energy&fuels

Article

Assessment of Combustion and Gasification Behavior in a Bubbling Fluidized Bed Reactor: A Comparison between Biomass with and without Chemical Additives

Cornelius Emeka Agu,* Britt M. E. Moldestad,* and Christoph Pfeifer*

Cite This: Energy Fuels 2020, 34, 9654−9663

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: During the storage of biogenic materials for energy utilization, destructions by microbial attacks are inevitable. Besides material degradation, self-ignition of wood chip piles also occurs consistently. Treating the feedstock with, for example, mineral additives such as Dolomite can inhibit the microbial destructions, though such treatment may affect the thermochemical conversion of the fuel particles. This study therefore demonstrates the effect of mixing 4 wt % calcium hydroxide with wood chips used as feedstock in a 20 kW (fuel input) bubbling fluidized bed reactor. The reactor consists of a 100 mm (inner diameter) cylindrical column with 1.0 m height, where both gasification and combustion modes can be applied. Six different tests within equivalence ratios of 0.1−1.1 are conducted, and in each run, both fluidization behavior and quality of the product gas at different reaction temperatures (750−900 °C) are analyzed and compared with the results from wood chips of the same particle size but without the additive. The results show that there is no significant difference in the product gas composition, but evidence shows that the chemical additive impacts on the bed pressure drop over the equivalence ratio tested. The gasification window is increased and the energy value of the product gas is higher with a lower hydrogen content. During the combustion, both the exit gas temperature and oxygen concentration are lower, suggesting that additional light molecules such as water vapor are released during the conversion of biomass mixed with additive.

1. INTRODUCTION

Wood is the most commonly used biogenic resource for production of heat and electricity. Typically, forest biomass is used in the form of high-quality wood chips as well as woody wastes such as bark, sawdust, and forest residues. After harvest, biomass is usually stored in the forest for natural drying over a period of time before utilization. During storage, destruction and conversion processes are inevitable. Different bacteria and mold fungi colonize the biomass, causing its degradation. These microbes originate from the natural microbial community present in the biogenic material as well as from atmospheric deposition.[1] Basidiomycetes are the main wood-rotters due to their ability to degrade cellulose, hemicellulose, and lignin. These fungi can overcome difficulties in wood decay such as limited nutrient accessibility and the presence of antibiotic compounds (essential oils).[2] Moreover, the microbes can grow over a wide temperature and pH range. The degradation of the wood components is carried out in aerobic conditions.[3] This degradation or respiration process results in an economical relevant dry-matter loss and consequently in a net-energy-value reduction. Comprehensive investigations are missing, and large fluctuations are reported based on season, biomass properties, storage technique, etc. However, different methods for quantifying dry-matter losses have been suggested. Annual losses of 10−40 wt % are reported,[4−10] and Buggeln[9] calculated a loss of about 1 wt % per month for outside storage of piles from high-quality wood chips. For wet and lower-quality materials, the values can be significantly higher. Some studies are also available to determine the periodic weight loss in wood chips piles, e.g., Lenz et al.[11]

Primary factors influencing the degradation rate are temperature, water content, and oxygen availability.[12] pH and nutrient availability are also the main microbial growth factors either promoting or inhibiting microbial growth. These factors are mainly influenced by the pile geometry, piling method, particle size, comminution method, storage season, storage location, and the tree species,[3,6,10,13,14] although the influencing factors are mostly not quantitatively reported in the literature.

One of the main drivers of microbial degradation is the temperature in the pile. As a result of limited air passage inside the wood chip piles and their low conductivity, temperatures of up to 80 °C can be achieved. Hence, self-heating and finally self-ignition can occur. Inhibiting the microbial growth is therefore crucial to lower or even eliminate the risk of self-ignition. To minimize the microbial degradation rate, the woody biomass has to be pretreated before storage. Such treatment can be via heating, mixing with chemicals, or their combination. Thermal treatment is often referred to as torrefaction, and it can be achieved in the absence of oxygen and at the temperature range
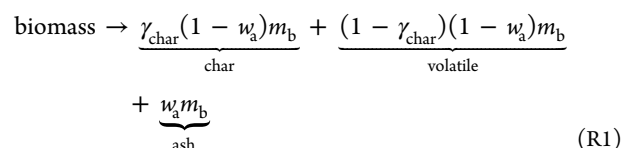
of 200−300 °C at a low heating rate.[15] The treatment can result in about 30% mass and 10% energy losses due to the release of volatile components consisting of mainly moisture and light oil.[15,16] The torrefied biomass has a better heating value and is more hydrophobic. These improved properties reduce the biomass susceptibility to biological decay, thus prolonging its storage time.[17−19] However, the torrefaction technology has some technical and economic challenges that have delayed the commercialization of some demonstrated plants.[20] Among the challenges is the high-energy requirement, as the process involves mainly biomass drying. To operate the process in a sustainable manner, Tregambi et al.[21] showed that solar radiation can be absorbed to deliver the necessary heat required with improved torrefied material quality.

Mixing of wood chips with chemical additives is a common method used to improve combustion or gasification behavior in fluidized bed applications. In particular, the removal of impurities such as sulfur or cracking of tars can be seen as state of the art. Different materials have been suggested,[22] which include those based on calcium, kaolin, sodium, potassium, etc. The application of those materials to change the pH and therefore avoid bacterial degradation of the organic structure is a novel approach. However, for both standard applications, i.e., gasification[23] and combustion,[24,25] agglomeration of particles is often a problem due to the increase in ash contents of low melting point[26,27] and interactions of bed material with the additives, forming low-melting eutectics.[28] Attrition and fragmentation are also important issues in fluidized bed combustion and gasification, respectively.[29] For residues from agriculture and forestry with typically high ash contents of about 5−10 wt %, bed agglomeration and slugging have been reported as major limitations.[30,31]

This study deals with the energetic utilization of solid fuel materials with and without additives and assessment of gasification and combustion of the fuel particles in a reactor. The study is aimed at investigating the effect of chemical additives on biomass conversion in a bubbling fluidized bed reactor by means of experimental measurement of product gas composition and analysis of the energy value. Although the fine chemical additive may influence the bed hydrodynamics as well as the biomass conversion route, no detailed analysis of these phenomena is obtained in this study. Interaction of additives with ash constituents as well as the bed material is of major importance for all industrial-scale fluidized bed applications, which are operated continuously. For pilot-scale applications, the time on stream is typically not sufficient to verify those effects, and therefore their investigations are not covered in this study. However, agglomeration of ash components including bed material particles has been studied in detail elsewhere.[32,33] Different models and methods have also been developed and proposed to verify the possible impacts of ash constituents as well as additives in fluidized beds.[34] In the present study, the reported results provide some insights into the extent the yield (product gas composition and energy content) of biomass conversion with additives deviates from that of the same solid fuel without additives.
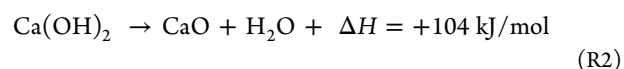
2. THEORY

The conversion of biomass in a fluidized bed results in an increase in the bed inventory. Biomass gasification or combustion begins with pyrolysis of the fuel particles, as described in the following one-step mechanism.

$$\text{biomass} \rightarrow \underbrace{\gamma_{\text{char}}(1 - w_{\text{a}})m_{\text{b}}}_{\text{char}} + \underbrace{(1 - \gamma_{\text{char}})(1 - w_{\text{a}})m_{\text{b}}}_{\text{volatile}}$$
$$+ \underbrace{w_{\text{a}}m_{\text{b}}}_{\text{ash}} \tag{R1}$$

Here, m_{b} is the mass of the given biomass, γ_{char} is the mass fraction of char released, and w_{a} is the mass fraction of ash in given biomass particles. The basic components of the released volatiles include CO_2, CO, H_2, CH_4, H_2O, and tar. Char is the solid fuel residue, which contains mainly the fixed carbon and with a trace of hydrogen. In the presence of air, all of the combustible gas components in addition to the active tar and char particles react with oxygen to release heat energy.

