

Torrefaction of Healthy and Beetle Kill Pine and Co-Combustion With Sub-Bituminous Coal

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Combustion of biomass and co-combustion with fossil fuels are viable means of reducing emissions in electricity generation, and local biomass resources are appealing to minimize life cycle emissions. In the Rocky Mountain Region of the U.S., a bark beetle epidemic is causing widespread forest death and associated safety hazards. This biomass has potential to be a feedstock resource, thereby achieving dual goals of improving forest health while supplying biomass for uses such as co-firing with coal in power plants. In this study, combustion and co-combustion of healthy pine (HP) and beetle kill pine (BK) with coal were conducted to assess the interchangeability of these feedstocks in raw and torrefied forms. HP and BK pine were torrefied at 200, 250, and 300 °C to increase energy density and improve grindability, both of which aid in seamless integration into power plants. Grindability was assessed for both feedstocks at each torrefaction condition. The raw feedstocks were pyrolyzed to assess their relative compositions. Raw and torrefied feedstocks were then combusted alone and co-combusted with sub-bituminous Powder River Basin coal using thermogravimetric analysis (TGA). Modulated TGA was used to derive kinetic parameters of coal, raw and torrefied biomass, and coal-biomass blends. Results show increased grindability and pyrolysis mass loss of BK as compared to HP, which are attributed to the degraded state of the wood. Combustion and co-combustion show favorable interchangeability of the HP and BK, and additive behavior when co-combusted with coal. [DOI: 10.1115/1.4038406]

Keywords: biomass, pine, beetle kill, sub-bituminous coal, co-combustion, torrefaction

1 Introduction

As the electricity generation sector seeks to reduce greenhouse gas emissions, the use of biomass as a feedstock alone and blended with coal for co-firing has been increasingly explored and implemented as a viable greenhouse gas mitigation option [1–3]. The Department of Energy recently released its Billion Ton Report, showing that plentiful biomass resources exist, including forest resources, within the U.S. to help meet energy demands [4]. Local biomass availability and needs must be considered when deciding on renewable energy strategies, as assessments of biomass resource location and demands in the U.S. have shown that supply and intended end use are not necessarily collocated [5]. Recent analyses have shown that, in order to achieve high levels of emissions reductions at minimal additional cost, transportation of biomass over significant distances should be avoided and local biomass resources should be considered for regional energy needs such as electricity [6]. Numerous studies have explored the use of biomass resources, including forest residues and dedicated crops like switchgrass, for co-firing with coal in power plants with an emphasis on local resources [2,7,8].

One biomass resource which is plentiful in the Rocky Mountain Region of the U.S. is lodgepole pine that has been killed by the blue stain fungi introduced by bark beetles. Estimates indicate that as much as 19.7 billion cu ft of standing dead timber could potentially be salvaged from across the western U.S. [9]. Additionally, if left unmanaged, devastating negative effects of large swaths of dead and dry forest on forest fire severity and risk to life and property have been identified [10]. Many different groups,

including the National Forest Service, recognize the potential for bioenergy development utilizing bark beetle kill trees and encourage bioenergy projects that utilize beetle kill biomass as a feedstock [11]. Furthermore, a recent technoeconomic assessment found that there are large amounts of standing and fallen dead pine in proximity to power plants in the region, and quantification of the co-firing potential of beetle kill pine (BK) by volume and proximity found it to be a plentiful resource [12]. Therefore, these assessments of beetle kill wood and the interest in increased use of biomass for electricity generation suggest that the investigation of beetle kill pine as a combustion and co-combustion feedstock is warranted.

There are technical challenges in co-firing biomass feedstock with coal in power plants, many of which are due to the differences in properties between coal and various biomasses [13]. Unfavorable properties of raw biomass include high moisture content and hygroscopicity, low energy density, and low grindability relative to coal. These properties can be improved for combustion with coal through mild pyrolysis, called torrefaction, in which raw biomass is heated in an inert atmosphere to temperatures between 200 and 300 °C. Torrefaction has been shown to significantly improve biomass properties, making biomass more suitable for co-firing applications [14,15]. Specifically, torrefaction reduces the oxygen and hydrogen contents of biomass, thereby concentrating the carbon content and increasing the heating value [16]. The hemicellulose portion of biomass is substantially degraded and the biomass is rendered hydrophobic during torrefaction due to the loss of –OH functional groups, which improves the storability of the biomass [17]. Additionally, torrefaction degrades the fibrous nature of raw biomass, thereby improving its grindability and handling [18,19]. As a result of these property changes, torrefaction can render biomass properties more similar to coal, improve combustion efficiency, and reduce transportation and storage costs of biomass [20].

