

## Article

# Production of Torrefied Solid Bio-Fuel from Pulp Industry Waste

Michael Huang <sup>1</sup> , Chia-Chi Chang <sup>1</sup>, Min-Hao Yuan <sup>2</sup>, Ching-Yuan Chang <sup>1,3,\*</sup>, Chao-Hsiung Wu <sup>4</sup>, Je-Lueng Shie <sup>5</sup>, Yen-Hau Chen <sup>1</sup>, Yi-Hung Chen <sup>6</sup>, Chungfang Ho <sup>7</sup>, Wei-Ren Chang <sup>1</sup>, Tzu-Yi Yang <sup>1</sup> and Far-Ching Lin <sup>8</sup>

<sup>1</sup> Graduate Institute of Environmental Engineering, National Taiwan University, Taipei 106, Taiwan; r01541105@ntu.edu.tw (M.H.); d92541005@ntu.edu.tw (C.-C.C.); p29681726@gmail.com (Y.-H.C.); a10022587@gmail.com (W.-R.C.); r99541115@ntu.edu.tw (T.-Y.Y.)

<sup>2</sup> Department of Occupational Safety and Health, China Medical University, Taichung 404, Taiwan; mhyuan@mail.cmu.edu.tw

<sup>3</sup> Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

<sup>4</sup> Department of Environmental Engineering, Da-Yeh University, Changhua 515, Taiwan; chwu@mail.dyu.edu.tw

<sup>5</sup> Department of Environmental Engineering, National I-Lan University, I-Lan 260, Taiwan; jlshie@niu.edu.tw

<sup>6</sup> Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan; yhchen1@ntut.edu.tw

<sup>7</sup> Department of International Business, Chung Yuan Christian University, Chung-Li 320, Taiwan; chunfang@cycu.edu.tw

<sup>8</sup> Department of Forestry and Resource Conservation, National Taiwan University, Taipei 106, Taiwan; farching@ntu.edu.tw

\* Correspondence: cychang3@ntu.edu.tw; Tel.: +886-2-23638994

Academic Editor: Thomas E. Amidon

Received: 6 January 2017; Accepted: 26 June 2017; Published: 3 July 2017

**Abstract:** The pulp industry in Taiwan discharges tons of wood waste and pulp sludge (i.e., wastewater-derived secondary sludge) per year. The mixture of these two bio-wastes, denoted as wood waste with pulp sludge (WPS), has been commonly converted to organic fertilizers for agriculture application or to soil conditioners. However, due to energy demand, the WPS can be utilized in a beneficial way to mitigate an energy shortage. This study elucidated the performance of applying torrefaction, a bio-waste to energy method, to transform the WPS into solid bio-fuel. Two batches of the tested WPS (i.e., WPS1 and WPS2) were generated from a virgin pulp factory in eastern Taiwan. The WPS1 and WPS2 samples contained a large amount of organics and had high heating values (HHV) on a dry-basis ( $H_{HD}$ ) of 18.30 and 15.72 MJ/kg, respectively, exhibiting a potential for their use as a solid bio-fuel. However, the wet WPS as received bears high water and volatile matter content and required de-watering, drying, and upgrading. After a 20 min torrefaction time ( $t_T$ ), the  $H_{HD}$  of torrefied WPS1 (WPST1) can be enhanced to 27.49 MJ/kg at a torrefaction temperature ( $T_T$ ) of 573 K, while that of torrefied WPS2 (WPST2) increased to 19.74 MJ/kg at a  $T_T$  of 593 K. The corresponding values of the energy densification ratio of torrefied solid bio-fuels of WPST1 and WPST2 can respectively rise to 1.50 and 1.25 times that of the raw bio-waste. The  $H_{HD}$  of WPST1 of 27.49 MJ/kg is within the range of 24–35 MJ/kg for bituminous coal. In addition, the wet-basis HHV of WPST1 with an equilibrium moisture content of 5.91 wt % is 25.87 MJ/kg, which satisfies the Quality D coal specification of the Taiwan Power Co., requiring a value of above 20.92 MJ/kg.