Biomass ash, in general, is inactive, but for the case of biomass with an additive, the inorganic chemical may undergo reactions including the decomposition process. For example, where calcium hydroxide $Ca(OH)_2$ is the biomass additive, the following reactions may also occur in the bed.

$$Ca(OH)_2 \rightarrow CaO + H_2O + \Delta H = +104 \text{ kJ/mol} \tag{R2}$$

$$CaO + CO_2 \rightarrow CaCO_3 + \Delta H = -178 \text{ kJ/mol} \tag{R3}$$

The decomposition reaction R2 is endothermic, occurring at temperatures over 500 °C. The CO_2 absorption by calcium oxide is highly exothermic and may likely not be favored at the reactor temperature over 700 °C in a bubbling bed. Depending on the proportion, the inert ash residue in addition to the unconverted char particles will influence the hydrodynamics of the bed, particularly in the gasification process. However, the effectiveness of the possible reactions occurring in a fluidized bed depends on the particle mixing behavior, which is affected by a number of factors including the size and density differences as well as the fluidization velocity. At low fluidization velocities, the tendency of different particle types to segregate is high. Biomass particles can float at the bed surface due to their relatively low density and irregularity in shape. As the density of the fuel particles increases, their sinking tendency increases.[35]

The bed hydrodynamics can be assessed through measurement of pressure drop and bed properties at the minimum fluidization condition, as expressed in eq 1

$$\Delta p_{\text{bed}} = (1 - \varepsilon_{\text{mf}})\rho_{\text{bed}}gh_{\text{mf}} \tag{1}$$

where Δp_{bed} is the bed pressure drop, and ε_{mf} and h_{mf} are the bed voidage and height at the minimum fluidization condition, respectively. Assuming that the bed contains two different particle types, solid fuel and inert particles (lumped biomass ash and bed material, e.g., sand particles), the average bed density ρ_{bed} can be estimated from

$$\rho_{\text{bed}} = \left(\frac{x_{\text{f}}}{\rho_{\text{f}}} + \frac{1 - x_{\text{f}}}{\rho_{\text{i}}}\right)^{-1} \tag{2}$$

where x_{f} is the mass fraction of the unconverted fuel particles, ρ_{f} is the solid fuel density, and ρ_{i} is the average density of the inert particles. Similar to eq 2, ρ_{i} can also be estimated from the densities of the individual inert solid components. The bed minimum fluidization velocity in the presence of biomass is usually difficult to estimate due to its dependency on the proportion of the different solid types in the bed. Particularly in a system where biomass is fed continuously and reactions occur, the amount of fuel particles accumulated in the bed is not

certainly known. However, if the mass fraction of the fuel particles x_f is estimated, the minimum fluidization velocity of the mixture can be predicted as described in Agu et al.[36] for a multicomponent system.

Assuming that biomass devolatilization takes place rapidly, the unconverted fuel particles contain mostly char. For biomass conversion with air in a bubbling fluidized bed, x_f can be determined from eqs 3 and 4 as described in Agu et al.[37]

$$\frac{x_f}{1-x_f} = (1-\alpha)\gamma_{char}(t_e - t_d)\frac{\dot{m}_{bio}}{m_i} \qquad (3)$$

$$\gamma_{char} = 0.414 X_{bio}^{0.245}\left(\frac{U_0}{U_{mfi}}\right)^{-0.463} \qquad (4)$$

Here, $\dot{m}_{bio}$ is the biomass feed rate and m_i is the total mass of the inert particles. The expressions for $t_e - t_d$ (char residence time) and X_{bio} (the ratio of the mass of biomass supplied over the extinction time t_e to the mass of the inert materials) are as given in ref 37. For wood chips, the degree of char conversion α is 0.6. U_0 is the superficial gas velocity corresponding to the airflow rate under the operating condition, and U_{mfi} is the minimum fluidization velocity of the inert particles, which can be estimated from the Wen and Yu[38] correlation. Equation 3 is derived assuming plug flow behavior, and depending on the degree of char conversion and devolatilization process, it gives the effective amount of biomass x_f accumulated in the bed. Equation 4 provides the amount of char yield γ_{char} at the end of devolatilization as a function of the operating parameter.

3. MATERIALS AND METHODS

The description of materials as well as the setup used in the test is presented in this section. As the comparison between the yields of the thermochemical conversion of biomass with and without additive is based on the product gas composition, the methods used for the gas sampling and analysis are also clearly described.

3.1. Material Description. In this study, sand particles of mean size 615 μm were used as the fluidized bed material. Two different samples of wood chips, shown in Figure 1, were prepared and used as feedstock

Figure 1. Two different samples of wood chips: without (A) and with (B) additive from spruce forest residues.

for gasification and combustion in bubbling fluidized beds. The two wood samples are plain wood chips made from spruce and wood chips mixed with 4 wt % calcium hydroxide, $Ca(OH)_2$. The biomass with additive was prepared by surface mixing of wood chips with calcium hydroxide powder in the ratio of 24:1 by mass. The mixing method is the same as that applied in preserving the wood chip pile against degradation during storage. The addition of fine $Ca(OH)_2$ particles may influence the biomass conversion route due to the possible decomposition of the additive and may also affect the bed hydrodynamics due to increase in attrition, elutriation, and axial segregation

of the solid particles. However, the analysis of these phenomena is not part of this study, but may be reported in a future study.

Both samples of the wood chips were dried and sieved to a size range of 20–50 mm. The properties of the different materials used in the tests are given in Table 1. The mean particle size of the sand particles was

Table 1. Properties of Different Particles Involved in the Tests

properties	sand	wood chips without additive	wood chips with additive	$Ca(OH)_2$
particle size [mm]	0.4–0.7	20–50	20–50	<0.2
bulk density [kg/m³]	1378	216	225	400
ash, w_a [%]		0.64	4.45	
moisture, w_{moit} [%]		15	15	
heating value, $\overline{LHV}_{bio}$ [MJ/kg]		20.05	18.72	

determined by the sieve analysis. The bulk densities of the sand particles and wood chips were measured by the gravimetric method, while the $Ca(OH)_2$ properties are as provided by the manufacturer, Schretter & Cie GmbH, Tyrol, Austria.

3.2. Experimental Setup and Procedure. Figure 2 illustrates the setup that consists of a cylindrical stainless steel column of effective internal diameter 10 cm and height 1.0 m. The reactor is lined internally with a refractory material and insulated externally with fiberglass to minimize the heat loss. The detailed description of this setup is given in Agu et al.[37] With three parallel electric heating elements, heat is supplied to the bed during the start up until a temperature of about 800 °C is achieved. The temperature and fluid pressure along the column are, respectively, monitored with five different thermocouples and five different pressure transducers arranged as shown in the figure.

Throughout the experiment, a bed of sand particles with initial height 22 cm was used. Biomass was fed continuously into the reactor by means of a screw conveyor driven at 8% full speed. The corresponding average feed rates of wood chips with and without additive over the 60 min operation are 2.03 and 1.95 kg/h, respectively. Six different airflow rates in the range of 1.7–12.5 kg/h were applied for each of the biomass sample types. The air supply was metered through a calibrated rotameter, and the chosen flow rates covered the range sufficient for both gasification and combustion in relation to the biomass feed rate. Moreover, the range of airflow rates was low to cause a significant particle entrainment. For a typical woody biomass with an elemental composition of 53.5% C, 5.9% H, 40.3% O, 0.1% N, and 0.2% S by weight, the stoichiometry air–fuel ratio $(AFR)_{th}$ to achieve combustion is about 6.[15] Table 2 gives the corresponding equivalence ratios (ERs) (ratio of the actual air–fuel ratio to the air–fuel ratio required for stoichiometry combustion of biomass) for the two different biomass samples in the range of the applied airflow rates. For ER < 1, the air–fuel mixture is rich with respect to the fuel supply, and the conversion process will tend toward gasification. When ER > 1, the mixture is lean, favoring the fuel combustion due to excess oxygen supply. The average bed temperature measured at the different equivalence ratios is within 830–950 °C.