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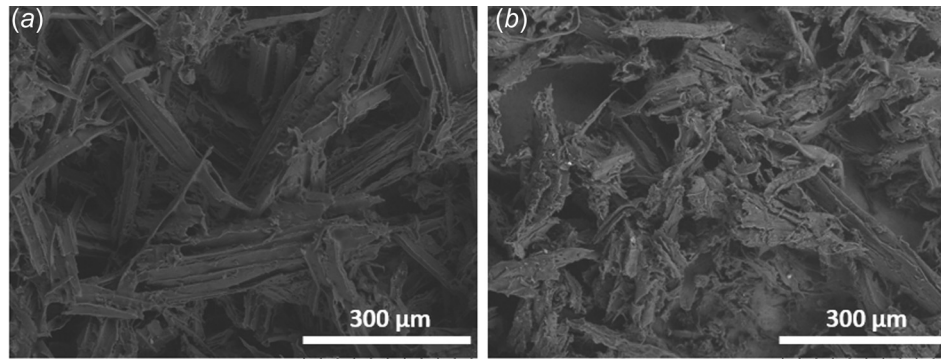


Fig. 1 Scanning electron microscopy images of (a) HP and (b) BK pine

Thermogravimetric analysis (TGA) has been widely used to examine thermochemical conversion and characteristics of biomass, including mass loss, mass yield, composition, and kinetic parameters [21,22]. Among thermochemical conversion techniques, the combustion of healthy raw and torrefied pine [23–25] and its co-combustion with coal have garnered particular interest because of their advanced technology readiness. Gil et al. [26] studied the combustion of bituminous coal and raw pine sawdust blends using TGA and found no significant synergistic behavior between the coal and biomass, as the blend behaved as an additive sum of the mass fractions and mass loss characteristics of each component. The coal, pine, and blends presented one, two, and three major mass loss events during combustion, respectively; these reaction steps were attributed predominantly to char oxidation for coal and volatile release followed by char oxidation for pine, with the blends demonstrating behavior of both coal and pine. Kinetic parameters were assessed using the Coats–Redfern method, with a first-order chemical reaction model fitting coal oxidation and the first stage of pine combustion and a diffusion model fitting second stage pine oxidation. Wang et al. [27] also studied the combustion of bituminous coal and pine sawdust using TGA and did observe both negative synergistic behavior at low conversion extents, which was attributed to coal restricting the devolatilization of biomass, and positive synergistic behavior which was attributed to the alkali content of the biomass ash. Zhang et al. [28] studied the co-combustion of coal gangue and pine sawdust using TGA and also observed synergistic behavior, which was attributed to a thermal effect in which heat release from pine combustion was lost to coal gangue, thereby slowing pine combustion and accelerating coal gangue combustion.

This study characterizes the torrefaction of beetle kill pine wood and its co-combustion with Powder River Basin coal in order to assess the technical viability of using beetle kill wood as a co-firing feedstock. Healthy pine (HP) is also assessed to elucidate the differences between beetle kill and healthy pine, as any co-firing strategy that purports to use beetle kill wood will need to plan for an alternative feedstock in the future as beetle kill wood is depleted. The combustion of beetle kill and healthy pine wood, torrefied at 200, 250, and 300 °C via TGA and a fixed bed reactor, and the grindability of the raw and torrefied feedstocks are assessed. The combustion of these feedstocks alone and their co-combustion with Powder River Basin coal in a 20/80% by energy blend of wood/coal, widely considered to be readily attainable in many furnaces [29], are also assessed. Mass loss, differential mass loss, and kinetic parameters evaluated by modulated TGA are presented. Differences in the composition, handling, and combustion characteristics of the feedstocks are discussed.

2 Materials and Methods

2.1 Feedstock Preparation. The biomass feedstocks used in this study were a sub-bituminous coal from the Powder River Basin in Wyoming (coal), pine sawdust produced from healthy

pine, and pine sawdust produced from standing dead beetle kill pine. The pine wood was collected from the Medicine Bow National Forest following all proper permitting requirements. Figure 1 shows scanning electron microscopy images of raw HP and BK, both of particle sizes nominally in a 75–150 μm particle size range achieved by sieving particles between 100 and 200 mesh size sieves. HP is observed to have more uniform fiber orientation as compared to BK, which exhibits greater variation in fiber orientation and appears more amorphous, suggestive of wood degradation in BK. Ultimate, proximate and heating values for the three tested feedstocks are summarized in Table 1. Biomass feedstock heating value, ultimate, and proximate analyses were performed by Wyoming Analytical Laboratories, Laramie, WY. Coal feedstock analyses were performed by Idaho National Laboratory.

Healthy and beetle kill pine sawdust in a particle size range of 0.425–3.35 mm were torrefied in a fixed bed reactor in order to produce samples for grindability assessment and combustion. The reactor was constructed from 316 SS pipe and fittings, and the main section of the reactor in which biomass was loaded for torrefaction was approximately 15 cm long with a 20 mm inside diameter. An inlet at the bottom of the reactor allowed inert gas to flow through the sample during torrefaction, and an outlet at the top permitted the venting of inert and evolved gases. A thermocouple was inserted into the sample and the sample temperature was continuously monitored during torrefaction. The reactor was loaded with approximately 5 g of predried sample and loaded into a preheated oven, while nitrogen (N₂) was flowed through the reactor at 0.5 L min⁻¹ in order to replace the interstitial gas with fresh N₂ approximately once per second. HP and BK samples underwent an average heating rate of 20 °C min⁻¹ up to a final torrefaction temperature of 200, 250, and 300 °C and were held at torrefaction temperature for one hour. Following torrefaction, samples were cooled in an inert environment to below 100 °C before they were removed from the oven. Samples were then transferred to glass

Table 1 Ultimate, proximate, and heating value analyses of as-received raw HP, BK pine, and coal are summarized. Results are on a weight by % basis unless otherwise specified.

