




## Article

# Sugarcane Bagasse Torrefaction for Fluidized Bed Gasification

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**Abstract:** Sugarcane bagasse has a great potential to be used as biofuel; however, its use as feedstock in fluidized bed reactors is hampered due to its fibrous nature, low apparent density, high moisture content, and difficulties with its fluidization. The present study evaluated the torrefaction of sugarcane bagasse to propose suitable process conditions that balance the properties of the fuel obtained in the torrefaction and the process's energy requirements. Based on the thermogravimetric analysis and previous reports, two final process temperatures (230 °C and 280 °C) and residence times (35 and 45 min) for the same heating rate (5 °C/min) and nitrogen flow (1 L/min) were evaluated. Within the experimental conditions evaluated, it can be concluded that for 30 min of residence time, the average target temperature of 230 °C should be high enough to produce a stable torrefacted bagasse with a 3.41% reduction in the volatile content and obtain 98.85% of energy yield. Higher temperatures increase the feedstock's carbon content and energy density, but the reduction in energy yield and the fraction of volatiles do not justify higher temperatures or longer residence times for pretreating the sugarcane bagasse.

**Keywords:** sugarcane bagasse; torrefaction; biomass; gasification; entrained flow gasifier

## 1. Introduction

The energy produced from the sugar industry by-products represents an essential contribution to the renewable energetic matrix in countries cultivating sugarcane worldwide [1–4]. In the 2019/2020 season, the estimated sugar production worldwide was roughly 166.18 million metric tons, with a forecasted production of 182.1 million metric tons for season 2020/2021 [5,6]. The sugarcane plant's world biomass generation capacity is high, averaging approximately 69 t.ha<sup>-1</sup> in 2018. The projection for this parameter for 2027 is 72.42 t.ha<sup>-1</sup> [5].

Sugarcane bagasse is the crushed outer stalk by-product formed after the juice extraction from sugarcane in the sugar and alcohol industry. This material represents between 25–40% of the mill's total processed material, depending on the sugarcane fiber contents and the process efficiency [7]. Sugarcane bagasse is an inhomogeneous material containing

around 30–35% of “pith” fiber, which derives from the core of the plant, and “rind” or “stem” fiber, which comprises the balance.

Conventionally, in the sugar factory, high moisture bagasse is used as fuel in boilers for power and steam generation through the Condensing-Extraction Steam-Turbine (CEST) technology, providing mechanical power, electricity, and heat required for the process. The CEST global efficiency ranges are typically 15–30% [8]. Therefore, this generation’s plant size with this technology has been restricted by these efficiencies and sugarcane bagasse availability within a tight transportation distance being economically sustainable.

This hurdle made imperative the development of more efficient technologies for sugarcane bagasse conversion technologies, allowing increases in the steam’s temperature and pressure, and leading to higher electric power cogeneration efficiency [9].

In sugar mills, the Biomass Integrated-Gasifier/Gas Turbine Combined Cycle (BIG/GTCC), a more advanced technology [10–13], is potentially cost-competitive with CEST technology while theoretically increasing the capacity for electricity generation per unit of biomass processed. In this type of technology, the characteristics of the sugarcane bagasse require fluidized bed or entrained flow gasification technologies to obtain more efficient conversion ratios.

The pretreatment of sugarcane bagasse for its use as feedstock in gasifiers is particularly problematic due to its high moisture content, fibrous structure, and tenacity. However, the physical composition of sugarcane bagasse varies slightly regardless of the mill used in the juice extraction process. Furthermore, the properties of bagasse as fuel have been studied extensively [4,14–17].

Several authors have reported problems during feedstock preparations and the feeding process to fluidized bed gasifiers in several demonstration projects. They feed the gasifiers with sugarcane bagasse after two pretreatment technologies, drying and milling [10,18–20] or pelletizing and grinding [21,22], respectively.

Torrefaction is an alluring biomass preprocessing path, as it may enhance the fuel characteristics of biomass and facilitate its grinding. This process also positively impacts storage and transportation because of the torrefied biomasses’ hydrophobic behavior and increased energetic density [23–26]. This process also allows pretreated sugarcane bagasse to be used as feedstock in entrained flow gasifiers designed to gasify coal [27].

Previous studies propose implementing sugarcane bagasse torrefaction to overcome the reported problems during this feedstock preparation and the feeding process to fluidized bed gasifiers [27,28]. Sugarcane bagasse torrefaction has been studied [23,29–31]. However, more experimental studies assessing the torrefaction conditions that balance the torrefied fuel properties and the process’s energy usages are required, allowing the maximization of the overall efficiency in the integrated technologies.

The present study’s objective was to assess the sugarcane bagasse torrefaction to propose adequate process conditions that balance the fuel properties obtained in sugarcane bagasse torrefaction and the energy requirements of the process. Thus, this technology could produce a hydrophobic, stable, energy-dense, and homogeneous in size solid fuel, and this may be able to be used in a fluidized bed or as entrained flow gasifiers.

## 2. The Torrefaction Process

Torrefaction is a thermochemical pretreatment process that improves the characteristics of biomass to be used as fuel in fluidized bed gasifiers. The enhancements are related to removing the volatiles and cracking part of the feedstock fibers. However, these improvements should be accomplished without losing too much energy to volatile products throughout the process.

Solid-phase forms the main torrefaction product, comparable to the pyrolysis process, and is referred to as the charred residue or torrefied feedstock. The chemical structure of feedstock is altered in the process, forming diverse volatile products, and some liquids at room temperature (condensable). Other than torrefied feedstock, the main process product is carbon monoxide, carbon dioxide, methanol, acetic acid, and water [32]. All these non-

solid reaction products contain relatively more oxygen compared to untreated biomass. Hence, the C/O ratio of torrefied biomass is higher than untreated biomass, increasing the torrefied feedstock's heating value.

High values of the C/O ratio (such as coal) are related to greater gasification efficiencies, while for low values of this ratio (such as biomass in general), the gasification efficiency drops. Therefore, fuels with high oxygen content are not ideal for gasification from an exergetic perspective [33].

In the torrefaction process, biomass loses its tenacious nature and part of its fibrous structure. The biomass usually has a darker color through torrefaction and becomes more suitable to be crushed into smaller pieces. Furthermore, the biomass is wholly dried during the process, and after it, the uptake of moisture is minimal, varying from 1–6% depending on the torrefaction conditions and the storage of the torrefied feedstock afterward.

The main reason for the hydrophobic behavior of torrefied biomass is the reduction of the hydrogen bonding capability by eliminating OH groups. The most reactive biomass polymer during torrefaction is hemicellulose [34–36]. After torrefaction, it has been entirely reacted to alternative char structures and volatiles. Most weight loss can be attributed to hemicellulose because torrefied biomass mainly consists of cellulose and lignin [25,37,38].

The temperatures of the torrefaction process range between 200 °C and 300 °C, according to previous studies [39,40]. Torrefaction above this temperature would result in extensive devolatilization and carbonization of the polymers, both undesirable for torrefaction products [39]. Also, the loss of lignin in biomass is very intensive above 300 °C. Furthermore, fast thermal cracking of cellulose causes tar formation, which starts around 300–320 °C [41]. These reasons fix the upper limit of torrefaction temperature as 300 °C for most biomasses.

