. The increase in tar was a result of increase in tertiary compounds like benzene, toluene, indene, styrene and naphthalene. In their seminal work on the nature of tar formation, Milne et al. [36] attributed tertiary tar formation at high temperature to the thermal conversion of primary and secondary tar compounds. However, at sufficiently high temperatures, all tar compounds undergo thermal cracking. Therefore, it is likely that the decrease in tar concentration beyond 935 °C was due to increasing thermal cracking of tar compounds.

The total tar yield reported was 1.94, 3.87 and 2.42 g/dry kg biomass at ER 0.20, 0.25 and 0.30, respectively. With an increase in ER from 0.20 to 0.25 the total tar yield increased, which was contradictory to what has been reported in literature [21,25,36,37] and perhaps was due to the small change in ER. Even though fractions of benzene and naphthalene have been reported to increase above ER

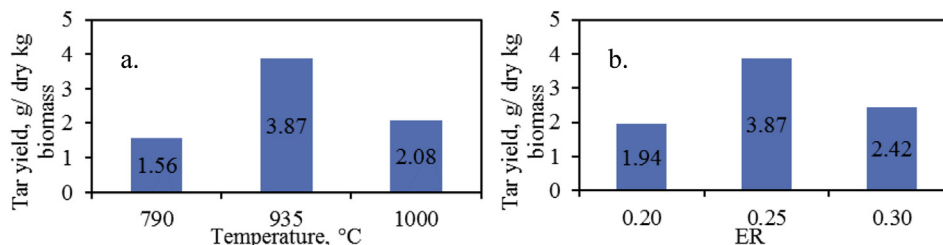


Fig. 6. Effect of temperature (a) and ER (b) on total tar yield.

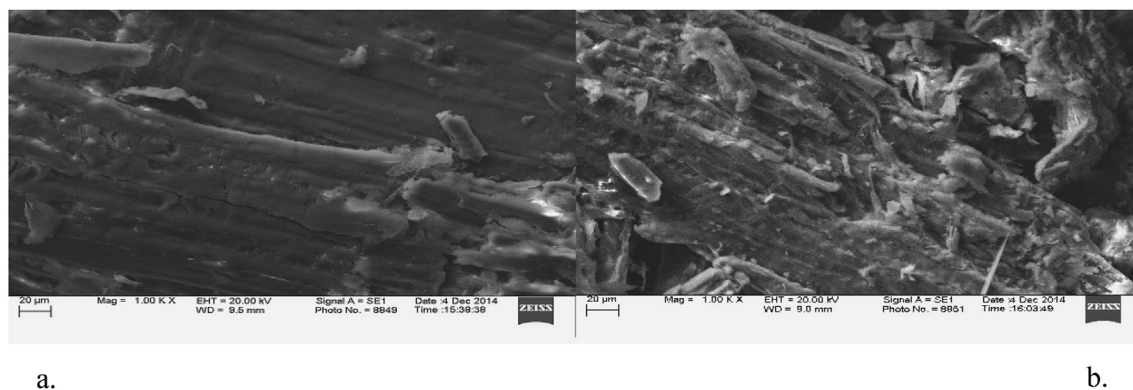


Fig. 7. SEM image of raw pine (a) and torrefied pine (b).

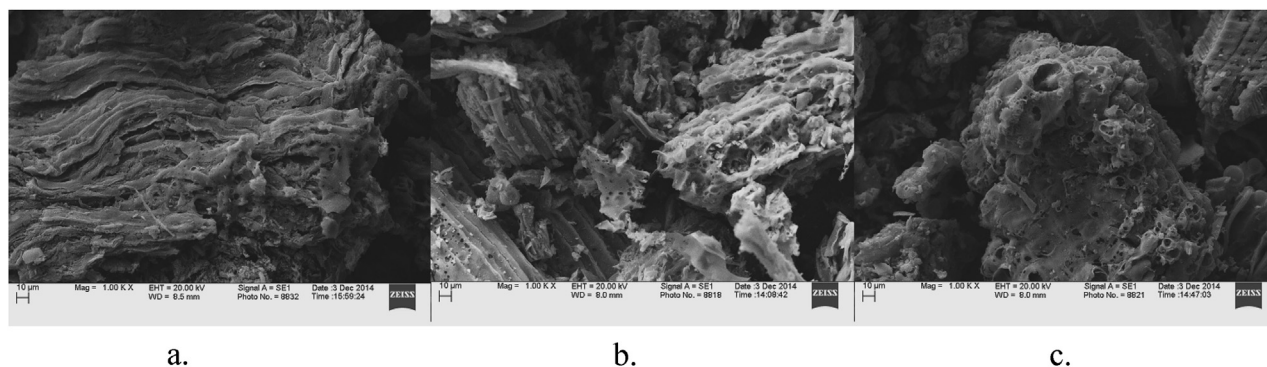


Fig. 8. SEM images of char obtained for experimental runs performed at 790 °C (a), 935 °C (b) and 1000 °C (c).