The mean air velocities corresponding to the operating airflow rates and temperatures are also given in Table 2. Based on the amount of accumulated biomass x_f predicted from eqs 3 and 4, the table also shows the estimated minimum fluidization velocity of the bed mixture. The data suggest that at 1.7 kg/h air supply, the beds are operated within the minimum fluidization condition, indicating that particle entrainment and attrition are at minimum. With an increase in airflow rate, the minimum fluidization velocity decreases due to reduction in the amount of biomass accumulated in the bed. The average value of U_{mf} for the pure sand particles over the operating temperatures is 0.132 m/s. This shows that the minimum fluidization velocity of the bed mixture containing the biomass with additive is about 1.16 times that of the sand particles, while the corresponding value for the bed with plain wood
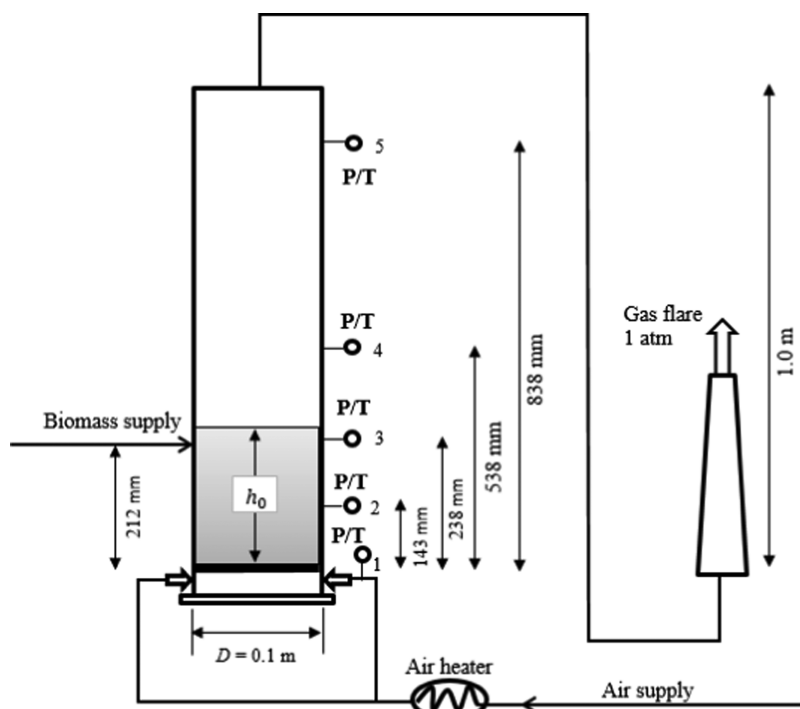
Figure 2. Schematic illustration of the reactor used for biomass conversion tests. P/T indicates the pressure and temperature sensor probe, and h_0 indicates the initial bed height.

Table 2. Equivalence Ratio at Applied Airflow Rates for the Two Wood Chip Samples Together with the Operating Air Velocities and the Estimated Minimum Fluidization Velocity of Each Bed Mixture

| airflow rate [kg/h]	operating air velocity [m/s]	equivalence ratio, ER		biomass fraction, x_f [wt %]		minimum fluidization velocity [m/s]	
		without additive	with additive	without additive	with additive	without additive	with additive
1.7	0.192	0.15	0.14	7.69	7.06	0.202	0.192
2.3	0.256	0.20	0.19	6.21	5.83	0.178	0.173
3.0	0.333	0.26	0.25	5.13	4.82	0.163	0.159
7.5	0.917	0.64	0.61	2.32	2.20	0.132	0.131
10.0	1.143	0.85	0.82	2.08	1.87	0.130	0.128
12.5	1.500	1.06	1.02	1.57	1.57	0.126	0.126
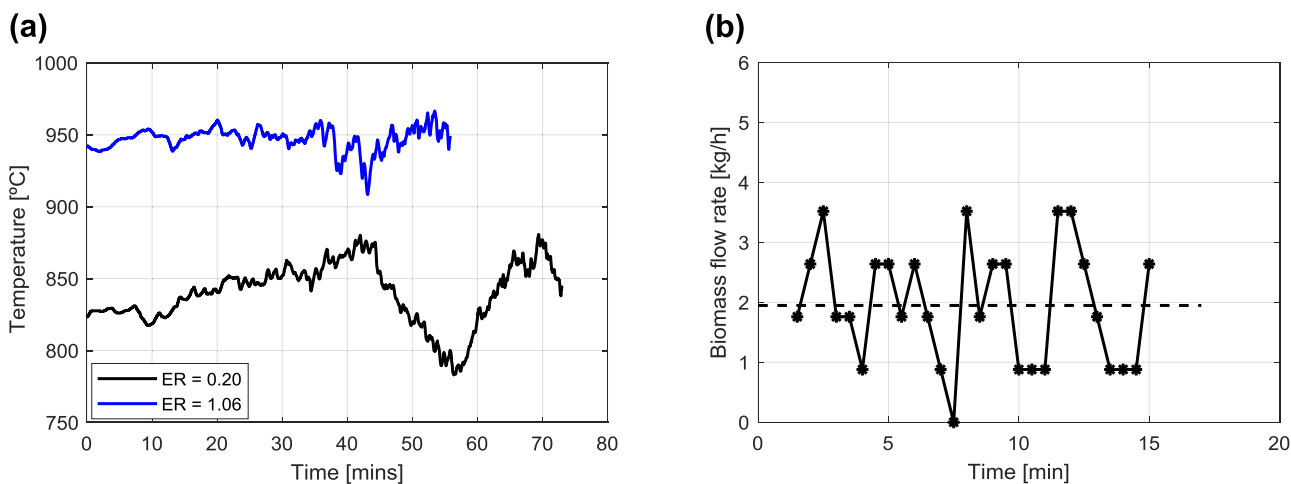
Figure 3. (a) Evolution of temperature in the bed, illustrating the autothermal behavior in the reactor; (b) evolution of biomass feed rate for bed instability control during the tests.

chips is about 1.18, which is in agreement with that reported in the literature.[39] In addition, the slightly lower values of U_{mf} suggests that the fluidization quality of the bed of biomass with additive will be better compared to the bed with plain biomass.

It is also important to emphasize that bed temperature control in each experimental run is self-driven and no external heat is supplied during the actual conversion process. External heaters are used to heat up the bed, but as soon as the required temperature is achieved, the heaters are turned off. Upon introduction of biomass and air into the reactor, the bed temperature regulates automatically by the oxidation of the fuel particles, making the process autothermal. Figure 3a shows the evolution of temperature in the bed at different equivalence ratios during conversion of wood chips without additive. With ER = 1.06, the temperature seems relatively stable compared to the process at the lower ER value. In the period when the temperature increases with time, the exothermic activities dominate the process. The temperature decreases when the endothermic activities are dominant, mainly due to accumulation of a large amount of unconverted char particles in the bed, as can be clearly seen with low equivalent ratios. Moreover, the periodic increase and decrease of temperature is also influenced by the feeding mode of biomass. If the same amount of biomass is continuously fed within the period the temperature is decreasing, the bed may become unstable and eventually may become defluidized due to the large amount of unconverted fuel particles. Figure 3b shows that the biomass feed rate varies between 1.0 and 3.5 kg/h over 3 min. The feed rate variation is achieved by pulsing the feed screw conveyor at regular intervals. However, this type of biomass supply mode may lead to a steady temperature increase over time, but this was not observed within the period of measurement in each run.