**Keywords:** torrefaction; bio-waste; biomass; torrefied bio-waste; solid bio-fuel; pulp industry waste

## 1. Introduction

There has been an increasing demand for fossil fuels over the past decades. With the consummation of fossil fuels, an increase in the emissions of greenhouse gases such as carbon dioxide has been confirmed to result in a severe global warming effect [1]. Globally averaged CO<sub>2</sub> levels have risen since the pre-industrial period from approximately 280 ppm in the 18th century to over 400 ppm in 2015 [2]. Therefore, the task concerning how to reduce fossil fuel usage and mitigate the greenhouse effect has been of vital importance towards creating a sustainable society [3,4].

One of the foremost solutions for a substitute energy source for fossil fuels is to accelerate the deployment of renewable energy sources, which includes solar energy, biomass energy, hydroelectricity, wind energy, wave energy, tidal energy, geothermal energy, and waste-derived energy [5]. Among these types of renewable energy, biomass energy from vegetable-derived feedstock has a property known as carbon neutrality and may not contribute to an increase in CO<sub>2</sub> in the atmosphere from a life cycle viewpoint [6]. In other words, vegetable-derived bio-energy feedstock can effectively use carbon derived from carbon dioxide in the atmosphere by way of photosynthesis during the growth process of the plants. Hence, the effective utilization of biomass energy is a preventive and strategic measure against global warming.

There are many successful examples of using biomass to produce bio-fuels such as bio-diesel and bio-ethanol. Bio-diesel is mainly used in transportation, and it can replace traditional diesel and be applied to a car engine directly. Biomass can come from agricultural products [7,8] and bio-wastes [9–11]. The production and application of solid bio-fuel from waste biomass, also known as refuse derived fuel, has been widely promoted [12,13]. However, the sources of biomass are complex and diverse, and the characteristics vary greatly. Thus, the torrefaction process has been used to make the characteristics of biomass more uniform [13–17].

Torrefaction is a mild pyrolysis process used to improve the properties of biomass as a fuel for combustion and gasification applications. Pyrolysis is a thermal chemical decomposition process that involves heating substances in the absence of oxygen with different heating rates [16–19]. The temperature of the torrefaction process is usually from 523 to 623 K [20–22]. The time and temperature of torrefaction can determine the quality of the torrefied product [23,24]. A higher heating rate results in a greater amount of volatile material being released thereby resulting in different physical features of the char [25]. During the process, the biomass is decomposed into solid, liquid, and gas products [17,24]. The goal of torrefaction is to remove part of the organic compounds and moisture, de-polymerize the long polysaccharide chains, and produce hydrophobic solid products with high energy densities and grindabilities [26–29]. Torrefied biomass yields range from 67% to 84%, and its energy yields about 77–90% [30]. These advantages make the transportation and packing of the char easier and more affordable [26,29]. Furthermore, torrefied char can be utilized as a solid fuel for home or industrial use [31–34].

In this study, the target biomass is a mixed waste consisting of wood waste and pulp sludge (i.e., wastewater-derived secondary sludge), denoted as wood waste with pulp sludge (WPS), from a pulp factory. The raw material used by the factory is mostly pure wood. There should therefore be a large portion of combustibles in the WPS. The main purpose of this study was to apply the torrefaction process to treat the WPS, enhancing its heating value and converting it into solid bio-fuel. The experimental factors include torrefaction temperature ( $T_T$ ) and torrefaction times ( $t_T$ ) for the optimal heating value of the torrefied products.