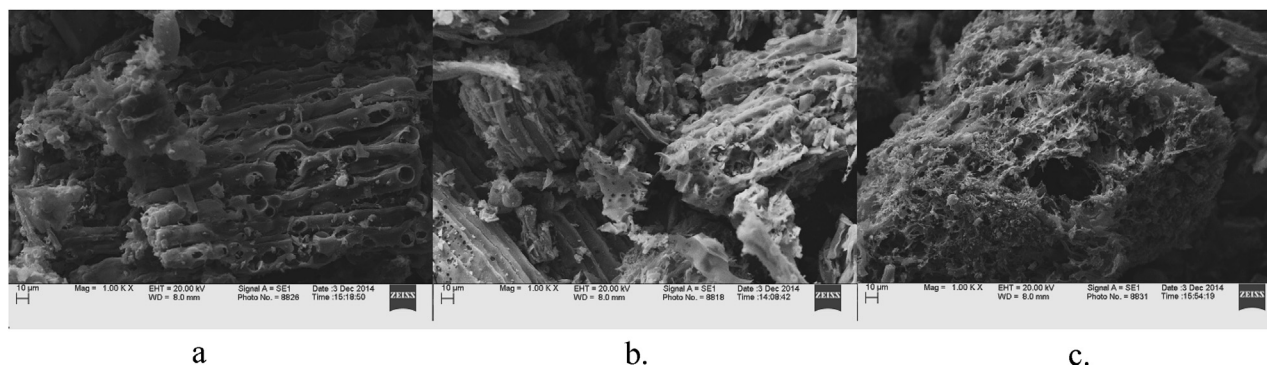


Fig. 9. SEM images of char obtained for experimental runs performed at ER: 0.20 (a), 0.25 (b) and 0.30 (c).

0.27 [37], other compounds tend to reduce due to oxidation. With further increase in ER (0.25–0.30) all the compounds and the total tar yield decrease, as expected.

It was observed that the highest yield obtained was that of benzene followed by toluene, indene, and naphthalene for all the conditions. The total and constituent yields agreed well with those reported with literature [21,25,26,38]. When a comparison was made between tar obtained from raw and torrefied pine. It was found that, for raw pine gasification tar produced was around 8 g/dry kg biomass and has been reported in a published article [21], at gasification temperature 935 °C and ER 0.25. While, it was observed that the torrefied pine produced less than half the amount of tar obtained for pine (as shown in Fig. 6a) under same temperature and ER. Thus, indicating that the torrefaction of biomass helps reduce the tar yield during gasification.

3.3.6. SEM images of char

In order to understand the effect of gasification parameters on the biomass particles, images from the scanning electron microscope (SEM) were taken. Fig. 7 shows the raw pine and torrefied pine at 1000x magnification. Fig. 7a shows that the cell walls of the ground biomass are still intact in the raw biomass, while they appear to be disintegrated due to torrefaction as seen in Fig. 7b [16,39,40].

As seen in Fig. 8, a higher degradation of the char particles is observed with the increase in temperature. It shows that even at higher temperatures such as 935 or 1000 °C cell walls are not completely damaged. This implies that either the actual temperature of the particles was much lower than what the gasification temperature was or some the particles were entrained during the gasification without decomposing totally during gasification. In

addition, as the gasification temperature increase, more voids are visible and it could be due to the ejection of volatile matter from cell walls.

Fig. 9 shows the microscopic structure of biomass of the char particles obtained through gasification at ER 0.20, 0.25 and 0.30. With higher oxygen supply, the disintegration of the char structure was more prominent, resulting in larger voids, which could be result of increase in the char reactivity or higher temperature of the particles with increase in ER.

4. Conclusions and remarks

This experimental study was performed to understand performance of torrefied pine as a gasification fuel in a bubbling fluidized bed gasifier and compare its performance with raw pine. A parametric study was performed to comprehend the effects of temperature and equivalence ratio on gasification of torrefied pine. Most importantly along with syngas composition, syngas contaminants (SO_2 , COS, HF, HCl, NH_3 , HCN and tar) were also studied. Nitrogen contaminants NH_3 and HCN were obtained in the range of 450–650 ppm and 90–180 ppm, respectively. H_2S was around 70 ppm, while SO_2 and COS were in reported between 80 to 100 ppm and 5–12 ppm respectively. HCl and HF were less than 2 ppm. The tar yield obtained was between 1.5 and 3.8 g/dry kg of biomass. The temperature and equivalence ratio did not have any significant effect on contaminant yield. Though temperature influenced the primary syngas composition to certain extent, equivalence ratio range in this study did not affect the syngas composition except for CO_2 .

From this study, it can be concluded that the higher carbon content in the torrefied pine did not translate to higher carbon in syngas, rather resulted in higher char formation, while producing lower liquid yield than raw pine when compared under similar gasification conditions (temperature and ER). One of the major advantages of torrefied pine gasification was lower tar production (3.8 g/kg of biomass) during gasification as compared to raw pine (8 g/kg of biomass). Also, torrefied pine produced lower amount of NH_3 (600 ppm) than raw pine (1100 ppm). Torrefaction of pine in infact resulted in lower heating value as compared to raw pine.

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