The residence time exerts a significant influence on the thermal degradation of biomass. Longer residence times usually lower the mass yield and increase the energy density. However, the residence time influences the torrefaction products; but it is not as dominant as the final torrefaction temperature. The effect of residence time on mass loss diminishes after 60 min [42].

### 3. Materials and Methods

#### 3.1. Characterization of the Sugarcane Bagasse

The samples were characterized before and after torrefaction, using the standard methodology for proximate analysis of solid biofuels (UNE-EN 15148:2010, UNE-EN 14774-3:2010, and UNE-EN 14775:2010). The elemental analysis was performed according to ABNT-NBR-8112 in a Leco TruSpec Elemental Analyzer CHN 628 and 628 S (Leco.co., St. Joseph, MI, USA). The calorific values were determined through a unified correlation of Channiwala and Parikh that includes 18 correlations and 50 fuels [43].

$$\text{HHV}_{db} = 349.1 C + 1178.3 H + 100.5 S - 103.4 O - 15.1 N - 21.1 \text{ASH} \left[ \frac{\text{kJ}}{\text{kg}} \right] \quad (1)$$

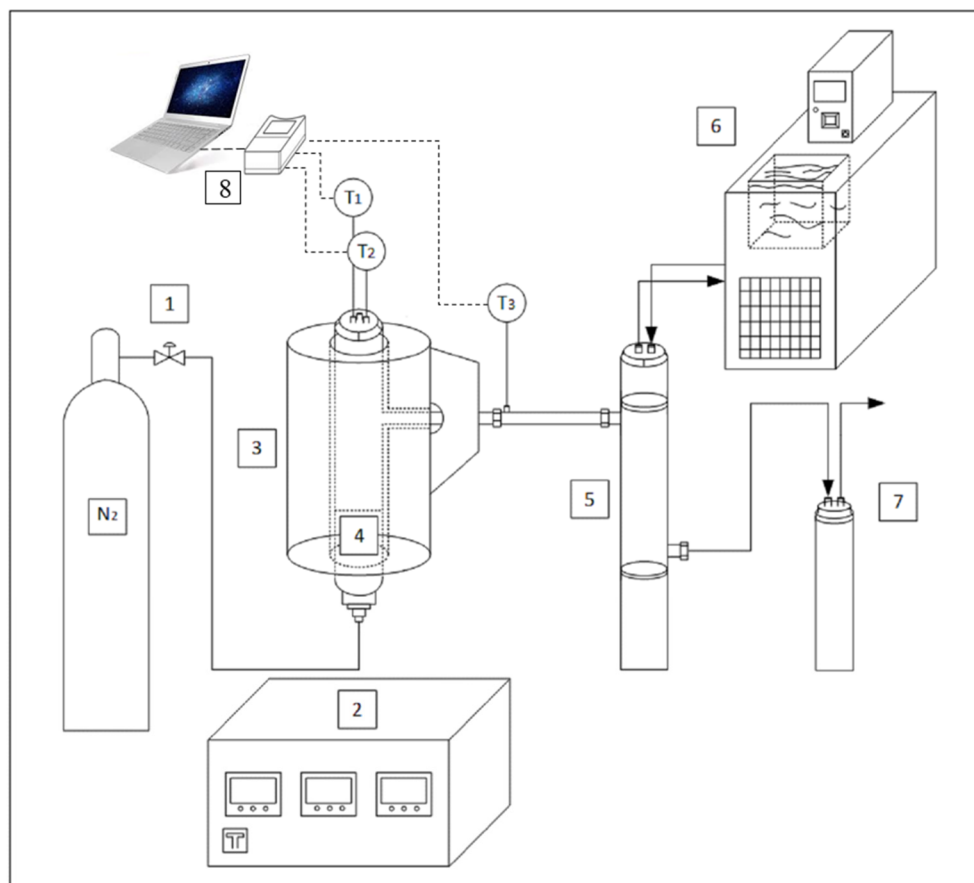
#### 3.2. Thermogravimetric Analysis (TGA)

The thermogravimetric studies were conducted with a thermobalance (Cahn–Ventron 2000) with a microprocessor, a temperature control unit, and thermal analysis data software. The samples (5–10 mg) were heated from 25 °C to 600 °C at a heating rate of 10 °C·min<sup>−1</sup>, using a nitrogen flow of 50 mL·min<sup>−1</sup>.

#### 3.3. Experimental Setup

Torrefaction experiments were performed in a lab-scale batch installation. Figure 1 shows a simplified diagram of the experimental setup. A flow regulator (1) fixes a nitrogen flow at 1 L/min to guarantee an inert atmosphere inside the reactor (4), loaded with 50 g of raw material by test. The reactor is heated through a 3-resistance furnace (3) with a heating rate of 5 °C/min in all tests. The controller (2) manages the furnace temperatures

and heating rate. Volatiles leave the reactor through a thermally insulated line. Condensed gases are collected in the condenser (5), coupled to a water-cooling bath, recirculating water at 7 °C (6). Finally, non-condensable volatiles are evacuated from the installation after passing by a water trap (7). The datalogger (8) registers the reactor temperatures ( $T_1$  and  $T_2$ ) and the gas temperature at the reactor exit ( $T_3$ ).



**Figure 1.** Experimental setup for torrefaction studies.

The experimental design evaluated the effect of the final process temperature ( $T_{\text{torr}}$ ) and residence time ( $t_{\text{R}}$ ) on the process products and the torrefied samples' physico-chemical properties. The process heating rate was the same for all the experimental runs.

An experimental design setup of two factors— $T_{\text{torr}}$  and  $t_{\text{R}}$ , and two levels for each factor (namely  $2^k$ ) was used. For the  $T_{\text{torr}}$  factor, the levels assessed were 230 °C and 280 °C, and for the  $t_{\text{R}}$ , the levels were 30 and 45 min. In addition, three experimental repetitions for each process condition were performed, totaling 12 experimental runs. The main output experimental variables observed in the experiments were the proximate and elemental composition and calorific value of torrefied bagasse.