	HP	BK	Coal
Moisture	7.16	6.53	26.8
Volatile matter	74.6	76.0	32.5
Fixed carbon	17.3	17.0	34.5
Ash	0.97	0.42	6.17
Carbon	47.2	48.6	48.6
Oxygen	38.9	38.4	14.0
Hydrogen	5.39	5.70	3.34
Nitrogen	0.38	0.28	0.58
Sulfur	0.02	0.02	0.47
HHV (kJ/kg)	18,401	19,006	19,725

Table 2 Heating values for torrefied HP and BK, as-received, are shown

	HHV (kJ/kg)
HP_200	18,908
HP_250	19,682
HP_300	22,551
BK_200	18,966
BK_250	19,757
BK_300	22,341

jars and flushed with N₂ for storage. Heating values for HP and BK torrefied at 200 °C (HP_200 and BK_200, respectively), 250 °C (HP_250 and BK_250, respectively) and 300 °C (HP_300 and BK_300, respectively) were measured and are summarized in Table 2.

2.2 Grindability. Grindability was assessed for raw and torrefied HP and BK samples in a particle size range of 0.425–3.35 mm. Prior to milling the samples, raw and torrefied BK and HP were sieved into size ranges of <75 μm, 75–150 μm, 150–425 μm, 0.425–1.18 mm, 1.18–2.00 mm, 2.00–3.35 mm, and >3.35 mm. A Gilson shaker was used to separate samples into the sieves using a shaking period of 2 min. After sieving, mass fractions were weighed and the fraction of total mass in each size range was calculated. After weighing all separated samples, the fractions were recombined and milled in an SPEX Industries ball mill for 1 min using a tungsten vessel and milling balls. The milled HP and BK samples were then sieved and weighed again. Some of the 75–150 μm fraction of each sample was retained and used for TGA combustion tests. The remainders of the milled samples were sent to Wyoming Analytical Laboratories for ultimate, proximate, and heating value analyses and further processed as necessary to fulfill the specifications of ASTM standards D5373, D7582, and D5865, respectively.

2.3 Thermogravimetric Analysis. Torrefaction mass loss, pyrolysis, combustion and combustion kinetic analysis were conducted using a TA Instruments Q500 TGA. Samples of biomass, coal, and biomass/coal blends of 20/80% by energy were loaded into alumina sample pans of 0.1 mL volume for all tests. N₂ (99.999%) and air (industrial compressed air, dried, and filtered) were used for inert and reactive gas environments, respectively, and flowed at 100 mL min⁻¹ for all tests. All tests were conducted at atmospheric pressure, which is 75 kPa in Laramie, WY. Torrefaction mass loss was quantified for HP and BK sawdust at each of the three tested torrefaction temperatures (200, 250, and 300 °C) by loading 5–7 mg of sawdust into a sample pan, and then carrying out torrefaction in the TGA. A temperature profile of heating to 100 °C at 100 °C min⁻¹, then a 10 min isothermal dehydration step, followed by heating at 20 °C min⁻¹ to the final torrefaction temperature of 200, 250, or 300 °C, and finally an isothermal step at torrefaction temperature for 1 h was applied. This method mimicked the heating profile used in larger scale torrefaction in the fixed bed reactor. Mass loss during torrefaction was determined on a dry basis following dehydration. Torrefaction was repeated five times to confirm repeatability and conduct statistical analysis on mass loss results.

Pyrolysis, combustion, and co-combustion of pulverized HP and BK, with particle sizes between 75–150 μm, were conducted using TA Instruments modulated TGA, in which feedstocks undergo a linear heating rate and a sinusoidal temperature modulation is imposed upon the linear heating profile in order to facilitate the assessment of Arrhenius kinetic parameters [30,31]. Activation energy (E_a) was evaluated using the following equation:

$$E_a = \frac{R(T^2 - Z^2) \ln \frac{dx_p}{dx_v}}{2Z} \quad (1)$$

where R is the ideal gas constant, T is the average value of the oscillating temperature, Z is the amplitude of the temperature oscillation, and dx_p/dx_v is the ratio of mass loss rates between adjacent peaks and valleys. The derivation of E_a is model free in that an assumed form of a kinetic function is not required. The Arrhenius pre-exponential factor (A) can be derived from modulated TGA assuming first order kinetics by the following equation:

$$\ln(A) = \ln \left[\frac{d\alpha}{1 - \alpha} \right] + \frac{E_a}{RT} \quad (2)$$

A linear heating rate of 2 °C min⁻¹ with an amplitude of 2 °C and a period of 200 s was used in all modulated TGA pyrolysis, combustion, and co-combustion tests. An advantage of using modulated TGA for determination of kinetic parameters is that E_a and A can be evaluated at every data point. In order to report a single representative value for each kinetic parameter at each stage of combustion, values of E_a and A were averaged between ±10% of the maximum derivative mass loss for each reaction stage.