## 2. Results and Discussion

### 2.1. Basic Properties of WPS

As received, the WPS is slurry-like containing a very large amount of water. Each sample has been prepared by open-air sun-drying over 3–4 days and then by oven treatment at 378 K over 24 h. Therefore, its water content was not measured. Instead, dry-basis contents were determined. As shown in Table 1, the values of dry-basis combustibles content ( $M_C$ ), fixed carbon ( $M_{FC}$ ), volatile matters

( $M_{VM}$ ), and ash ( $M_A$ ) (i.e.,  $M_{CD}$ ,  $M_{FCD}$ ,  $M_{VMD}$ , and  $M_{AD}$ ) are 95.19, 20.79, 74.41, and 4.81 wt % for WPS1, and 80.30, 18.75, 61.55, and 19.70 wt % for WPS2, respectively. The dried sample when exposed to air gained equilibrium moisture content ( $M_{WE}$ ). For WPS1 and WPS2, the values of  $M_{WE}$  are 12.75 and 3.77 wt %, respectively. It is noted that the initial moisture content of the WPS batches would vary depending on the source and pretreatment procedures. The results of this study showed two cases of WPS samples with high and low amounts of initial equilibrium moisture.

**Table 1.** Characteristics of WPS and torrefied WPS.

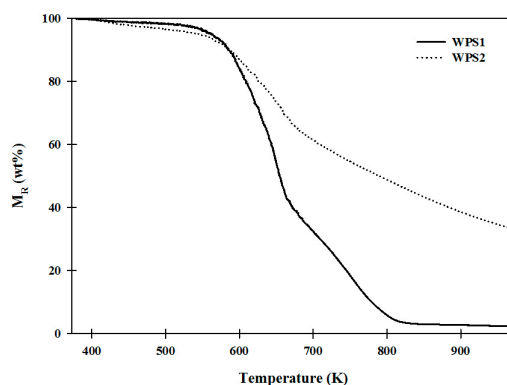
Properties or Compositions	WPS1	WPST1-300-20	WPS2	WPST2-320-20	Rice Straw [35]	Torrefied Rice Straw-280-50 [35]
<b>Heating Value (MJ/kg) <sup>a</sup></b>						
$H_{HD}$	18.30 ± 0.07	27.49	15.72 ± 0.01	19.74	16.64	21.63
<b>Proximate Analyses (wt %) <sup>a</sup></b>						
Combustibles, $M_{CD}$	95.19 ± 0.05	91.41 <sup>d</sup>	80.30 ± 3.09	74.61 ± 2.56	88.7	78.8
Fixed carbons, $M_{FCD}$	20.79 ± 0.09	42.74	18.75 ± 2.16	20.86 ± 2.46	16.7	45.5
Volatile matter, $M_{VMD}$	74.41 ± 0.12	48.67	61.55 ± 1.27	53.75 ± 0.10	72.0	33.4
Ash, $M_{AD}$	4.81 ± 0.09	8.59 <sup>e</sup>	19.70 ± 3.04	25.39 ± 2.56	11.3	21.2
<b>Equilibrium Moisture (wt %) <sup>b</sup></b>						
$M_{WE}$	12.75 ± 0.13	5.91 ± 0.01	3.77 ± 0.49	2.15 ± 0.01	9.6	2.8
<b>Ultimate Analyses (wt %) <sup>c</sup></b>						
C	49.07 ± 0.05	54.35 ± 0.87	44.53 ± 0.33	50.46 ± 1.27	38.96	50.89
H	6.10 ± 0.00	5.32 ± 0.14	5.82 ± 0.09	5.12 ± 0.24	6.05	4.40
O	43.56 ± 3.29	39.00 ± 0.33	45.23 ± 0.05	40.28 ± 0.32	43.33	23.74
N	1.06 ± 0.06	1.16 ± 0.05	2.44 ± 0.021	2.74 ± 0.035	0.55	0.89
S	0.18 ± 0.01	0.17 ± 0.09	1.84 ± 0.75	1.30 ± 0.40	0.79	0.15
Cl	0.02 ± 1.12	0.00 ± 4.06	0.14 ± 2.66	0.11 ± 1.12	0.12	0.31
Atomic H/C	1.49	1.18	1.57	1.22	1.86	1.04
Atomic O/C	0.67	0.54	0.76	0.60	0.83	0.35

<sup>a</sup> Dry basis. <sup>b</sup> Equilibrium moisture content of sample. <sup>c</sup> Dry ash free. <sup>d</sup> Calculated by balance of  $M_{AD}$ . <sup>e</sup> Computed from mass yield ( $Y_M$ ) = 0.56 by assuming all ash in WPS1 were retained in WPST1. ND: Not detected. WPST1-T-t or WPST2-T-t (e.g., WPST1-300-20): T-t denotes torrefaction temperature (°C) and time (min), respectively.