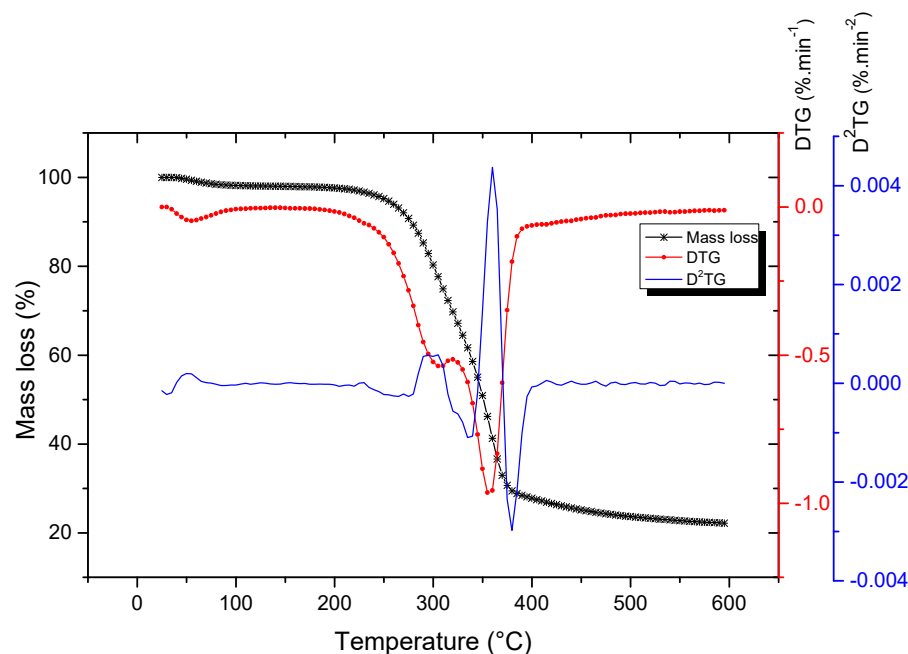
In order to assess the impact of  $T_{\text{torr}}$ , temperatures of 230 °C and 280 °C were selected considering previously reported experiences with similar feedstocks [25,39,40,44,45] and the TGA analysis results, which are presented in the next section.

## 4. Results and Discussion

### 4.1. Thermogravimetric Analysis (TGA)

Figure 2 shows the thermal degradation of raw sugarcane bagasse under N<sub>2</sub> atmosphere, and it is observed that the thermal degradation profile of sugarcane bagasse showed three stages of mass loss, according to the DTG curve. The first one was below 113 °C and belonged to the biomass moisture evaporation, accounting for a water loss of 2.3%.

Besides, the pyrolysis was concentrated in the temperature range 178–478 °C and reached the maximum decomposition rate at 356 °C, which is in line with previously reported results for this agro-fiber [35,46,47].



**Figure 2.** Thermogravimetric curve (TG), its derivative (DTG), and second-order derivative ( $D^2TG$ ) for sugarcane bagasse biomass under  $N_2$  atmosphere and heating rate  $10\text{ °C min}^{-1}$ .

The second decomposition stage contributes to the mass loss of 28.8%, in the temperature range of 178–321 °C, and the maximum decomposition rate is peaking at 307.4 °C. Then, a third decomposition stage can be observed at a higher temperature range of 322–478 °C, with a maximum decomposition rate at 356 °C, and an associated mass loss of 45.1%. Finally, 22.1% of char is obtained, which belongs to inorganics and the remaining condensed material. Table 1 summarizes the thermal analysis results. The results were obtained from the graphical analysis of the DTG curve shown in Figure 2.

**Table 1.** Results from thermal degradation of sugarcane bagasse in  $N_2$  atmosphere and heating rate of  $10\text{ °C min}^{-1}$ .

Sugarcane Bagasse	Temperature (°C)			Weight Loss (%)	Char (%)
	$T_{ONSET}$	$T_{PEAK}$	$T_{OFFSET}$		
First stage	30	58	113	2.3	
Second stage	178	307	321	28.8	22.1
Third stage	322	356	478	45.1	

Lignin, hemicellulose, and cellulose are macromolecular compounds that display different thermal decomposition behavior under pyrolysis conditions [34]. Moreover, their chemical composition can influence biomass pyrolytic behavior due to the interaction of their components [46]. It has been reported that sugarcane bagasse pyrolysis can be represented as an independent parallel reaction model [48]. Each component (hemicellulose, cellulose, and lignin) could decompose at temperature intervals that overlap among each other instead of starting to decompose only after the other one ends.

In Figure 2, it is observed that the thermal degradation profile of sugarcane bagasse showed three zones of mass loss. The first one was below 113 °C and belonged to the

biomass moisture evaporation, accounting for a water loss of 2.3%. The second zone corresponds to the predominant thermal decomposition of hemicellulose, and in the third zone, the degradation of cellulose was the predominant event that took place, while the lignin decomposition starts [34].

For sugarcane biomass, the pyrolysis was concentrated in the temperature range 178–478 °C and reached the maximum decomposition rate at 356 °C, which is in line with previously reported results for this agro-fiber [35,46,48]. The decomposition of hemicellulose contributes to the mass loss of 28.8%, in the temperature range of 178–321 °C, and the maximum decomposition rate is peaking at 307.4 °C.

Cellulose pyrolysis occurs in a higher temperature range of 322–478 °C, with a maximum decomposition rate at 356 °C. The associated mass loss for this temperature range is 45.1%, mainly related to cellulose degradation. Meanwhile, according to several authors, the lignin decomposition occurred in the broader range from 200 to 500 °C, overlapping with the polysaccharide degradation [34–36]. Therefore, this mass loss can also be associated with lignin degradation but in a smaller proportion.

In Figure 2, it is observed that the thermal degradation profile of sugarcane bagasse showed three stages of mass loss, according to the DTG curve. The first one was below 113 °C and belonged to the biomass moisture evaporation, accounting for a water loss of 2.3%. Besides, the pyrolysis was concentrated in the temperature range 178–478 °C and reached the maximum decomposition rate at 356 °C, which is in line with previously reported results for this agro-fiber [35,46,48].

The second decomposition stage contributes to the mass loss of 28.8%, in the temperature range of 178–321 °C, and the maximum decomposition rate is peaking at 307.4 °C. Then, a third decomposition stage can be observed at a higher temperature range of 322–478 °C, with a maximum decomposition rate at 356 °C, and an associated mass loss of 45.1%. Finally, 22.1% of char is obtained, which belongs to inorganics and the remaining condensed material.

The second stage corresponds to the thermal decomposition of hemicellulose, which is less thermal stable than cellulose. The third stage belongs to cellulose degradation, a semicrystalline ordered polymer with higher thermal stability [34]. Besides, the lignin decomposition occurred in the broader range from 160–500 °C, overlapping with the polysaccharide degradation [34–36]. However, it has been demonstrated that those processes overlapped and do not belong to pure compounds because those components can have complex interactions during thermal degradation, and different profiles can be obtained for different lignocellulosic sources [49,50].

Considering that the torrefaction temperature must be lower than 300 °C, and as observed in Figure 2, the changes in the monotony of DTG before that temperature occur at around 230 °C, where we see an increase in the temporal rate of mass loss, and in the vicinity of 280 °C where it reaches the maximum of the temporal rate of mass loss before 300 °C. Considering previous studies [25,39,40,44,45] and the sugarcane bagasse thermal degradation behavior observed, those values were fixed as the torrefaction temperature levels in the experimental runs.

#### 4.2. Proximate Analysis of Unprocessed Sugarcane Bagasse

According to Table 2, the volatile matter forms more than 88% of the studied raw sugarcane bagasse's overall composition, which is high compared with the previously reported compositions. On the contrary, the fixed carbon content of the studied sample is lower than the average content for this component. The overall ash content rounds 2% within the average content for this biomass if compared with previously reported data. In the combustion of this feedstock, the low ash content could prevent deposits in the combustion appliances. Deposits can bridge across tube bundles, increasing the combustion side pressure drop and increasing the fan work needed to sustain proper flow.