Pyrolysis was conducted in a N₂ environment up to a pyrolysis temperature of 800 °C in order to examine the relative hemicellulose, cellulose, and lignin contents of the feedstocks as well as the pyrolysis kinetics for the two feedstocks. Combustion was conducted in air at temperatures up to 800 °C of nine unblended samples: raw HP and BK; HP and BK each torrefied at 200, 250, and 300 °C; and coal. Co-combustion of blends of HP or BK with coal was prepared by blending 20% by energy of HP or BK with coal, and these blends were combusted in the TGA. For all pyrolysis, combustion and co-combustion tests, samples of 5–7 mg were used to avoid mass and heat transfer limitation effects and tests were repeated twice to confirm repeatability.

The presence of additive or synergistic behavior was assessed by calculating theoretical derivative mass loss curves for feedstock blends from the derivative mass loss curves of the individual components using the following equation:

$$dm/dt_{\text{model}} = x_{\text{coal}}(dm/dt)_{\text{coal}} + x_{\text{biomass}}(dm/dt)_{\text{biomass}} \quad (3)$$

where x_{coal} and x_{biomass} are the mass fractions of coal and biomass in the blends, respectively, and $(dm/dt)_{\text{coal}}$ and $(dm/dt)_{\text{biomass}}$ are the individual experimental derivative mass loss curves of coal and biomass, respectively. TGA is an excellent method for testing for the presence of synergistic or additive behavior between two feedstocks because feedstock particles are maintained in contact throughout the duration of the heating process.

3 Results and Discussion

3.1 Torrefaction Mass Loss. Figure 2 summarizes the mass loss due to torrefaction, as determined by TGA. The average uncertainty, calculated using Student t -distribution with a 95% confidence interval for five replicates, for all data sets is ±0.9% and is not shown in Fig. 2 due to its small magnitude. Results show that BK mass loss is slightly greater than HP mass loss at 200 °C torrefaction at 10.2% and 9.3%, respectively. The difference in mass loss increases at a torrefaction temperature of 250 °C, where BK loses 28.4% of its initial mass and HP loses 26.4% of its initial mass. The greatest difference in mass loss is observed at 300 °C torrefaction temperature, where BK and HP lose 68.5% and 64.7% of their initial masses, respectively. These results suggest that HP is more recalcitrant to degradation at torrefaction temperatures, which could be attributed to the natural degradation that BK undergoes upon death by infestation of bark

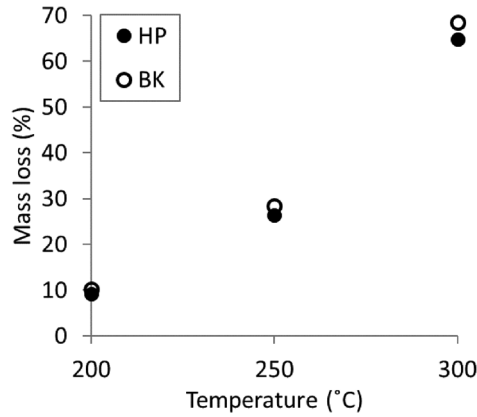


Fig. 2 Mass loss of HP and BK due to torrefaction at 200, 250, and 300 °C are shown

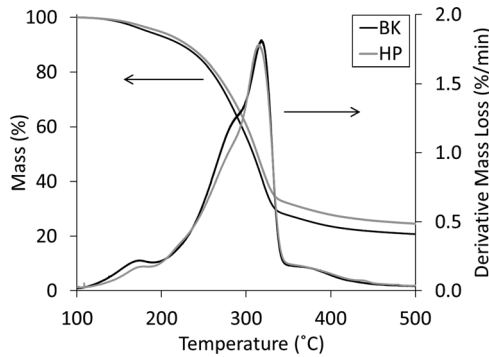


Fig. 3 Mass loss and derivative mass loss of raw HP and raw BK during pyrolysis

beetles and the fungi that the bark beetles introduce to the tree [32,33].

Figure 3 shows the mass loss and derivative mass loss during pyrolysis of raw HP and BK. Results are presented on a dry basis and abbreviated to between 100 °C and 500 °C in Fig. 3 in order to better visualize the predominant region of mass loss during pyrolysis; minimal and gradual mass loss was observed beyond 500 °C and until the end of pyrolysis experiments. BK is observed

to lose more mass during pyrolysis as compared to HP, with BK and HP losing 79% and 75% of their original dry mass at 500 °C and eventually losing 83% and 80% of their original dry mass at the end of pyrolysis experiments at approximately 800 °C, respectively. Examining the derivative mass loss, the small peak at approximately 180 °C is attributed to loss of light volatiles and water bound in the cellulose component [34] and is observed to be slightly larger in BK as compared to HP. BK also shows a larger derivative mass loss shoulder than HP at a pyrolysis temperature of 285 °C. This shoulder is widely attributed to hemicellulose degradation, which degrades at lower temperatures than cellulose and lignin during pyrolysis [35]. The increased magnitude observed in BK results suggests that cellulose and/or lignin degradation due to beetle infestation forms less recalcitrant compounds which are prone to degradation at lower temperatures, and further investigation of the chemical compositions of BK and HP is suggested to understand BK degradation pathways.