The dry-basis high heating value ( $HHV_D$  or  $H_{HD}$ ), wet-basis HHV of a sample with equilibrium moisture ( $HHV_{WE}$ ), and wet-basis low heating value of a sample with equilibrium moisture ( $LHV_{WE}$ ) are 18.30, 15.97, and 14.60 wt % for WPS1, and 15.72, 15.13, and 14.19 wt % for WPS2, respectively. These results indicate that WPS1 possesses a higher amount of combustibles and a higher heating value while possessing lower ash content than WPS2. Thus, the quality of WPS1 is better than WPS2 and would yield a better torrefied biomass. The dry-basis metal compositions of Na, Ca, and Mg of WPS1 are 0.059, 0.761, and 0.089 wt %, respectively, which are much lower than those of WPS2, which are 0.168, 5.27, and 0.842 wt %, respectively. The high contents of Na, Ca, and Mg of WPS2 are attributed to its high ash content which was discharged from the process using alkaline oxides and would hinder the pyrolysis and torrefaction.

## 2.2. TGA Characteristics of Pyrolysis and Torrefaction

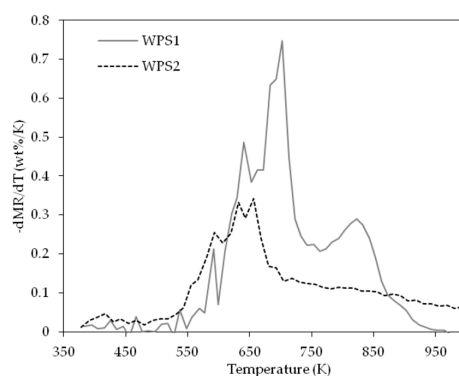
Figure 1 depicts the diagrams of thermal gravimetric analysis (TGA) for WPS1 and WPS2. It presents the variation of the residual mass fraction of the WPS ( $M_R$ , wt %) with temperature (T) during the pyrolysis process. The T started from 378 K (105 °C) because the  $M_R$  was calculated by the initial WPS on a dry-basis. Before the pyrolysis process, the WPS was maintained at 378 K in order to remove the moisture. According to the study by Bergman et al. [20], the pyrolysis process can be divided into three regions. Under 473 K, it involves de-polymerization, re-condensation, and softening. Before 523 K, the process consists of limited de-volatilization and carbonization. After 523 K, the biomass begins to proceed with extensive de-volatilization and carbonization.



**Figure 1.** TGA curves of residual mass fraction ( $M_R$ ) vs. temperature ( $T$ ) for WPS with conditions: pre-heating at 378 K for 20 min, heating rate of 10 K/min, sample weight of 20 mg.