**Table 2.** Proximate analysis of sugarcane bagasse sample compared with other studies (wt.%, dry basis).

	Present Study	[51]	[52]	[53]	[4]	[54]	[55]	[56]	[57]
Volatile matter (wt.%, dry basis)	88.48	87.06	83.0	85.61	88.7	82.1	85.43	79.35	n.a.
Ash (wt.%, dry basis)	2.1	n.a.	4.0	2.44	2.0	1.6	1.68	3.66	6.8
Fixed Carbon (wt.%, dry basis)	9.41	12.94	13.0	11.95	9.3	16.3	12.89	17.88	n.a.
Higher heating value (MJ. kg <sup>-1</sup> , dry basis)	15.96	18.6	18.9	18.99	18.7	19.19	19.14	19.41	18.85

In the sugarcane bagasse, the leaching process during the juice extraction removes a significant quantity of alkaline constituent from the sugarcane, significantly reducing the alkaline index and the potential formation of fouling and slagging in the combustion of this feedstock. Considering this fact, 2% of ash content in this fuel can be considered acceptable. The obtained higher heating value of the studied unprocessed sugarcane bagasse is roughly 15% lower than the expected value for this feedstock. The proximate analysis shows that the sugarcane bagasse is feedstock with a high potential for gasification.

#### 4.3. Ultimate Analysis of Unprocessed Sugarcane Bagasse

Table 3 shows the elemental composition of unprocessed sugarcane bagasse, i.e., the fractions of the elemental Carbon (C), Hydrogen (H), Nitrogen (N), Sulfur (S), Chlorine (Cl), and Oxygen (O). The studied sample of sugarcane bagasse contains more than 41% of carbon, a relatively lower value than the mean for the previously studied samples, but not out of order for sugarcane bagasse [4,43–49]. This is the main reason for the comparatively lower HHV reported in Table 2. Hydrogen contributes 5.51%, in line with the previously reported value for this feedstock. Oxygen credits roughly 50% of the overall composition, relatively high compared to the other sugarcane bagasse samples reported in Table 2. All other elements studied here (N, S, Cl) are lower than 1%. In the case of sulfur content demeanor, as expected, the concentration remains in the order of 0.05%, reducing the potential formation of the common pollutant throughout the combustion of this biomass, caused by the probable combination of sulfur with hydrogen and oxygen. These values are within the range found in herbaceous and non-woody biomasses [58].

**Table 3.** Ultimate analysis of sugarcane bagasse sample compared with other studies (wt.%, dry basis).

Element	Present Study	[51]	[52]	[53]	[4]	[54]	[55]	[56]	[57]
C	41.45	47.0	46.3	48.65	42.9	48.81	49.0	48.4	46.7
H	5.51	5.9	6.4	5.87	5.9	6	5.87	6.01	6.2
O *	50.37	45.81	43.0	42.82	49.0	43.1	43.27	41.61	39.8
N	0.51	0.33	n.a.	0.16	0.20	0.46	0.1	0.17	0.2
S	0.054	0.05	0.1	0.04	n.a.	0.1	0.06	0.02	0.02
Cl	n.a.	n.a.	n.a.	0.03	n.a.	<0.01	0.02	n.a.	0.06

\* by difference.

#### 4.4. Improving Energy Properties of Sugarcane Bagasse by Torrefaction

Tables 4 and 5 summarize the obtained composition of the torrefied sugarcane bagasse at temperatures of 230 °C and 280 °C and for residence times of 30 and 45 min, respectively.

Torrefaction causes reductions in biomass energy yields on an ash-free basis (DAF) [59] because of partial devolatilization but also causes an increase in the energy density (DAF). In the case of the sugarcane bagasse torrefaction at 230 °C (Table 4), it was noticed that by reducing 3% to 5% of the energy yields, the feedstocks lost between 18% to 19% of its original mass. Thus, it increases by 19% to 20% in the bagasse samples' energy density for those experimental conditions, increasing its higher heating value by 20%.

**Table 4.** The proximal and ultimate composition of torrefied sugarcane bagasse at 230 °C.

Property	Raw Bagasse	Torrefaction Time (min)	
		30	45
Volatiles (%)	88.48	85.67	85.71
Ash (%)	2.11	5.97	5.48
Fixed Carbon (%)	9.41	8.36	8.81
C (%)	41.45	47.07	46.90
H (%)	5.514	6.02	6.02
O (%) *	50.37	40.62	41.21
N (%)	0.509	0.28	0.33
C/O	0.823	1.159	1.138
H/C	0.133	0.128	0.128
Increase C/O ratio (%)	-	40.82	38.29
Decrease H/C ratio (%)	-	3.75	3.75
Higher heating value (HHV) (MJ/kg product)	15.96	19.19	19.08
Mass yield DAF (%)	-	82.21	81.03
Energy yield DAF (%)	-	98.85	96.87
Energy density (% Energy yield/% Mass yield)	-	1.20	1.19
Rise in HHV (%)	-	20.24	19.55

\* by difference.