The Arrhenius kinetic parameters of HP and BK pyrolysis, derived from modulated TGA, are useful in consideration of not only the first stage of combustion, which involves pyrolysis of the biomass, but also in the context of forest fires where BK can present a significant fuel source and hazard. Averaged over $\pm 10\%$ of the peak derivative mass loss, the activation energies (E_a) of HP and BK pyrolysis are 145.0 and 143.5 kJ mol⁻¹, respectively, and the logarithms of pre-exponential factors ($\log(A)$) of HP and BK pyrolysis are 11.4 and 11.3 min⁻¹, respectively. Thus, the kinetic parameters support the observed earlier onset of mass loss by BK as compared to HP during pyrolysis.

3.2 Grindability. Table 3 summarizes the size distributions of raw and torrefied BK and HP before and after milling. The majority of unmilled biomass, including both raw and torrefied samples, is observed to be between 0.425–3.35 mm before milling as expected, although small fractions were measured to be larger and smaller than this range. Significant size reduction occurs after milling for all samples, with the greatest fraction of small particle sizes observed at the highest torrefaction level of 300 °C. Size reduction with respect to the increase in torrefaction temperature is attributed to the decomposition of hemicellulose, cellulose, and lignin at torrefaction temperatures. Limited devolatilization and carbonization of hemicellulose begins at 200 °C, followed by cellulose and lignin at higher temperatures. After torrefaction at 300 °C, all three biomass components have undergone extensive devolatilization and carbonization. Hence, as observed in Table 3, higher torrefaction temperatures result in increased grindability and particle size reduction [34]. In addition to the effective size

Table 3 The results of grindability are shown, with the percentages of particles found in each size range before and after milling given

	<75 μm	75–150 μm	150–425 μm	0.425–1.18 mm	1.18–2.00 mm	2.00–3.35 mm	>3.35 mm
Size range percentages (before milling)							
BK_raw	0.0	0.2	2.5	40.4	37.1	16.9	2.9
BK_200	0.0	0.2	2.2	42.9	35.2	17.8	1.6
BK_250	0.1	0.4	3.8	46.6	34.2	12.9	2.1
BK_300	0.1	0.6	5.0	45.9	33.1	11.8	3.4
HP_raw	0.0	0.0	1.1	34.4	32.8	30.4	1.3
HP_200	0.0	0.1	1.7	37.2	32.9	25.5	2.6
HP_250	0.0	0.1	2.7	46.3	31.1	18.4	1.3
HP_300	0.1	0.1	2.1	37.1	35.8	22.6	2.1
Size range percentages (after milling)							
BK_raw	0.1	2.9	18.0	62.2	14.9	1.9	0.2
BK_200	0.4	6.2	33.9	56.7	2.9	0.0	0.0
BK_250	0.8	9.3	49.1	39.9	0.7	0.1	0.0
BK_300	5.8	22.3	59.5	12.5	0.0	0.0	0.0
HP_raw	0.0	1.6	10.8	47.9	27.8	11.2	0.7
HP_200	1.1	4.5	18.6	54.9	20.6	0.1	0.3
HP_250	0.4	11.4	33.4	48.1	6.3	0.4	0.0
HP_300	14.5	39.8	36.2	9.5	0.1	0.0	0.0

reduction achieved by torrefaction at 300 °C, it is noteworthy that torrefaction at this level altered BK and HP to have heating values which exceed that of coal (Table 2). In contrast, BK and HP torrefied at 200 °C have heating values below that of coal, and HP and BK torrefied at 250 °C have heating values nearly equal to coal. Thus, the benefit of torrefaction in altering biomass to improve its suitability in co-firing with or substituting for coal is seen, with 300 °C torrefaction being particularly effective, in terms of size reduction and heating value increase.

In order to further interpret the results in Table 3, a weighted average particle size was calculated for raw and torrefied BK and HP. The fractions of particles in each size range and an average particle size in each size range, based on the upper and lower bounds of the range, were used to calculate the overall weighted average. For the <75 μm size range, an average particle size of 37.5 μm was used, and for the largest size range (>3.35 mm), a particle size of 3.35 mm was used. Figure 4 summarizes the average particle sizes for each sample before and after milling. Raw BK (BK_raw) sawdust was initially slightly smaller than raw HP (HP_raw) before milling, with average particle sizes of 1.47 mm and 1.66 mm, respectively. This could be attributed to the natural degradation that the BK undergoes upon beetle- and fungus-induced death, leading to smaller sawdust particles formed during sawing. Premilled torrefied samples were generally observed to reduce in size slightly with increased torrefaction temperature. After milling, BK_raw and torrefied BK at 200 °C and 250 °C (BK_200 and BK_250, respectively) were more substantially reduced in size as compared to their equivalent HP counterparts, with average particle sizes of 0.85, 0.61, and 0.49 mm for BK_raw, BK_200, and BK_250, respectively, and average particle sizes of 1.18, 0.84, and 0.61 mm for HP_raw, HP_200, and HP_250, respectively. Again, this is attributed to natural degradation of BK due to beetle infestation and fungal degradation. Interestingly, HP had a smaller average particle size than BK when torrefied at 300 °C with average postmilled HP_300 and BK_300 particle sizes of 0.23 and 0.30 mm, respectively. This might be attributed to the more severe degradation that biomass undergoes at 300 °C torrefaction, where substantial amounts of cellulose and some lignin degrades. Overall, the results suggest better grindability of BK as compared to HP, which means that BK requires less energy to process than HP.