3.3. Gas Sampling and Analysis. At each equivalence ratio, measurements were taken over 60 min. Both the temperature and pressure along the reactor axis were logged in continuously at 1 s interval. The product gas was sampled from the reactor exit at 10 min intervals for offline analysis using an SRI 8610C gas chromatograph (GC). The GC uses a thermal conductivity detector (TCD) and helium as carrier gas with an installed column comprising a packed molecular sieve 5A. Figure 4 provides the technical description of gas
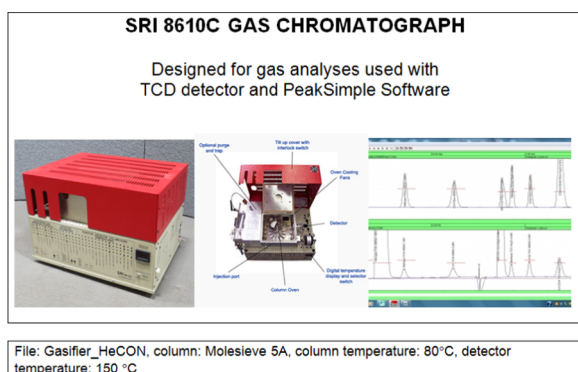

Figure 4. Description of the gas chromatography used for gas analysis in the test.

chromatography. The gas analyzer only detects N_2, O_2, CO, CH_4, and H_2, which are the only gas species experimentally measured in this study. In addition to tar, other gases including CO_2, H_2O, and C+ compounds were not measured because there was no available equipment at the time of this study for the same.

However, the estimation of CO_2 and H_2O concentrations can be provided by the elemental and mass balances to enhance the evaluation of the quality of biomass conversions under the given operating conditions. Assuming that the same amount of biomass supplied at a given time is totally converted into gas (i.e., neglecting the char accumulation and entrainment), the concentrations of CO_2 and H_2O can be predicted using eqs 5 and 6, which are derived by balancing the number of hydrogen and carbon atoms between the feed and the product streams as well as noting that the total mole fraction of product gas species is unity.

$$y_{CO_2} = \frac{W}{n_p} - (y_{CO} + y_{CH_4}) \tag{5}$$

$$y_{H_2O} = \frac{Y + Z}{2n_p} - (y_{H_2} + 2y_{CH_4}) \tag{6}$$

$$n_p = \frac{W + \frac{1}{2}(Y + Z)}{1 + 2y_{CH_4} - y_{N_2} - y_{O_2}} \tag{7}$$

$$\left. \begin{array}{l} W = (1 - \alpha_A)\frac{w_C}{M_{AC}} \sum_i (w_i M_{Ai}) \\ Y = (1 - \alpha_A)\frac{w_H}{M_{AH}} \sum_i (w_i M_{Ai}) \\ Z = \alpha_A \frac{2}{M_{Ca(OH)_2}} \end{array} \right\} \tag{8}$$

Here, y_i is the mole fraction of the species, $i = \{CO, CO_2, CH_4, H_2, H_2O, O_2, N_2\}$ in the product gas, w_i is the mass fraction of the element, $i = \{C, H, O, N, S\}$ in the biomass, M_{Ai} is the corresponding atomic mass, $M_{Ca(OH)_2}$ is the molecular weight of the additive, and α_A is its weight fraction in the mixture with biomass. For biomass without the additive, $\alpha_A = 0$. Note that the concentration of compounds associated with sulfur, nitrogen, and C+ in the product gas is also neglected in eqs 5−7.

4. RESULTS AND DISCUSSION

The results obtained over the six equivalence ratios for each of the biomass samples are discussed in this section to explore the effect of chemical additive on the product gas composition and energy content. As exothermic reactions dominate the conversion processes, the temperature in the reactor increases with increasing equivalence ratio. Figure 5a compares the temperatures measured in the middle of the beds for the different biomass samples. As can be seen, the temperature variation at different ER values is similar in both cases with and without additive. However, for ER < 0.6, where the gasification process dominates, the temperature in the bed of biomass with additive is slightly lower, suggesting that there are relatively higher endothermic activities in the bed. Figure 5b shows that the profile of pressure drop in the bed is a reflection of the temperature profile shown in Figure 5a. This indicates that changes in gas properties due to changes in the bed temperature affect the pressure drop in the fluidized state. The higher pressure drop at the lower ER values can be associated with a high accumulation of char in the bed. In comparison, the pressure drop is higher in the bed containing biomass and the mineral additive at a given equivalence ratio.

The temperature variations in the bed and along the freeboard will influence the composition of the product gas. Table 3 summarizes the gas compositions from the different experimental runs including their measurement uncertainties. The mole fractions of CO_2 and H_2O predicted from eqs 5−8 are also reported.

4.1. Variation in Gas Composition. Figure 6 shows the composition of the product gas at different equivalence ratios. The yield of H_2 effectively decreases in the bed within the different ranges, ER < 0.35 and > 0.6, for both biomass samples. Between ER = 0.35 and 0.6, the concentration of H_2 in the product gas increases, possibly due to the increase in the bed temperature, as shown in Figure 5a. The trend of H_2 mole fraction with changes in ER for the bed without biomass additive is similar to those reported in the literature[40] but at the expense of decreasing temperature. The slight difference in the gas composition between the two different biomass samples may be associated with the biomass pyrolysis since lower temperature
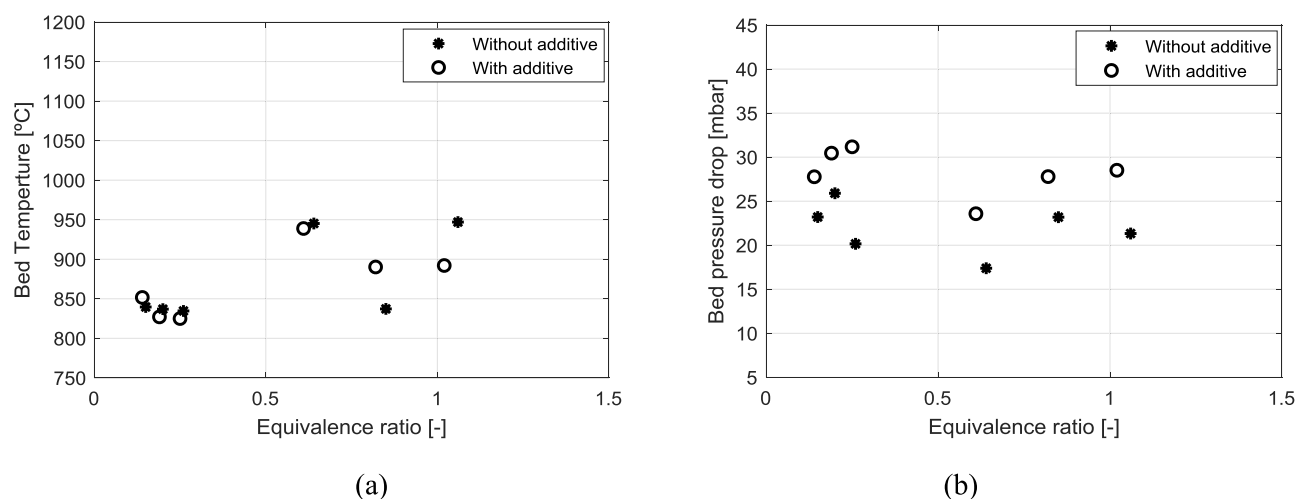
(a)

(b)

Figure 5. Comparison between the behaviors of two different beds containing wood chips with and without additive at different equivalence ratios: (a) temperature, T3; (b) pressure, P3.