**Table 5.** The proximal and ultimate composition of torrefied sugarcane bagasse at 280 °C.

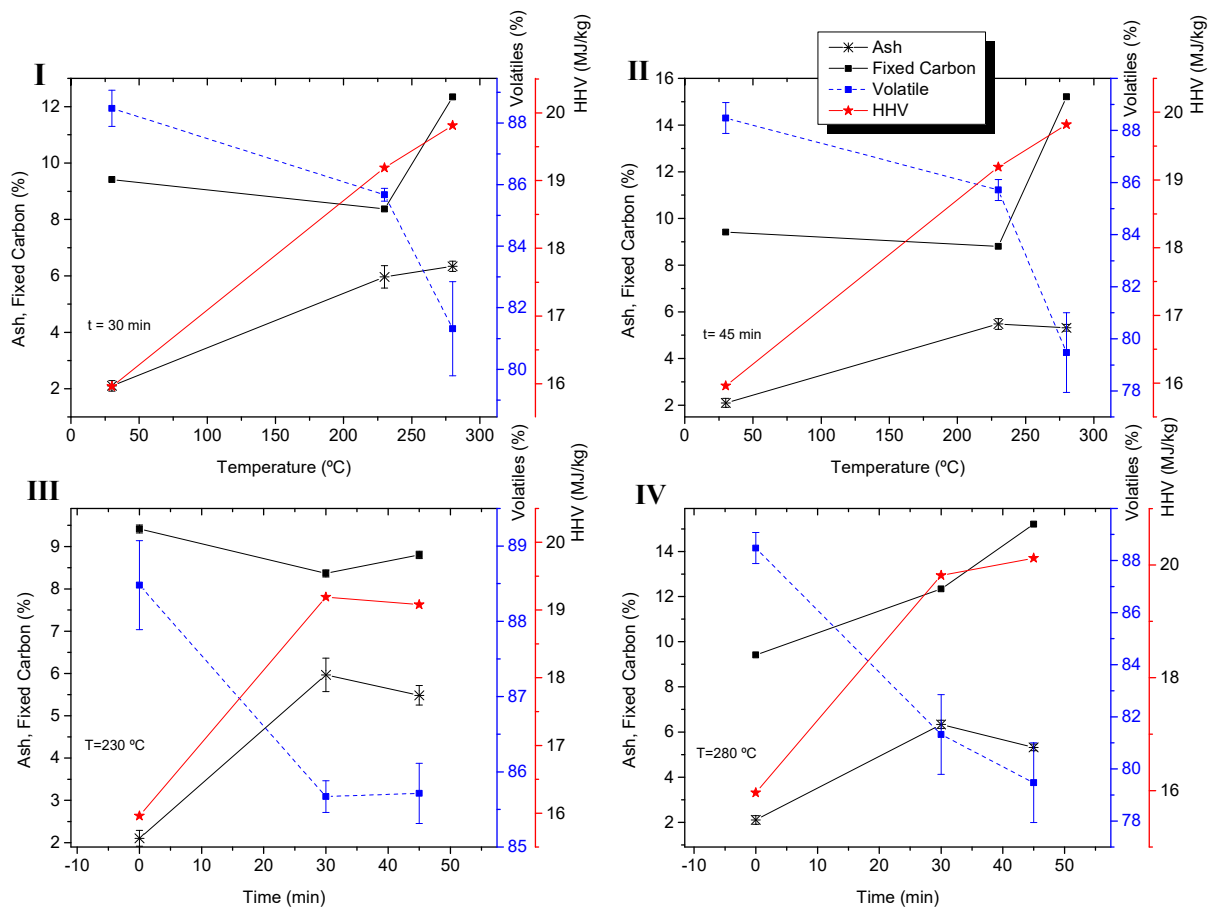
Property	Raw Bagasse	Torrefaction Time (min)	
		30	45
Volatiles (%)	88.48	81.32	79.47
Ash (%)	2.11	6.34	5.32
Fixed Carbon (%)	9.41	12.34	15.21
C (%)	41.45	48.20	49.53
H (%)	5.51	6.08	5.94
O (%) *	50.37	39.04	39.16
N (%)	0.51	0.29	0.01
C/O	0.82	1.24	1.27
H/C	0.133	0.126	0.120
Increase C/O ratio (%)	-	50.05	53.71
Decrease H/C ratio (%)	-	5.26	9.77
Higher heating value (HHV) (MJ/kg product)	15.96	19.81	20.12
Mass yield DAF (%)	-	71.01	72.60
Energy yield DAF (%)	-	88.10	91.41
Energy density (% Energy yield/% Mass yield)	-	1.24	1.26
Rise in HHV (%)	-	24.11	26.05

\* by difference.

Table 5 shows a similar behavior on the analyzed parameters for the sugarcane bagasse torrefaction at 280 °C. At this temperature, reductions in the biomass energy yield ash-free basis reach 12%, increasing the sample's energy density by 26%.

Figure 3 shows the effects of the studied torrefaction temperatures and residence times on the proximate analysis of sugarcane bagasse. Figure 3-I presents the variation of ash, fixed carbon, volatiles, and higher heating value for 30 min. Figure 3-II presents the same effects for 45 min. The results have shown that the fuel composition has the same behavior with the temperature increment for both residence times.

The percentage of volatiles in the composition is reduced at higher treatment temperatures with a significant increment in the variation rate for the temperature of 280 °C, as previously observed in Figure 2. Fixed carbon has less than 1% of the variation for 230 °C, increasing more than 4% when the temperature increases by 50 °C.



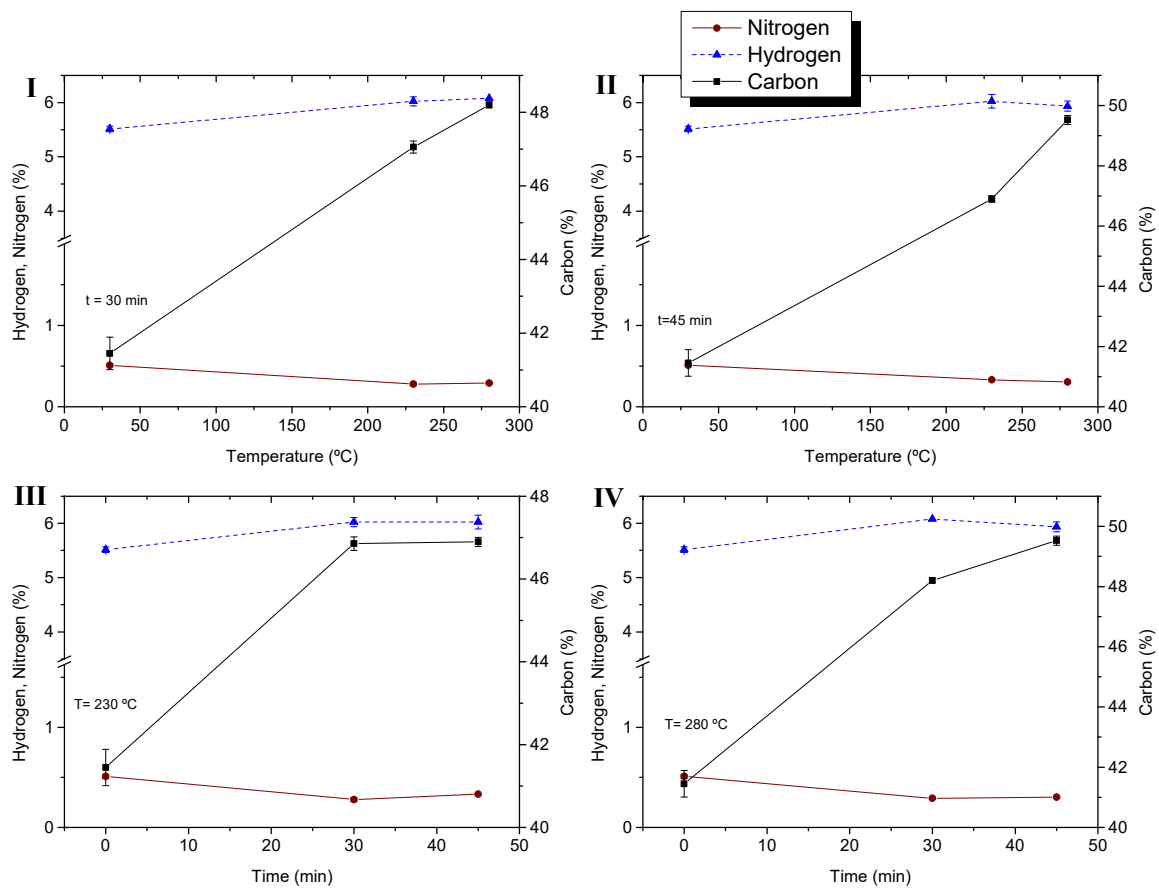
**Figure 3.** Effects of torrefaction temperatures (I,II) and residence times (III,IV) on proximate analysis of sugarcane bagasse.

For the residence time of 45 min, the fixed carbon has the same behavior for the temperature of 230 °C, but with a more significant increment for 280 °C. Ash content showed the primary increment for the temperature of 230 °C, with the same tendency for the temperature increase for the residence time of 30 min; ash remains almost in its totality in the solid product of the torrefaction. On the other hand, the tendency is slightly reverted for the residence time of 45 min.

The higher heating value shows a similar trend for both residence times, opposite to volatiles and fixed carbon, with the lower increments at the temperature of 280 °C for both residence times.