3.3 Combustion and Co-Combustion. Figure 5 shows the mass loss of coal, raw HP and BK, and 300 °C torrefied HP and BK during combustion. Results are abbreviated to show the region of most significant mass loss between 100 °C and 500 °C, after which the raw and torrefied biomass show negligible mass loss but coal continues to gradually lose mass via oxidation. In contrast to coal, raw and torrefied HP and BK clearly show multiple stages

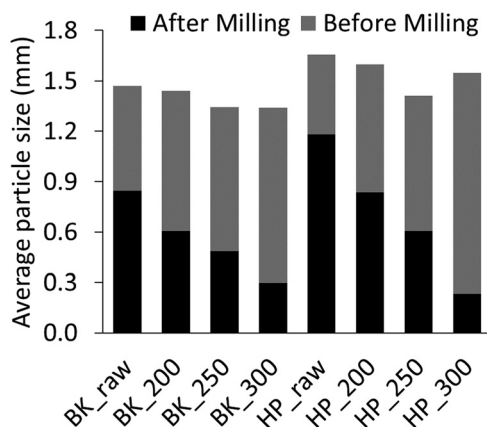


Fig. 4 Average particle size for each sample before and after milling are shown

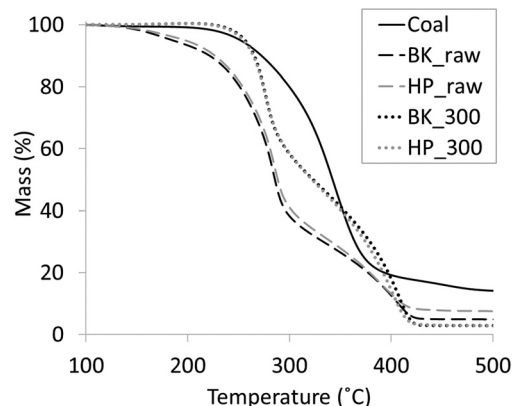


Fig. 5 Mass loss profiles of coal, raw BK and HP, and 300 °C torrefied HP and BK during combustion are shown

of mass loss. These two regions of mass loss correspond to stage 1 of biomass combustion, which is devolatilization of biomass by pyrolysis and homogeneous gas phase combustion, and stage 2 of combustion of the devolatilized biomass char, which is a heterogeneous carbon oxidation process. BK and HP generally behave quite similarly, particularly when torrefied at 300 °C, although raw BK shows slightly earlier onset of mass loss as compared to raw HP. The mass loss from 300 °C torrefied pine that occurs before 300 °C is due to low temperature oxidation. Severe torrefaction includes extensive devolatilization during which the oxygen content of the biomass is significantly reduced and the solid carbon fraction is increased. This process increases the amount of available oxidation sites in the biomass [36]. Hence, once the HP and BK torrefied samples were exposed to air during combustion tests, they were readily susceptible to oxidation at these available sites as demonstrated by the onset of mass loss at approximately 260 °C for BK_300 and HP_300. Since HP and BK behave quite similarly, mass loss during combustion of BK, including raw and torrefied at 200, 250, and 300 °C, is shown in Fig. 6 to highlight the impact of torrefaction level on combustion behavior, with the understanding that raw and torrefied HP exhibit similar behavior. Mass loss behavior is observed to be quite similar between raw, 200, and 250 °C BK, although the torrefied biomass shows later pyrolysis onset, likely due to the loss of light volatiles during torrefaction. Notably, raw and 200 °C torrefied BK lose mass monotonically at combustion temperatures above 100 °C, while 250 °C torrefied BK gains 0.1% mass and 300 °C torrefied BK gains 0.4% mass before losing mass. This mass gain is attributed to oxygen adsorption, and the observed increase in more highly torrefied BK

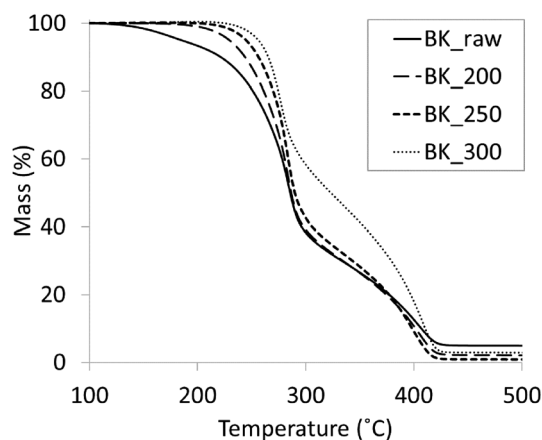


Fig. 6 Mass loss profiles of raw and 200, 250 and 300 °C torrefied BK during combustion are shown

is attributed to the higher level of carbonization which provides more active sites for oxygen adsorption.

Figure 7 shows the derivative mass loss profiles of coal, raw HP and BK, and 300 °C torrefied HP and BK. The derivative mass loss profiles for 200 °C and 250 °C torrefied biomass are not shown for brevity but exhibit similar dual peak characteristics to the raw and torrefied biomasses. These dual peaks correspond to pyrolysis (stage 1 of biomass combustion) and char oxidation (stage 2 of biomass combustion). In contrast, coal shows a single stage of combustion, consisting predominantly of solid carbon oxidation.