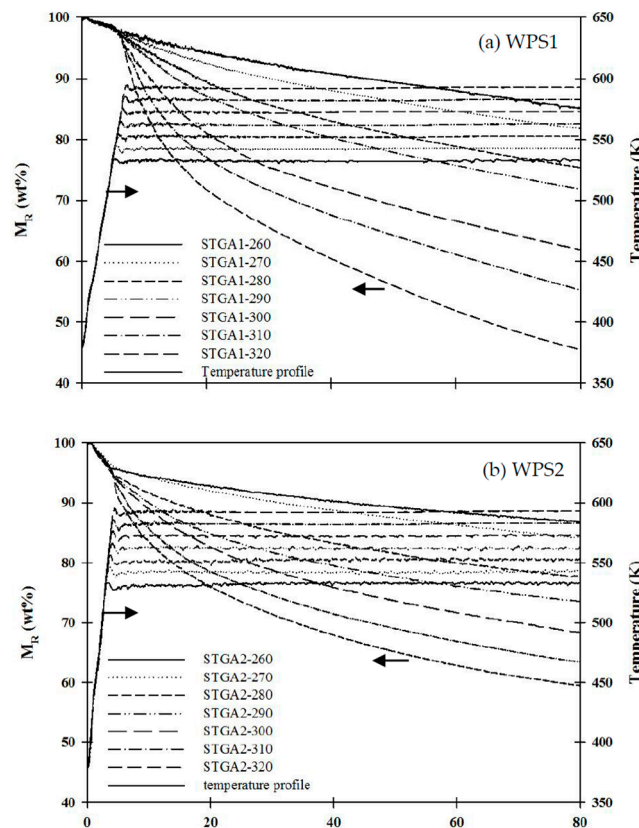
The results of Figure 1 show that the WPS exhibits no extensive decomposition at a temperature below 523 K. It starts to decompose significantly (e.g., mass loss of 5 wt %) at around 553 K and 573 K, respectively, for WPS2 and WPS1, which implies that the torrefaction process has begun. The WPS1 decomposed easier than WPS2 at 773 K by mass amounts of about 87 and 50 wt %, respectively. This is consistent with the assertion that WPS1 has a higher content of volatile matter. A significant residual mass is left in the case of WPS2, due to its high ash content.

The DTG (differential thermogravimetric) curves reveal a rough composition ratio of the constituents in WPS1 and WPS2, which allows for the estimation of the mild temperature for torrefaction [20]. The value of  $-dM_R/dT$  is related to the time variation of  $M_R$ , i.e., the reaction rate  $-dM_R/dt$  is related by  $-dM_R/dt = (-dM_R/dT) \text{ HR}$ , where HR represents the heating rate (10 K/min). A higher peak indicates a higher reaction rate. As reported by previous studies [36], hemi-cellulose has a sharp pyrolysis rate around 550–585 K. As soon as 628 K is reached, the intense decomposition of cellulose can be observed. However, the decomposition of lignin is difficult to identify in the DTG curve because the temperature at which this occurs overlaps with that of cellulose [36]. As shown in Figure 2, the DTG curves indicated that both WPS1 and WPS2 possess low hemi-cellulose composition, and they are both predominantly composed of cellulose and lignin. This is because the WPS is a mixed waste of waste wood and pulp sludge with no significant hemi-cellulose content. Figure 2 reveals that WPS1 and WPS2 exhibit four and three significant peaks, respectively, and that their first peaks appear at about 593 K at about 10 wt % of the WPS having been decomposed. Notice that the highest peak of WPS1 at around 683 K is twice as high as that of WPS2 at about 633–653 K. This again indicates that the properties of WPS1 make it easier and faster to decompose than WPS2. Furthermore, the significant peak at 820 K for WPS1 is similar to the DTG pattern of secondary pulp mill sludge obtained from the aerobic biological treatment [37].



**Figure 2.** DTG curve of  $-dM_R/dT$  vs.  $T$  for WPS1 and WPS2 in  $N_2$ : Pre-heating at 378 K for 20 min, heating rate of 10 K/min, sample weight of 20 mg.

Simulated torrefactions by TGA were performed at  $T_T$  in the range of 533 to 593 K with 10 K intervals. Figure 3 shows the influences of  $t_T$  on  $M_R$  at various  $T_T$  values for WPS1 and WPS2. For both WPS1 and WPS2, a higher  $T_T$  as well as a longer  $t_T$  induces higher mass reduction. Most of the biomass torrefaction tests have been set to retain a torrefied biomass of about 70 wt % while allowing for the decomposition of the hemi-cellulose and cellulose constituents. For WPS1, the  $M_R$  was about 72 wt % after 40 min of torrefaction at 573 K. However, the  $M_R$  decreased to about 68 and 61 wt % at 583 and 593 K, respectively. This suggests that the  $T_T$  for WPS1 may be properly operated at 573–583 K or lower. For WPS2, the mass reduced slightly after 60 min of torrefaction for the cases with  $T_T$  lower than 553 K (e.g., 533 and 543 K). At 40 min, the values of  $M_R$  were 75, 71, and 68 wt % at 573, 583, and 593 K, respectively, suggesting the appropriate  $T_T$  value of 583–593 K for WPS2.