Table 3. Mole Fractions [%] Showing Gas Composition at Different Airflow Rates for Both Wood Chips with and without Additive

				mole fraction [%]				
ER [-]	N_2	O_2	CO	CH_4	H_2	$^aCO_2$	^aH_2O	T_{exit} [°C]
				Wood Chips Without Additive				
0.15	45.4 ± 1.9	0.93 ± 0.2	21.1 ± 1.4	6.08 ± 0.7	6.16 ± 3.4	12.5	7.90	850 ± 30
0.20	50.2 ± 3.6	1.12 ± 0.3	17.6 ± 2.3	5.22 ± 0.9	9.69 ± 5.2	12.7	3.40	809 ± 42
0.26	52.9 ± 7.1	0.96 ± 0.2	16.3 ± 4.2	4.57 ± 1.4	7.92 ± 2.5	12.4	4.95	809 ± 24
0.64	69.9 ± 3.9	2.25 ± 0.6	5.73 ± 2.9	1.04 ± 0.6	7.20 ± 3.4	11.3	2.66	887 ± 30
0.85	72.2 ± 2.3	3.11 ± 0.7	3.41 ± 1.5	0.68 ± 0.4	5.44 ± 2.4	11.6	3.56	857 ± 21
1.06	74.9 ± 1.8	13.7 ± 1.7	0.93 ± 1.1	0.45 ± 0.3	0.00	6.01	3.99	930 ± 9
				Wood Chips With Additive				
0.14	44.8 ± 3.5	0.82 ± 0.1	22.4 ± 2.0	5.84 ± 0.9	8.33 ± 0.4	11.5	6.32	813 ± 33
0.19	47.0 ± 2.8	0.95 ± 0.2	19.1 ± 1.4	5.57 ± 0.7	6.54 ± 3.0	13.4	7.50	875 ± 22
0.25	50.1 ± 5.0	0.92 ± 0.1	17.0 ± 2.7	5.08 ± 1.1	5.34 ± 2.5	13.5	8.10	831 ± 42
0.61	69.3 ± 4.8	2.37 ± 1.3	5.85 ± 3.1	1.30 ± 0.8	7.53 ± 3.3	11.5	2.20	918 ± 5
0.82	72.6 ± 3.8	2.98 ± 1.3	3.70 ± 2.9	0.80 ± 0.7	6.79 ± 3.1	11.2	2.00	886 ± 41
1.02	74.5 ± 1.7	6.14 ± 3.7	1.89 ± 1.5	0.46 ± 0.4	0.00	9.85	7.16	887 ± 13

^{a}Estimated gas composition.

favors CO, CO_2, and CH_4 yields and decreases H_2 yield.[41] In both biomass samples, CO and CH_4 decrease while N_2 and O_2 mole fractions increase since oxidation of the combustible gases is enhanced with increasing equivalence ratio. N_2 is lower in the gasification process (ER < 0.6) in the case of biomass with additive due to the higher amount of the combustible gases, but indifferent between the two biomass samples in the combustion process. On the other hand, the trend of O_2 is slightly opposite to that of N_2 when compared between the two different biomass samples. CO_2 slightly increases for ER < 0.35 and then decreases thereafter due to increasing concentration of the lighter gases, N_2, O_2, and H_2O. The H_2O concentration increases accordingly as the oxidations of H_2 and CH_4 are enhanced. In the combustion process, the additional release of H_2O from the decomposition of the additive, $Ca(OH)_2$, increases the gas concentration compared to the case without the additive.

Moreover, the mixing pattern in the bed might also have influenced the results including the variations of H_2, H_2O, and CO_2 within ER < 0.35 due to the relatively low effective velocity, $U_0 - U_{mf}$ for the bed fluidization. Note that the feeding position of biomass is close to the top of the bed. Therefore, its mixing

with the bed material will depend on the degree of fluidization. Considering the density difference between the different biomass types, the sample with additive may have a better mixing behavior with the bed material, which essentially supplies the necessary heat required for the reactions. The lower H_2 mole fraction indicates that a higher concentration of O_2 is available within the vicinity of the gas species, thereby enhancing its oxidation. Since the affinity of H_2 for oxygen is higher compared to the other combustible gases, the slightly higher concentrations of CO and CH_4 for biomass with additive may result from a lesser amount of oxygen available for their oxidations. For biomass without additive, the lower amount of H_2 at ER = 0.15 is an evidence that the bed may not have been properly fluidized if at all with the supplied air velocity, thereby reducing the biomass contact with the bed and thus the necessary heat required for the release of H_2 during the devolatilization process.

The presence of oxygen over the entire range of equivalence ratio suggests that there is no sufficient time for the active gas species (CO, CH_4, and H_2) to react with the available oxygen before exiting the reactor, possibly due to the relatively short length of the freeboard. Especially in the lower ER values, the
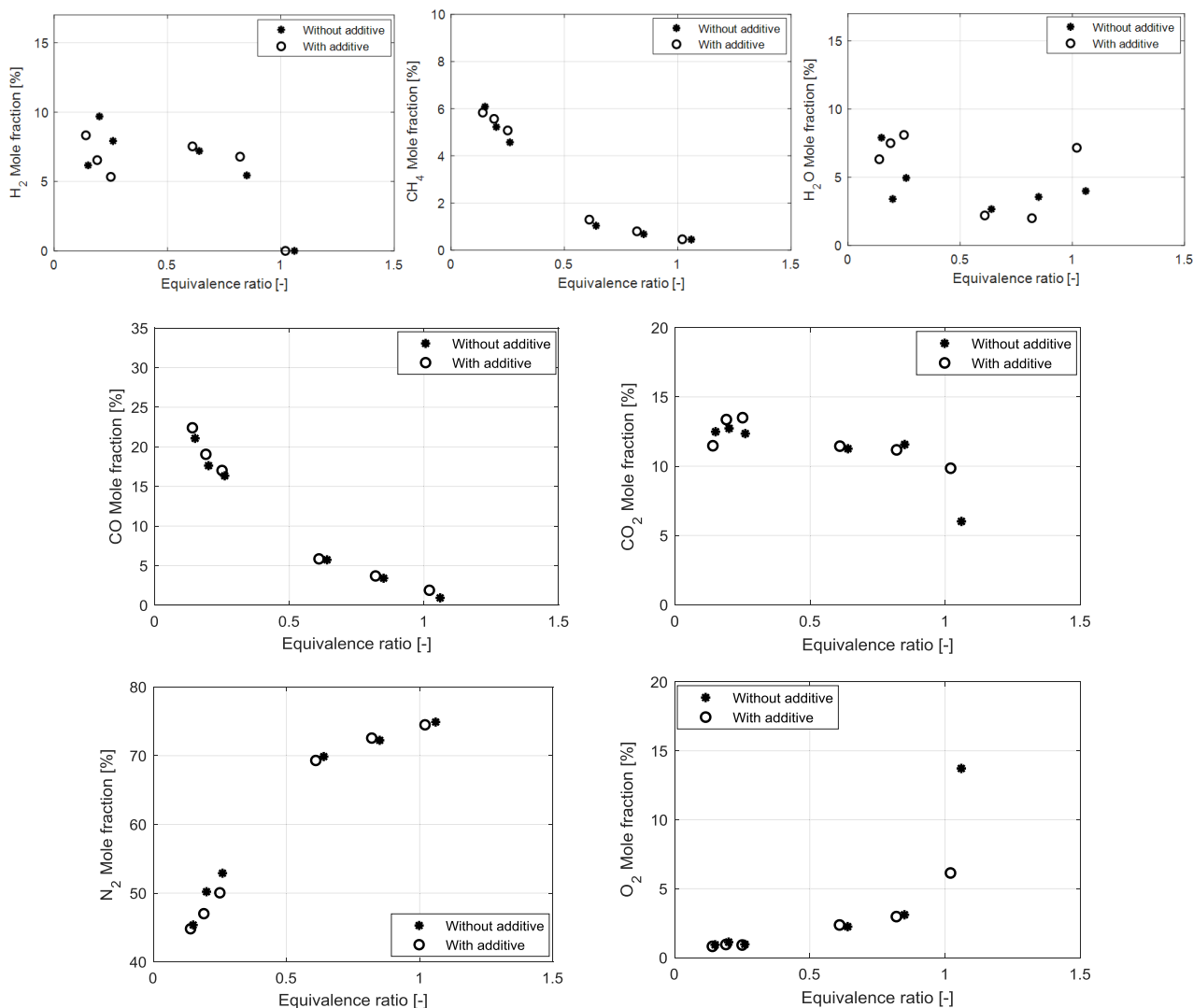
Figure 6. Mole fractions of gas species in the product gas, comparing the conversion of two different wood chips (with and without additive) at different equivalence ratios.