Figure 3-III presents the variation of fuel properties with residence time increase for the temperature of 230 °C. Figure 3-IV presents the same effects for the temperature of 280 °C. For the temperature of 230 °C, no significant variation is observed after the obtained composition at 30 min. Conversely, for 280 °C, a substantial enhancement is observed for the fixed carbon content after 30 min. The torrefaction process also causes a noticeable reduction of the volatiles and ash composition for a residence time of 45 min, compared with the obtained composition at 30 min. A slight increment of the higher heating value is observed for a residence time of 45 min.

Figure 4 shows the effects on sugarcane bagasse elemental composition of studied torrefaction temperatures and residence times. Figure 4-I presents the carbon, hydrogen, and nitrogen composition at different temperatures, for the residence time of 30 min. Figure 4-II presents the same results for a residence time of 45 min.



**Figure 4.** Effects of torrefaction temperatures (I,II) and residence times (III,IV) on the elemental composition of sugarcane bagasse.

The elemental composition has the same behavior for both residence times when the temperature increases. However, the nitrogen concentration has a minor reduction, with the temperature for both residence times differing from the behavior observed for hydrogen and carbon when increasing the temperature increment. The increase of hydrogen concentration is lower than 1%, with carbon being the component with the most significant increment for the studied conditions, raising 8% for a residence time of 30 min and more than 9% for 45 min. The primary increment occurs for the temperature of 230 °C, with 6% and 7% for 30 and 45 min residence times, respectively.

Figure 4-III presents the variation of the elemental composition with the variation of the residence time for the temperature of 230 °C. Figure 4-IV presents the same effects for the temperature of 280 °C. No significant variation is observed in the torrefied samples' elemental composition after the attained composition at 30 min of residence time, similar to results at 230 °C. On the contrary, for a temperature of 280 °C, the fixed carbon composition increases, after 30 min. For the temperature of 280 °C, the torrefaction process causes a slight reduction of hydrogen concentration for a residence time of 45 min when compared with the obtained composition at 30 min.

The increase of the elemental carbon fraction in the feedstock composition is essential for biomass as feedstock in combustion devices. For gasification, it is also essential not to significantly reduce the volatile fraction of the processed feedstock [60–62]. In the torrefaction process, the volatile release rate, mainly hydrogen and oxygen, increases with temperature. The volatile fraction reduction increases the C/O ratio to 40.82% and 50.05% for 230 °C and 280 °C, respectively. Reduction in the volatile content also caused a decrease in the H/C ratio to 3.75% for 230 °C and 5.26% for 280 °C, both for 30 min of residence time.

In addition, the yield of volatiles was also reduced by 3.41% and 8.09% at 230 °C and 280 °C, respectively, for 30 min of residence time. The variation is partially balanced with the increment of HHV and the energy yield (98.85% at 230 °C, and 88.10% at 280 °C), keeping viable the uses of torrefacted sugarcane bagasse as feedstock for thermal gasification (Tables 4 and 5).

For the torrefaction at 230 °C, the HHV of sugarcane bagasse increased 20.24% for 30 min of residence time and, for 280 °C, the HHV increased 24.11%—less than 4% higher if compared with the observed increment for 230 °C. The energy yield in these conditions was also higher than the value reported by Basu et al. [63] for 30 min of residence time and Manatura [29] at 225 °C for 30 and 60 min of residence time.

Daniyanto et al. [62] obtained a similar composition for the torrefied Indonesian sugarcane bagasse at 220 °C but for a longer residence time of 60 min. The torrefied bagasse gasification with the later torrefaction parameter was also reported [56], showing comparatively better results than the torrefied bagasse at a higher temperature and same residence time. Even though obtained HHV was inferior to other conventional gasification fuels [53,64,65], the obtained benefits associated with the torrefaction of sugarcane bagasse suggest using the process as a pretreatment technology for gasification.

## 5. Conclusions

Due to the torrefied biomass's hydrophobic character, the results have proven that it is possible to avoid natural degradation of the untreated bagasse due to water content, sugar, and dirt that occurs during storage.

This work corroborates the hypothesis that torrefaction temperature affects the resulting torrefaction yield and quality. Furthermore, the residence time was also revealed to have an essential role in the torrefied sample's chemical properties.

Considering as main purpose the usage of torrefied biomass as feedstock for gasification, within the range of the temperatures in this work, it can be concluded that for 30 min of residence time, the middle target temperature used of 230 °C should be high enough to produce stable torrefied sugarcane bagasse with a reduction of 3.41% in the volatile content and obtaining 98.85% of energy yield. The previously reported studies also support this conclusion. Higher temperatures increase the carbon content and the feedstock energy density, but the reduction of energy yield and volatile fraction do not justify higher temperatures or longer residence times for pretreatment of sugarcane bagasse. Further studies about the heating rate effects while using this temperature should be performed.