**Figure 3.** Simulated torrefaction of (a) WPS1 and (b) WPS2 via TGA at different setting temperatures. STGA1-260 and STGA2-260: torrefaction of WPS1 and WPS2 via TGA at 260 °C, respectively.  $t_T$ : torrefaction time.

### 2.3. Energy Densification

Key parameters reflecting the performances of the torrefaction system assessed are the mass yield ( $Y_M$ ), energy yield ( $Y_E$ ), and energy densification ratio ( $E_D$ ).  $Y_M$  is the ratio of the mass of the product to the feed, as calculated by Equation (1).  $Y_E$  is the ratio of the energy output of the product to the input of the feed, as computed by Equation (2), or the multiplication of  $Y_M$  and the ratio of  $H_{HDT}$  of the product to the feed ( $H_{HDTD}/H_{HTRD}$ ).  $E_D$  can be calculated from  $Y_E/Y_M$  or  $H_{HDTD}/H_{HTRD}$  by Equation (3). A higher energy densification ratio implies a higher enhancement of the heating value of the torrefied product:

$$Y_M = m_{TD}/m_{RD}, \quad (1)$$

$$Y_E = m_{TD}H_{HDTD}/m_{RD}H_{HTRD} = Y_M(H_{HDTD}/H_{HTRD}), \quad (2)$$

$$E_D = Y_E/Y_M = H_{HDTD}/H_{HDDR}, \quad (3)$$

where

$H_{HD}$  = dry-basis high heating value,

$H_{HDDR}$ ,  $H_{HDTD}$  =  $H_{HD}$  of dried raw and torrefied samples,

$m_{RD}$ ,  $m_{TD}$  = mass of dried raw and torrefied samples.

Referring to the TGA results of Section 2.2, the lab-scale torrefactions using a tubular furnace were conducted at  $T_T = 533$ , 553, and 573 K for WPS1 and 553, 573, and 593 K for WPS2, both with  $t_T = 20$ , 40, and 60 min. The heating values for the torrefied WPS are shown in Table 2. For WPST1, the  $H_{HD}$  generally increases with an increasing  $t_T$  at a moderate  $T_T$  of 533 and 553 K. However, at high a  $T_T$  of 573 K, the torrefaction is vigorous, resulting in a reduction of  $H_{HD}$  as  $t_T$  increases. For WPST2, similar enhancing trends at 553 and 573 K were observed, while a tendency to decrease at 593 K with time resulted. The  $T_T$  as  $H_{HD}$  decreased with the  $t_T$  at 573 K for WPST1 was lower than that at 593 K for WPST2, because WPS1 contains more combustibles making it easier to decompose. In general, a higher  $T_T$  produced a higher  $H_{HD}$ , except at  $T_T = 573$  K with a  $t_T$  value of 60 min for WPST1. The  $H_{HD}$  was raised from 18.30 MJ/kg for WPS1 to its highest value of 27.49 MJ/kg for the WPST1, which occurred at 573 K with a  $t_T$  value of 20 min (WPST1-300-20). That of WPS2 was raised from 15.72 MJ/kg to 19.74 MJ/kg for the WPST2, which occurred at 593 K with a  $t_T$  value of 20 min (WPST2-320-20). Again, the values of  $H_{HD}$  for WPS1 were higher than those of WPS2, as expected. The  $H_{HD}$  values of WPST1-280-60, WPST1-300-20, WPST1-300-40, and WPST1-300-60 were 25.19, 27.49 (highest), 24.98, and 24.58 MJ/kg, respectively, and are all within the  $H_{HD}$  range of bituminous coal which is 24–35 MJ/kg [38]. Table 2 also presents the  $HHV_{WE}$  values of WPS1, WPS2, torrefied WPS1 (WPST1) and WPS2 (WPST2), and the  $LHV_{WE}$  values of WPS1, WPS2, WPST1-300-20, and WPST2-320-20. The wet-basis  $HHV_{WE}$  of the above mentioned cases of WPST1-280-60, WPST1-300-20, WPST1-300-40, and WPST1-300-60 were 23.75, 25.87 (highest), 23.51, and 23.13 MJ/kg, respectively, which also satisfy the Quality D coal specification of the Taiwan Power Co. (TPC) (City, Country), which is 20.92 MJ/kg minimum [39].