presence of O_2 may also be associated with severe gas bypass resulting from poor fluidization of the bed. The unexpected high amount of oxygen in the product gas at ER = 1.06, which also affects the amount of predicted CO_2 and H_2O, is attributed to the poor gas sampling at this point probably due to partial blockage of the sampling line, since a similar O_2 concentration was measured over six different samples. As the O_2 mole fraction is close to the value in the atmospheric air, it possibly means that each sample contains mostly air with residues of other gases in the sampling line. On average, the results show that there is no significant difference in the composition of the product gas obtained from conversion of the two different wood chip samples except for the H_2O concentration at ER > 1.0 due to the additional amount from the decomposition of the additive.

4.2. Variation in the Energy Value. Particularly in the gasification process aimed at converting biomass into gas of higher energy content, evaluating energy value of the product gas can help to ascertain the influence of additives on the conversion efficiency. The gross energy value depends on both mass and the gas calorific value. Neglecting the char loss due to entrainment, the total mass rate of the gas, $\dot{m}_{gas}$, can be estimated

from eq 9 based on the predicted mass fraction, x_f, of the accumulated char particles.

$$\dot{m}_{gas} = \dot{m}_{air} + (1 - x_f)(1 - w_a)\dot{m}_{bio} \tag{9}$$

The gas calorific value can be derived from the specific energy value, $\widehat{LHV}_i$, and the mass fractions, x_i, of the gas species as expressed in eq 10, where $\hat{M}_i$ is the molecular weight of the species. For the combustible gas species CO, CH_4, and H_2, the respective values 10.1, 50, and 120 MJ/kg for $\widehat{LHV}$ are applied, while for other gas species, the energy values are set to zero.

$$\widehat{LHV}_{gas} = \sum_i (x_i \widehat{LHV}_i); \quad x_i = \frac{y_i \hat{M}_i}{\sum_i (y_i \hat{M}_i)} \tag{10}$$

The energy conversion efficiency η_c from biomass to syngas in each experimental run can therefore be obtained from

$$\eta_c = \frac{\dot{m}_{gas} \widehat{LHV}_{gas}}{(1 - w_a)\dot{m}_{bio} \widehat{LHV}_{bio}} \tag{11}$$

The thermal conversion efficiency, η_{th}, which is of importance for the combustion process can be based on the sensible heat

(a)   (b)
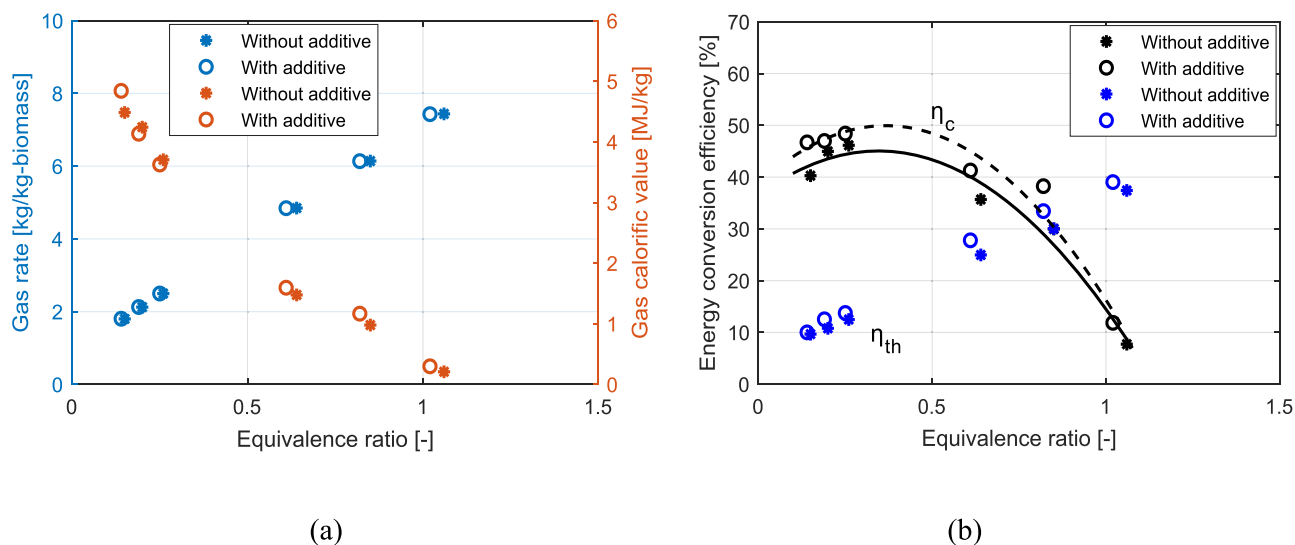
Figure 7. (a) Product gas specific yield and (b) energy conversion efficiency, comparing the conversion of two different wood chips (with and without additive) at different equivalence ratios.

content of the exit gas, as given in eq 12, where $\tilde{c}_{p,gas}$ is the gas specific heat capacity and T_{amb} = 30 °C is the ambient temperature at the feed stream condition.

$$\eta_{th} = \frac{m_{gas}\tilde{c}_{p,gas}(T_{exit} - T_{amb})}{(1 - w_a)m_{bio}\widehat{LHV_{bio}}}; \quad \tilde{c}_{p,gas} = \sum_i (x_i\tilde{c}_{p,i}) \quad (12)$$

The gas rate relative to the biomass feed rate as well as the product calorific value is shown in Figure 7a. As can be seen, the respective quantities are similar for both biomass types at the same equivalence ratio. The slight difference in the specific gas rate at ER > 0.5 is probably due to the release of additional H_2O from $Ca(OH)_2$ decomposition since the process temperature in this ER range is significantly high to favor the reaction. Figure 7b shows that the conversion ratio, η_c (i.e., the cold gas efficiency) first increases to a peak value and then decreases with an increase in the ER value. The η_c value peaks at ER ≈ 0.37 and 0.35 for the biomass with and without additive, respectively, which is in agreement with the ER value reported in the literature[15,42] for optimum biomass gasification. For ER < 1, the energy conversion is considerably higher for the biomass with additive. At the optimum ER, the corresponding efficiencies in converting the different biomass types to syngas are about 50 and 45%. The thermal energy conversion η_{th} increases with the equivalence ratio, but it is slightly higher for biomass with additive at the same ER value as shown in Figure 7 due to the higher specific gas rate.