Figures 8 and 9 show the experimentally measured derivative mass loss profiles of raw and 300 °C torrefied HP and BK blends with coal, respectively, as well as the calculated model derivative mass loss (Eq. (3)). Results are abbreviated between 100 °C and 500 °C in order to highlight the region of maximum substantial mass loss, and results are not shown for 200 °C and 250 °C torrefied BK and HP blended with coal for brevity because results exhibit quite similar trends to those observed for raw and 300 °C torrefied BK and HP. Results show generally excellent agreement between experimentally measured and calculated theoretical derivative mass loss, suggesting that the combustion behavior of both raw biomass/coal and torrefied biomass/coal blends is additive. This indicates that there is no significant catalytic behavior

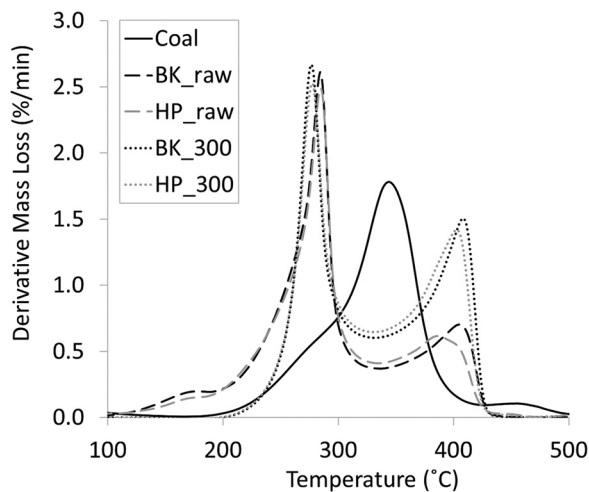


Fig. 7 Derivative mass loss profiles for combustion of coal, raw HP and BK, and 300 °C HP and BK are shown

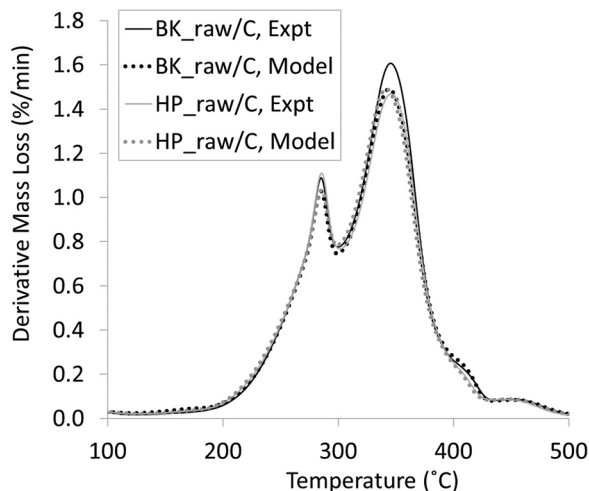


Fig. 8 Experimental (Expt) and calculated (Model) derivative mass loss during combustion of raw BK and raw HP blended with coal (BK_raw/C and HP_raw/C, respectively)

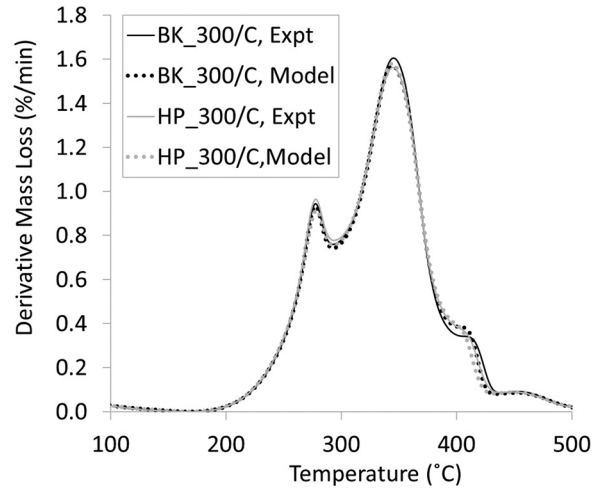


Fig. 9 Experimental (Expt) and calculated (Model) derivative mass loss during combustion of 300 °C torrefied BK and 300 °C torrefied HP blended with coal (BK_300/C and HP_300/C, respectively)

resulting from the ash contents of biomass or coal, nor is there any apparent alteration to biomass devolatilization imposed by the presence of coal among the feedstocks tested in this study. Raw HP and BK blends with coal (Fig. 8) both show a maximum rate of stage 1 (pyrolysis) mass loss at 286 °C, and a maximum rate of stage 2 (char combustion) mass loss at 346 °C. The 300 °C torrefied biomass/coal blends (Fig. 9) exhibit lower pyrolysis peaks as compared to raw biomass/coal blends, as expected due to the loss of volatiles during torrefaction, with 300 °C HP/coal and 300 °C BK/coal blends showing maximum stage 1 mass loss at 278 °C. Stage 2 maximum mass loss for 300 °C HP and BK blends with coal occur at 346 °C, as was observed for raw biomass/coal blends. While not shown for brevity, 200 °C and 250 °C HP and BK blends with coal also exhibit maximum stage 2 mass loss at 346 °C. Thus, following pyrolysis of the raw or thermally pre-treated biomass/coal blends, stage 2 combustion proceeds in a uniform manner regardless of feedstock blend. Stage 1 peak mass loss for 200 °C biomass/coal blends and 250 °C biomass/coal blends (not shown) occurs at 285 °C and 284 °C, respectively.