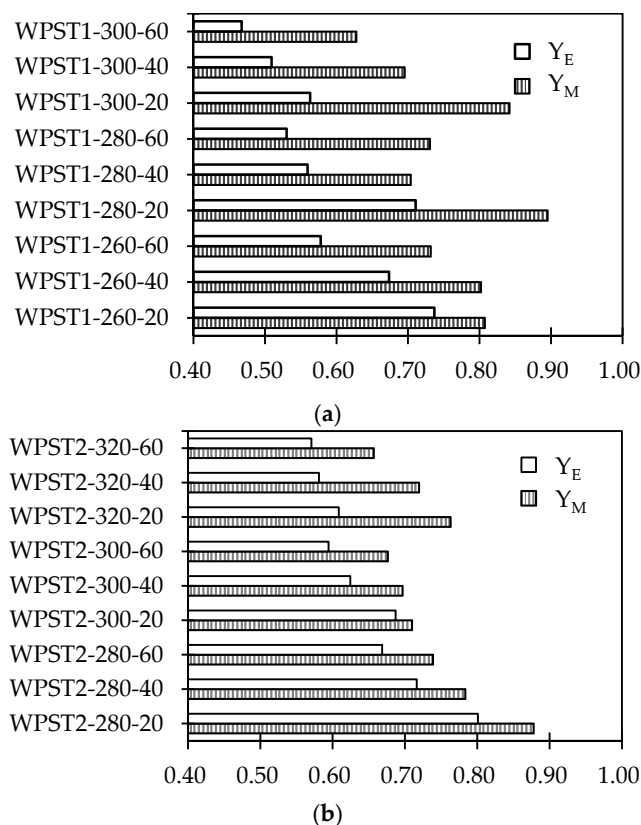
**Table 2.** Heating values of WPS and torrefied WPS of WPST at different torrefaction conditions.

Sample	$H_{HD}$ (MJ/kg)	$HHV_{WE}$ (MJ/kg)	$LHV_{WE}$ (MJ/kg)
WPS1	18.30 ± 0.07	15.97	14.60
WPST1-260-20	19.99	18.81	-
WPST1-260-40	21.79	20.50	-
WPST1-260-60	23.20	21.83	-
WPST1-280-20	23.05	21.69	-
WPST1-280-40	22.96 ± 0.07	21.67	-
WPST1-280-60	25.19	23.75	-
WPST1-300-20 (optimal)	27.49	25.87	-
WPST1-300-40	24.98	23.51	-
WPST1-300-60	24.58	23.13	-
WPS2	15.72 ± 0.01	15.13	14.19
WPST2-280-20	17.03 ± 0.03	16.87	-
WPST2-280-40	17.30 ± 0.12	16.82	-
WPST2-280-60	17.48 ± 0.10	17.00	-
WPST2-300-20	17.52	17.14	-
WPST2-300-40	17.55 ± 0.01	17/17	-
WPST2-300-60	17.89	17.50	-
WPST2-320-20 (optimal)	19.74	19.31	18.57
WPST2-320-40	19.46	19.05	-
WPST2-320-60	18.10	17.71	-

WPS1, WPS2: Batches 1 and 2 of wood waste with pulp sludge (WPS). WPST: Torrefied WPS. WPST1-T-t or WPST2-T-t (e.g., WPST1-300-20): T-t denote temperature (°C) and time (min), respectively.  $H_{HD}$ : High heating value (HHV) in dry basis.  $HHV_{WE}$ : Wet-basis HHV of sample with equilibrium moisture.  $LHV_{WE}$ : Wet-basis low heating value of sample with equilibrium moisture.