Overall, Figure 8 shows that the maximum hot gas efficiency ($\eta_c + \eta_{th}$) can be as high as 73% at an ER of about 0.57 for the biomass with additive and significantly lower (within 65% at ER ≈ 0.56) for the plain wood chips due to the enhanced gasification in the former (accompanied with higher CO and CH_4 yields). This indicates that the chemical additive increases the gasification window of the woody biomass. Moreover, since the specific yield of the product gas is similar in both biomass types, the overall efficiency shows that the additive improves the energetic utilization of the fuel material in addition to preserving it against rot. Though tar concentration was not analyzed in these tests, the CaO particles released from the decomposition of $Ca(OH)_2$ might have influenced the tar conversion, thereby improving the conversion efficiency of the biomass with the
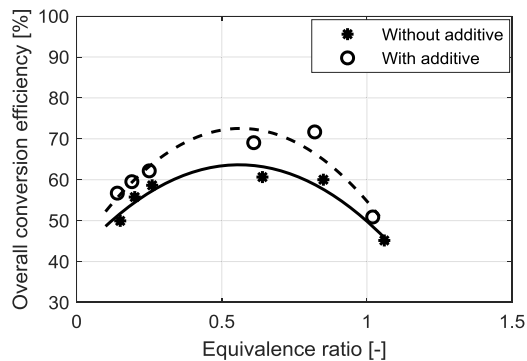

Figure 8. Overall energy conversion efficiency, comparing the conversions of two different wood chips (with and without additive) at different equivalence ratios.

additive. Comparing Figures 7b and 8, it is clear to conclude that the overall efficiency in each case at ER slightly >1.0 is equivalent to the corresponding cold gas efficiency, η_c, at the optimum gasification process.

Although there are no measurements taken in this study to confirm if the $Ca(OH)_2$ additive in the wood chips influences both the conversion and bed hydrodynamics, yet there are significant evidences from the results presented above that the $Ca(OH)_2$ particles play some roles.

Based on the relatively small bulk density of the $Ca(OH)_2$ particles, the volume of the particles released from a unit mass of biomass will be considerably high, resulting in a decrease in the average bed voidage. With a lower bed voidage compared to the bed without additive, the pressure drop will be higher, as shown in Figure 5b, and the minimum fluidization velocity will be lower, as shown in Table 2. The lower bed temperature shown in Figure 5a can be a result of the endothermic decomposition of the $Ca(OH)_2$ particles into CaO and H_2O and an increase in the sensible heat loss due to the additional amount of inert particles, CaO, gas flow rate, and H_2O through the bed. The decomposition reaction increases the concentration of water in the bed, which may also contribute to the higher CO yield compared to the bed with plain wood chips, as can be seen in Figure 6. The lower O_2 mole fraction for the case with additive in

the combustion process is also an evidence of increase in the release of lighter molecules such as H_2O. The possible release of H_2O during combustion (ER = 1.02) may lead to an increase in sensible heat loss, thereby lowering the exit temperature, as shown in Table 3.

5. CONCLUSIONS

This study investigated the performance of biomass mixed with 4 wt % calcium hydroxide during gasification and combustion of the fuel particles in a bubbling fluidized bed. The study was based on the experimental measurements of gas composition, pressure drop, and gas temperature along the reactor axis. To further gain insight into the influence of the additive on the bed behavior, theoretical evaluations of the minimum fluidization velocity were also carried out.

Compared to wood chips of the same kind but with no chemical additive, the results showed that mixing biomass with $Ca(OH)_2$ has some positive influences on the gasification process. The chemical energy content of the product gas is significantly higher although the hydrogen yield is lower. The analysis also provided evidence that the additive decomposes into CaO and H_2O. The additional H_2O released increases the sensible heat loss during the combustion process. The release of fine particles of CaO results in an increase in the bed pressure drop and reduction in the minimum fluidization velocity.

This study opens up a need for further studies to investigate the use of lime to improve the gasification process and to determine how much of such additive is required to avoid inhibiting the combustion process under the desired operating condition. In addition, further analysis of the process using bed material of different particle sizes is also necessary to investigate the gas bypass phenomenon.

■ AUTHOR INFORMATION

Corresponding Authors

Cornelius Emeka Agu − *Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, 3918 Porsgrunn, Norway;* ⓘ orcid.org/0000-0002-5339-9794; Email: cornelius.e.agu@usn.no

Britt M. E. Moldestad − *Department of Process, Energy and Environmental Technology, University of South-Eastern Norway, 3918 Porsgrunn, Norway;* Email: britt.moldestad@usn.no

Christoph Pfeifer − *Department of Material Sciences and Process Engineering, University of Natural Resources and Life Sciences, 1190 Vienna, Austria;* ⓘ orcid.org/0000-0002-7747-9297; Email: christoph.pfeifer@boku.ac.at

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.energyfuels.0c01408

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ NOMENCLATURE

Symbols

A [m^2] = bed cross-sectional area
$\tilde{c}_p$ [J/kg-K] = specific heat capacity
D [m] = bed diameter
g [m/s^2] = acceleration due to gravity
h [m] = height above distributor
$\widehat{LHV}$ [J/kg] = lower heating value
$\hat{M}$ [kg/kmol] = molecular weight
m [kg] = mass
$\dot{m}$ [kg/s] = mass flow rate
p [Pa] = fluid pressure
T [K] = temperature
t [s] = time
U [m/s] = superficial gas velocity
w [-] = weight fraction of biomass component
X [-] = mass ratio between biomass and inert particles
x [-] = species mass fraction
y [-] = species mole fraction

■ GREEK LETTERS

α [-] = degree of conversion completeness
ε [-] = void fraction of bulk material
η [-] = energy conversion ratio
ρ [kg/m^3] = density
γ_{char} [-] = pyrolysis char yield

■ SUBSCRIPTS

a = ash
amb = ambient
bio = biomass
d = devolatilization
e = extinction
f = fuel particles
i = inert
j = species
mf = minimum fluidization
s = sand
0 = entry point

■ REFERENCES

(1) Noll, M.; Jirjis, R. Microbial communities in large-scale wood piles and their effects on wood quality and the environment. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 551−563.

(2) Martínez, A. T.; Speranza, M.; Ruiz-Dueñas, F. J.; Ferreira, P.; Camarero, S.; Guillén, F.; et al. Biodegradation of lignocellulosics: Microbial, chemical and enzymatic aspects of the fungal attack of lignin. *Int. Microbiol.* **2005**, *8*, 195−204.

(3) Boer, W. d.; Folman, L. B.; Summerbell, R. C.; Boddy, L. Living in a fungal world: Impact of fungi on soil bacterial niche development. *FEMS Microbiol. Rev.* **2005**, *29*, 795−811.

(4) Scholz, V.; Idler, C.; Daries, W.; Egert, J. Lagerung von Feldholzhackgut. *Agrartechnische Forschung* **2005**, *4*, 100−113.

(5) Thörnqvist, T. Drying and storage of forest residues for energy production. *Biomass* **1985**, *7*, 125−134.

(6) Barontini, M.; Scarfone, A.; Spinelli, R.; Gallucci, F.; Santangelo, E.; Acampora, A.; et al. Storage dynamics and fuel quality of poplar chips. *Biomass Bioenergy* **2014**, *62*, 17−25.

(7) Whittaker, C.; Macalpine, W.; Yates, N. E.; Shield, I. Dry Matter Losses and Methane Emissions During Wood Chip Storage: The Impact on Full Life Cycle Greenhouse Gas Savings of Short Rotation Coppice Willow for Heat. *BioEnergy Res.* **2016**, *9*, 820−835.

(8) He, X.; Lau, A. K.; Sokhansanj, S.; Jim, L. C.; Bi, X. T.; Melin, S. Dry matter losses in combination with gaseous emissions during the storage of forest residues. *Fuel* **2012**, *95*, 662−664.

(9) Buggeln, R. Outside storage of wood chips. *BioCycle* **1999**, *40*, 32−34.