The Arrhenius kinetic parameters of coal and raw and torrefied HP and BK combustion and co-combustion, derived from modulated TGA and averaged within $\pm 10\%$ of the peak derivative mass loss, are summarized for single and blended feedstocks in Table 4. These results are generally in good agreement with other studies of pine oxidation kinetics, such as the study by Shen et al. [23] in which first- and second-stage activation energies were found to be 119 and 146 kJ mol⁻¹, respectively, at a heating rate of 10 °C min⁻¹, and the study by Yorulmaz and Atimtay [24] in which a range of activation energies between 123–136 kJ mol⁻¹ were derived. Perhaps, most notably in this study, the kinetic parameters of the second stage combustion of feedstock blends closely resemble the single stage combustion parameters of coal. These results indicate that blend combustion behavior is dominated by coal combustion behavior, which is likely attributable to the high concentration of coal in the blends. The practical implications of this are important for industrial co-firing of coal and biomass, since a coal/biomass blend such as those tested in this study are expected to combust at rates similar to coal, and these feedstock blends are therefore anticipated to be interchangeable from a combustor performance standpoint. This finding is in agreement with observations that 20% by energy co-firing is feasible in industrial scenarios with minimal combustion efficiency losses [37,38]. Furthermore, the results suggest that HP and BK combustion behavior is similar enough that a seamless transition from BK to HP could be made in the future when BK resources are depleted.

Table 4 Kinetic parameters, including activation energy (E_a , kJ mol⁻¹) and the logarithm of the pre-exponential factor (A , min⁻¹), are summarized for combustion of single feedstocks, including coal (C) and raw and torrefied BK and HP, and feedstock blends

Feedstock	Stage 1		Stage 2	
	E_a	log(A)	E_a	log(A)
C	96.0	6.7	—	—
BK_raw	141.0	11.9	120.8	8.1
BK_200	135.7	11.5	118.8	8.2
BK_250	132.0	11.2	119.3	8.3
BK_300	135.5	11.4	117.5	8.1
HP_raw	136.1	11.4	123.6	8.3
HP_200	152.4	13.1	119.8	8.3
HP_250	135.8	11.4	116.4	8.0
HP_300	136.9	11.5	114.8	7.9
BK_raw/C	140.0	11.3	96.1	6.7
BK_200/C	136.8	11.0	95.9	6.7
BK_250/C	134.9	10.9	95.1	6.6
BK_300/C	136.9	14.7	96.7	6.7
HP_raw/C	135.2	10.8	96.1	6.7
HP_200/C	143.7	11.7	95.1	6.6
HP_250/C	138.5	11.1	95.1	6.6
HP_300/C	136.7	11.0	97.4	6.8

4 Conclusions

This study assessed beetle kill pine as a potential feedstock for combustion and co-combustion with coal and compared its performance with healthy pine. Healthy and beetle kill pine were torrefied at 200, 250, and 300 °C using thermogravimetric analysis and a fixed bed reactor. Increased mass loss was observed in torrefaction of beetle kill pine, as well as during assessment of relative beetle kill and healthy pine compositions via pyrolysis, which was attributed to the natural degradation of the wood that occurs after beetle- and associated fungus-induced death. Torrefaction of both healthy and beetle kill pine feedstocks was found to improve fuel properties by increasing energy density and grindability. Beetle kill pine was found to have a generally higher grindability than healthy pine, which would translate to decreased processing energy required when beetle kill pine is used as a feedstock. Combustion of raw and torrefied healthy and beetle kill pine alone and co-combustion of these feedstocks blended with coal in an amount of 20% by energy were conducted using thermogravimetric analysis. Combustion and co-combustion results, including mass loss and derivative mass loss for all fuels and blends tested, showed similar trends for beetle kill and healthy pine at each torrefaction level. These results suggest the interchangeability of these fuels in combustion and co-combustion applications, which has important implications for the use of both beetle kill and healthy pine as combustion feedstocks, as healthy pine can be readily utilized when beetle kill pine is depleted without substantial combustor performance changes. Kinetic parameters were derived using modulated thermogravimetric analysis for the combustion of coal and raw and torrefied beetle kill and healthy pine, and results showed two distinct combustion stages for biomass as compared to a single combustion stage for coal. Kinetic parameters for the blends were found to be dominated by coal, suggesting that a 20% by energy blend of healthy or beetle kill pine with coal can be substituted for coal with little effect on the operation of the combustor. Additive analysis of the blend results showed no synergistic or inhibiting effects in co-combustion of the coal and biomass. Thus, in summary, the results of this study show a viable path for beetle kill pine utilization in energy applications, whereby beetle kill pine has favorable pretreatment behavior but otherwise behaves similarly to healthy pine during conversion.

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