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## References

1. Taylor, R.D. 2016 Outlook of the U.S. and World Sugar Markets, 2016–2025. *Agribus. Appl. Econ. Rep.* **2016**, *751*. [CrossRef]
2. de Sousa, E.L.L.; de Carvalho Macedo, I. *Ethanol and Bioelectricity: Sugarcane in the Future of the Energy Matrix*; Unica: São Paulo, Brazil, 2011.
3. EPE Balanço Energético Nacional. 2019. Available online: <https://www.epe.gov.br/sites-pt/publicacoes-dados-abertos/publicacoes/PublicacoesArquivos/publicacao-377/topico-494/BEN%202019%20Completo%20WEB.pdf> (accessed on 2 January 2020).
4. De Filippis, P.; Borgianni, C.; Paolucci, M.; Pochetti, F. Gasification process of Cuban bagasse in a two-stage reactor. *Biomass Bioenergy* **2004**, *27*, 247–252. [CrossRef]
5. FAO; OECD. *OECD-FAO Agricultural Outlook 2018–2027*; FAO-OECD: Rome, Italy, 2018; ISBN 978-92-5-130501-0.
6. USDA. *Sugar: World Markets and Trade*; USDA: Washington, DC, USA, 2021.
7. Pernalet, Z.; Piña, F.; Suarez, M.; Ferrer, A.; Aiello, C. Fraccionamiento del Bagazo de Caña de Azúcar Mediante Tratamiento Amoniacal: Efecto de la Humedad del Bagazo y la Carga de Amoniaco. *Bioagro* **2008**, *20*, 3–10.
8. Barroso, J.; Barreras, F.; Amaveda, H.; Lozano, A. On the optimization of boiler efficiency using bagasse as fuel. *Fuel* **2003**, *82*, 1451–1463. [CrossRef]
9. Brito, A.L.; Beaton, P.A.; Ballester, J.; Dopazo, C. *Novel Approach for the Analysis of Heat Transfer in Bagasse-Fired Furnaces*; Overend, R.P., Chornet, E., Eds.; Pergamon: Oxford, UK, 1999; ISBN 0080430198.
10. Larson, E.D.; Williams, R.H.; Leal, M.R.L. A review of biomass integrated-gasifier/gas turbine combined cycle technology and its application in sugarcane industries, with an analysis for Cuba. *Energy Sustain. Dev.* **2001**, *5*, 54–76. [CrossRef]
11. Bridgwater, A.V. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* **2012**, *38*, 68–94. [CrossRef]
12. Jana, K.; De, S. Biomass integrated gasification combined cogeneration with or without CO<sub>2</sub> capture—A comparative thermodynamic study. *Renew. Energy* **2014**, *72*, 243–252. [CrossRef]
13. Babu, S. Thermal gasification of biomass technology developments: End of task report for 1992 to 1994. *Biomass Bioenergy* **1995**, *9*, 271–285. [CrossRef]
14. Gómez, E.O.; Cortez, L.A.B.; Alarcon, G.R.; Rocha, G.J.D.M.; Da Silva, V.F.N.; De Almeida, E. Some simplified geometrical properties of elephant grass and sugarcane trash particles. *Fuel Process. Technol.* **2012**, *104*, 234–244. [CrossRef]
15. Driemeier, C.; Oliveira, M.M.; Mendes, F.M.; Gómez, E.O. Characterization of sugarcane bagasse powders. *Powder Technol.* **2011**, *214*, 111–116. [CrossRef]
16. Alarcon, G.; Olivares Gómez, E.; Barbosa Cortez, L.; Glauco Sánchez, C.; Alarcon, G.; Olivares Gómez, E.; Barbosa Cortez, L.G.S. Caracterización del bagazo de la caña de azúcar. Parte I: Características físicas. In Proceedings of the VI Encontro Energia no Meio Rural AGRENER 2006, Campinas, Brazil, 6–8 June 2006; NIPE/Unicamp: Campinas, Brazil, 2006; p. 10.
17. Rasul, M.; Rudolph, V.; Carsky, M. Physical properties of bagasse. *Fuel* **1999**, *78*, 905–910. [CrossRef]
18. van den Enden, P.J.; Lora, E.S. Design approach for a biomass fed fluidized bed gasifier using the simulation software CSFB. *Biomass Bioenergy* **2004**, *26*, 281–287. [CrossRef]
19. Pellegrini, L.; Deoliveira, S. Exergy analysis of sugarcane bagasse gasification. *Energy* **2007**, *32*, 314–327. [CrossRef]
20. Gómez, E.O.; Cortez, L.A.B.; Lora, E.E.S.; Sanchez, C.G.; Bauen, A. Preliminary tests with a sugarcane bagasse fueled fluidized-bed air gasifier. *Energy Convers. Manag.* **1999**, *40*, 205–214. [CrossRef]
21. Gabra, M.; Salman, H.; Kjellström, B. Development of a sugar cane residue feeding system for a cyclone gasifier. *Biomass Bioenergy* **1998**, *15*, 143–153. [CrossRef]
22. Gabra, M.; Pettersson, E.; Backman, R.; Kjellström, B. Evaluation of cyclone gasifier performance for gasification of sugar cane residue—Part 1: Gasification of bagasse. *Biomass Bioenergy* **2001**, *21*, 351–369. [CrossRef]
23. Basu, P. (Ed.) *Torrefaction. In Biomass Gasification, Pyrolysis and Torrefaction*; Academic Press: New York, NY, USA, 2013; pp. 93–154. ISBN 9780128129920.
24. Leal-Arcas, R.; Minas, S. Renewable energy. *Res. Handb. Int. Law Nat. Resour.* **2016**, 261–280. [CrossRef]
25. Pach, M.; Zanzi, R.; Björnbo, E. Torrefied biomass a substitute for wood and charcoal. In Proceedings of the 6th Asia-Pacific International Symposium on Combustion and Energy Utilization, Kuala Lumpur, Malaysia, 20–22 May 2002; Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Ed.; Universiti Teknologi Malaysia: Skudai, Malaysia, 2002; p. 6.
26. Anukam, A.; Mamphweli, S.; Reddy, P.; Meyer, E.; Okoh, O. Pre-processing of sugarcane bagasse for gasification in a downdraft biomass gasifier system: A comprehensive review. *Renew. Sustain. Energy Rev.* **2016**, *66*, 775–801. [CrossRef]
27. Blanco Machin, E. *Análise Técnica, Econômica e Ecológica da Incorporação de Sistemas de Gaseificação de Bagaço de Cana-de-Açúcar No Setor Sucroalcooleiro: Uso de Ciclos Combinados Para o Aumento da Oferta de Eletricidade*; Universidade Estadual Paulista (UNESP): Guaratinguetá, Brazil, 2015.
28. Pedroso, D.T.; Machin, E.B.; Perez, N.P.; Braga, L.B.; Silveira, J.L. Technical assessment of the Biomass Integrated Gasification/Gas Turbine Combined Cycle (BIG/GTCC) incorporation in the sugarcane industry. *Renew. Energy* **2017**, *114*, 464–479. [CrossRef]
29. Manatura, K. Inert torrefaction of sugarcane bagasse to improve its fuel properties. *Case Stud. Therm. Eng.* **2020**, *19*, 100623. [CrossRef]
30. Granados, D.A.; Ruiz, R.; Vega, L.; Chejne, F. Study of reactivity reduction in sugarcane bagasse as consequence of a torrefaction process. *Energy* **2017**, *139*, 818–827. [CrossRef]
31. Shehzad, M.; Asghar, A.; Ramzan, N.; Aslam, U.; Bello, M.M. Impacts of non-oxidative torrefaction conditions on the fuel properties of indigenous biomass (bagasse). *Waste Manag. Res.* **2020**, *38*, 1284–1294. [CrossRef]