(10) Pecenka, R.; Lenz, H.; Idler, C.; Daries, W.; Ehlert, D. Development of bio-physical properties during storage of poplar chips from 15 ha test fields. *Biomass Bioenergy* **2014**, *65*, 13−19.

(11) Lenz, H.; Pecenka, R.; Idler, C.; Dumfort, S.; Whittaker, C.; Ammon, C.; Hartung, E. Continuous weighing of a pile of poplar wood chips − A comparison of methods to determine the dry matter losses during storage. *Biomass Bioenergy* **2017**, *96*, 119−129.

(12) Kazemi, S. M.; Dickinson, D. J.; Murphy, R. J. Effects of initial moisture content on wood decay at different levels of gaseous oxygen concentrations. *J. Agric. Sci. Technol.* **2001**, *3*, 293−304.

(13) Ferrero, F.; Malow, M.; Noll, M. Temperature and gas evolution during large scale outside storage of wood chips. *Eur. J. Wood Prod.* **2011**, *69*, 587−595.

(14) Brand, M. A.; de Muñiz, G. I. B.; Quirino, W. F.; Brito, J. O. Storage as a tool to improve wood fuel quality. *Biomass Bioenergy* **2011**, *35*, 2581−2588.

(15) Basu, P. Gasification Theory. In *Biomass Gasification, Pyrolysis, and Torrefaction − Practical Design and Theory*, 2nd ed; Elsevier Inc: London, U.K., 2013; pp 199−248.

(16) van der Stelt, M. J. C.; Gerhauser, H.; Kiel, J. H. A.; Ptasinski, K. J. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass Bioenergy* **2011**, *35*, 3748−3762.

(17) Kamdem, D. P.; Pizzi, A.; Triboulot, M. C. Heat-treated timber: Potentially toxic byproducts presence and extent of wood cell wall degradation. *Holz Roh- Werkst.* **2000**, *58*, 253−257.

(18) Acharjee, T. C.; Coronella, C. J.; Vasquez, V. R. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. *Bioresour. Technol.* **2011**, *102*, 4849−4854.

(19) Almeida, G.; Brito, J. O.; Perre, P. Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: The potential of mass loss as a synthetic indicator. *Bioresour. Technol.* **2010**, *101*, 9778−9784.

(20) Eseyin, A. E.; Steele, P. H., Jr.; Pittman, C. U. Current trends in the production and applications of torrefied wood/biomass − A review. *BioResources* **2015**, *10*, 8812−8858.

(21) Tregambi, C.; Montagnaro, F.; Salatino, P.; Solimene, R. Solar-driven torrefaction of a lignin-rich biomass residue in a directly irradiated fluidized bed reactor. *Combust. Sci. Technol.* **2019**, *191*, 1609−1627.

(22) Pfeifer, C.; Koppatz, S.; Hofbauer, H. Catalysts for dual fluidised bed biomass gasification − an experimental study at the pilot plant scale. *Biomass Convers. Biorefin.* **2011**, *1*, 63−74.

(23) Wilk, V.; Kitzler, H.; Koppatz, S.; Pfeifer, C.; Hofbauer, H. Gasification of waste wood and bark in a dual fluidized bed steam gasifier. *Biomass Convers. Biorefin.* **2011**, *1*, 91−97.

(24) Grimm, A.; Etula, J.; Salh, R.; Kalén, G.; Segerström, M.; Brücher, J.; Söderberg, C.; Soukup, D.; Pfeifer, C.; Larsson, S. H. Slagging and fouling characteristics during co-combustion of Scots pine bark with low-temperature dried pulp and paper mill chemical sludge. *Fuel Process Technol.* **2019**, *193*, 282−294.

(25) Scala, F.; Chirone, R. Characterization and early detection of bed agglomeration during the fluidized bed combustion of olive husk. *Energy Fuels* **2006**, *20*, 120−132.

(26) Natarajan, E.; Öhman, M.; Gabra, M.; Nordin, A.; Liliedahl, T.; Rao, A. N. Experimental determination of bed agglomeration tendencies of some common agricultural residues in fluidized bed combustion and gasification. *Biomass Bioenergy* **1998**, *15*, 163−169.

(27) Morris, J. D.; Daood, S. S.; Chilton, S.; Nimmo, W. Mechanisms and mitigation of agglomeration during fluidized bed combustion of biomass: A review. *Fuel* **2018**, *230*, 452−473.

(28) Anicic, B.; Lin, W.; Dam-Johansen, K.; Wu, H. Agglomeration mechanism in biomass fluidized bed combustion − Reaction between potassium carbonate and silica sand. *Fuel Process. Technol.* **2018**, *173*, 182−190.

(29) Scala, F.; Chirone, R.; Salatino, P. Attritionphenomena Relevant to Fluidized Bed Combustion and Gasification Systems. In *Fluidizedbed Technologies for Near-Zero Emission combustion and gasification*; Woodhead Publishing Series in Energy; Woodhead Publishing, 2013; pp 254−315.

(30) https://phyllis.nl/, visited 06.07.2020, 8:00.

(31) Kitzler, H.; Pfeifer, C.; Hofbauer, H. Combustion of Reeds in a 3 MW District Heating Plant. *Int. J. Environ. Sci. Dev.* **2012**, *3*, 407−411.

(32) Furuvik, N. C. I.; Jaiswal, R.; Moldestad, B. M. E. Flow behavior in an agglomerated fluidized bed gasifier. *Int. J. Energy Environ.* **2019**, *10*, 55−64.

(33) Furuvik, N. C. I.; Jaiswal, R.; Thapa, R. K.; Moldestad, B. M. E. CPFD Model for Prediction of Flow Behavior in an Agglomerated Fluidized Bed Gasifier. *Int. J. Energy Prod. Manage.* **2019**, *4*, 105−114.

(34) Miccio, F.; Landi, A.; Barletta, D.; Poletto, M. Preliminary Assessment of a Simple Method for Evaluating the Flow Properties of Solid Recovered Fuels. *Part. Sci. Technol.* **2009**, *27*, 139−151.

(35) Agu, C. E.; Tokheim, L.-A.; Pfeifer, C.; Moldestad, B. M. E. Behaviour of biomass particles in a bubbling fluidized bed: A comparison between wood pellets and wood chips. *Chem. Eng. J* **2019**, *363*, 84−98.

(36) Agu, C. E.; Pfeifer, C.; Moldestad, B. M. E. Prediction of void fraction and minimum fluidization velocity of a binary mixture of particles: Bed material and fuel particles. *Powder Technol.* **2019**, *349*, 99−107.

(37) Agu, C. E.; Pfeifer, C.; Eikeland, M.; Tokheim, L.-A.; Moldestad, B. M. E. Measurement and characterization of biomass mean residence time in an air-blown bubbling fluidized bed gasification reactor. *Fuel* **2019**, *253*, 1414−1423.

(38) Wen, C. Y.; Yu, Y. H. A Generalized method for predicting the minimum fluidization velocity. *AIChE J.* **1966**, *12*, 610−612.

(39) Narváez, I.; Orio, A.; Aznar, M. P.; Corella, J. Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas. *Ind. Eng. Chem. Res.* **1996**, *35*, 2110−2120.

(40) Robinson, T.; Bronson, B.; Gogolek, P.; Mehrani, P. Comparison of the air-blown bubbling fluidized bed gasification of wood and wood−PET pellets. *Fuel* **2016**, *178*, 263−271.

(41) Gopalakrishnan, P. Modelling of Biomass Steam Gasification in a Bubbling Fluidized Bed Gasifier. PhD. Thesis, The University of Canterbury, 2013.

(42) Kumar, A.; Jones, D. D.; Hanna, M. A. Thermochemical biomass gasification: A review of the current status of the technology. *Energies* **2009**, *2*, 556−581.