32. Bourgois, J.; Guyonnet, R. Characterization and analysis of torrefied wood. *Wood Sci. Technol.* **1988**, *22*, 143–155. [[CrossRef](#)]
33. Prins, M.J.; Ptasinski, K.J.; Janssen, F.J.J.G. More efficient biomass gasification via torrefaction. *Energy* **2006**, *31*, 3458–3470. [[CrossRef](#)]
34. Stefanidis, S.D.; Kalogiannis, K.G.; Iliopoulou, E.F.; Michailof, C.M.; Pilavachi, P.A.; Lappas, A.A. A study of lignocellulosic biomass pyrolysis via the pyrolysis of cellulose, hemicellulose and lignin. *J. Anal. Appl. Pyrolysis* **2014**, *105*, 143–150. [[CrossRef](#)]
35. Zanatta, E.R.; Reinehr, T.O.; Awadallak, J.A.; Kleinübing, S.J.; Santos, J.; Bariccatti, R.A.; Arroyo, P.; Da Silva, E.A. Kinetic studies of thermal decomposition of sugarcane bagasse and cassava bagasse. *J. Therm. Anal. Calorim.* **2016**, *125*, 437–445. [[CrossRef](#)]
36. Mohomane, S.M.; Motaung, T.E.; Revaprasadu, N. Thermal Degradation Kinetics of Sugarcane Bagasse and Soft Wood Cellulose. *Materials* **2017**, *10*, 1246. [[CrossRef](#)] [[PubMed](#)]
37. Basu, P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*, 2nd ed.; Elsevier: New York, NY, USA, 2013; ISBN 9780123964885.
38. Wang, L.; Barta-Rajnai, E.; Skreiberg, Ø.; Khalil, R.; Czégény, Z.; Jakab, E.; Barta, Z.; Grønli, M. Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark. *Appl. Energy* **2018**, *227*, 137–148. [[CrossRef](#)]
39. Bergman, P.C.A.; Kiel, J.H.A. Torrefaction for biomass upgrading. In Proceedings of the 14th European Biomass Conference, Paris, France, 17–21 October 2005; pp. 17–21.
40. Basu, P. Introduction. In *Biomass Gasification, Pyrolysis and Torrefaction*; Academic Press: New York, NY, USA, 2013; pp. 1–27.
41. Prins, M.J.; Ptasinski, K.J.; Janssen, F.J.J.G. Torrefaction of wood. Part 1. Weight loss kinetics. *J. Anal. Appl. Pyrolysis* **2006**, *77*, 28–34. [[CrossRef](#)]
42. 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. [[CrossRef](#)]
43. Channiwalla, S.; Parikh, P. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel* **2002**, *81*, 1051–1063. [[CrossRef](#)]
44. Chen, W.-H.; Du, S.-W.; Tsai, C.-H.; Wang, Z.-Y. Torrefied biomasses in a drop tube furnace to evaluate their utility in blast furnaces. *Bioresour. Technol.* **2012**, *111*, 433–438. [[CrossRef](#)]
45. Itoh, T.; Fujiwara, N.; Iwabuchi, K.; Narita, T.; Mendbayar, D.; Kamide, M.; Niwa, S.; Matsumi, Y. Effects of pyrolysis temperature and feedstock type on particulate matter emission characteristics during biochar combustion. *Fuel Process. Technol.* **2020**, *204*, 106408. [[CrossRef](#)]
46. Wang, S.; Guo, X.; Wang, K.; Luo, Z. Influence of the interaction of components on the pyrolysis behavior of biomass. *J. Anal. Appl. Pyrolysis* **2011**, *91*, 183–189. [[CrossRef](#)]
47. Munir, S.; Daood, S.S.; Nimmo, W.; Cunliffe, A.; Gibbs, B. Thermal analysis and devolatilization kinetics of cotton stalk, sugar cane bagasse and shea meal under nitrogen and air atmospheres. *Bioresour. Technol.* **2009**, *100*, 1413–1418. [[CrossRef](#)]
48. Santos, K.G.; Lira, T.; Giancesella, M.; Lobato, F.S.; Murata, V.V.; Barrozo, M. Bagasse pyrolysis: A comparative study of kinetic models. *Chem. Eng. Commun.* **2012**, *199*, 109–121. [[CrossRef](#)]
49. Cheng, K.; Winter, W.T.; Stipanovic, A.J. A modulated-TGA approach to the kinetics of lignocellulosic biomass pyrolysis/combustion. *Polym. Degrad. Stab.* **2012**, *97*, 1606–1615. [[CrossRef](#)]
50. Zhao, S.; Liu, M.; Zhao, L.; Zhu, L. Influence of Interactions among Three Biomass Components on the Pyrolysis Behavior. *Ind. Eng. Chem. Res.* **2018**, *57*, 5241–5249. [[CrossRef](#)]
51. Rein, P. *Cane Sugar Engineering*; Verlag Dr. Albert Bartens KG: Berlin, Germany, 2017; ISBN 9783870401672.
52. Camargo, C.; Hakuo Ushima, A. *Conservação de Energia na Indústria do Açúcar e do álcool: Manual de Recomendações*; Instituto de Pesquisas Tecnológicas, Ed.; Instituto de Pesquisas Tecnológicas: São Paulo, Brazil, 1990.
53. Jenkins, B.M.; Baxter, L.L.; Miles, T.R. Combustion properties of biomass. *Fuel Process. Technol.* **1998**, *54*, 17–46. [[CrossRef](#)]
54. García-Pérez, M.; Chaala, A.; Yang, J.; Roy, C. Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: Thermogravimetric analysis. *Fuel* **2001**, *80*, 1245–1258. [[CrossRef](#)]
55. Miles, T.R.; Baxter, L.L.; Bryers, R.W.; Jenkins, B.M.; Oden, L.L. Boilers. Fuels and deposit formation. In *Alkali Deposits Found in Biomass Power Plants*; National Techrucd Motation Service (NTIS): Golden, CO, USA, 1995; Volume I, pp. 1–122. ISBN 9788578110796.
56. Agblevor, F.A.; Besler-Guran, S.; Montane, D.; Wiseloge, A.E. Biomass Feedstock Variability and Its Effect on Biocrude Oil Properties. In *Developments in Thermochemical Biomass Conversion*; Springer: Dordrecht, The Netherlands, 1997; pp. 741–755.
57. Natarajan, E.; Öhman, M.; Gabra, M.; Nordin, A.; Liliedahl, T.; Rao, A. Experimental determination of bed agglomeration tendencies of some common agricultural residues in fluidized bed combustion and gasification. *Biomass Bioenergy* **1998**, *15*, 163–169. [[CrossRef](#)]
58. Felfli, F.F.; Luengo, C.A.; Bezzon, G.; Soler, P.B. Bench unit for biomass residues torrefaction. In Proceedings of the 10th European Conference Biomass for Energy & Industry, Würzburg, Germany, 8–11 June 1998; EU: Würzburg, Germany, 1998; p. 12.
59. Basu, P. Chapter 2. Biomass Characteristics. In *Biomass Gasification and Pyrolysis: Practical Design and Theory*; Academic Press: New York, NY, USA, 2010; ISBN 9780123749888.
60. Basu, P. Gasification Theory. In *Biomass Gasification, Pyrolysis and Torrefaction*; Academic Press: New York, NY, USA, 2013; pp. 199–248.
61. Anukam, A.; Mamphweli, S.; Reddy, P.; Okoh, O.; Meyer, E. An Investigation into the Impact of Reaction Temperature on Various Parameters during Torrefaction of Sugarcane Bagasse Relevant to Gasification. *J. Chem.* **2015**, *2015*, 235163. [[CrossRef](#)] [[PubMed](#)]

62. Daniyanto, S.; Deendarlianto, B.A. Torrefaction of Indonesian Sugar-cane Bagasse to Improve Bio-syngas Quality for Gasification Process. *Energy Procedia* **2015**, *68*, 157–166. [[CrossRef](#)]
63. Pimchuai, A.; Dutta, A.; Basu, P. Torrefaction of Agriculture Residue to Enhance Combustible Properties. *Energy Fuels* **2010**, *24*, 4638–4645. [[CrossRef](#)]
64. Zaharioiu, A.; Bucura, F.; Ionete, E.I.; Ionete, R.E.; Ebrasu, D.; Sandru, C.; Marin, F.; Oancea, S.; Niculescu, V.; Miricioiu, M.G.; et al. Thermochemical Decomposition of Sewage Sludge—An Eco-Friendly Solution for a Sustainable Energy Future by Using Wastes. *Rev. Chim.* **2020**, *71*, 171–181. [[CrossRef](#)]
65. Vassilev, S.V.; Baxter, D.; Andersen, L.K.; Vassileva, C.G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89*, 913–933. [[CrossRef](#)]