Figure 4 presents the  $Y_M$  and  $Y_E$  values for WPST1 and WPST2 at various conditions. The values of  $Y_E$  are higher than those of  $Y_M$ , indicating that more energy was retained than mass for the torrefied product. In general, both  $Y_M$  and  $Y_E$  decrease with increasing  $t_T$  and  $T_T$ , revealing that more energy and mass are lost as  $t_T$  and  $T_T$  increase. The corresponding values of  $E_D$  are listed in Table 3 and all listed values are higher than 1, indicating that the torrefaction is beneficial for the energy densification of the WPS. The  $E_D$  is generally enhanced with increasing  $T_T$ . At moderate  $T_T$  values, e.g., 533 and 553 K for WPST1 and 553 and 573 K for WPST2 (depending on the raw materials), a longer  $t_T$  yields a higher  $E_D$ . However, at a high  $T_T$  value such as 573 K for WPST1 and 593 K for WPST2, the extent of torrefaction is very significant resulting in a reduction of  $E_D$  with an increasing energy loss as  $t_T$  increases.



**Figure 4.** Energy yield ( $Y_E$ ) and mass yield ( $Y_M$ ) at different torrefaction conditions for (a) WPST1 and (b) WPST2.

**Table 3.** Energy densification ratios  $E_D$  of WPS at various torrefaction temperatures.

$t_T$ (min)	533 K		553 K		573 K		593 K	
	WPST1-260	WPST2-260	WPST1-280	WPST2-280	WPST1-300	WPST2-300	WPST1-320	WPST2-320
20	1.10	-	1.26	1.10	1.50	1.03	-	1.26
40	1.19	-	1.26	1.09	1.36	1.12	-	1.24
60	1.27	-	1.38	1.11	1.34	1.14	-	1.15

For the cases of WPST1-280-60, WPST1-300-20, WPST1-300-40, and WPST1-300-60, the values of  $HHV_{WE}$  qualify the Quality D coal specification (20.92 MJ/kg minimum). The obtained values of  $H_{HD}$  are also within the range of bituminous coal (24–35 MJ/kg), and these  $E_D$  values are 1.38, 1.50, 1.36, and 1.34 while those of  $Y_M$  are 0.53, 0.56, 0.51, and 0.47, respectively. Excellent energy densification was observed for these cases, however, with a low mass yield of the torrefied product. Some cases, such as WPST1-260-60, WPST1-280-20, and WPST1-280-40, possess respective  $HHV_{WE}$  of 21.83, 21.69, and 21.67 MJ/kg, satisfying the Quality D coal specification, whereas the respective  $H_{HD}$  values of 23.20, 23.05,

and 22.96 MJ/kg are slightly lower than that of bituminous coal. The respective  $E_D$  values of 1.27, 1.26, and 1.26 are satisfactory with corresponding  $Y_M$  values of 0.58, 0.71, and 0.56. Hence, WPST1-300-20 with an  $H_{HD}$ ,  $HHV_{WE}$ ,  $E_D$ , and  $Y_M$  of 24.79 MJ/kg, 25.87 MJ/kg, 1.50, and 0.56, respectively, seems to be the optimal case among all WPST1 samples. The highest  $E_D$  for WPST1 is 1.50 for the WPST1-300-20 torrefied at 573 K for 20 min; however, this sample possesses a low  $Y_M$  value of 0.56.

As for the torrefaction of WPS2, the  $E_D$  and  $Y_M$  values respectively range from 1.09–1.11 and 0.67–0.80 for WPST2-280, 1.03–1.14 and 0.59–0.69 for WPST2-300, and 1.15–1.26 and 0.57–0.61 for WPST2-320. The highest  $E_D$  value of 1.26 was observed in the case of WPST2-320-20. The corresponding  $Y_M$ ,  $H_{HD}$ , and  $HHV_{WE}$  values for this sample are 0.61, 19.74 MJ/kg, and 19.31 MJ/kg, respectively. The  $HHV_{WE}$  value is close to the Quality D coal specification of the TPC.

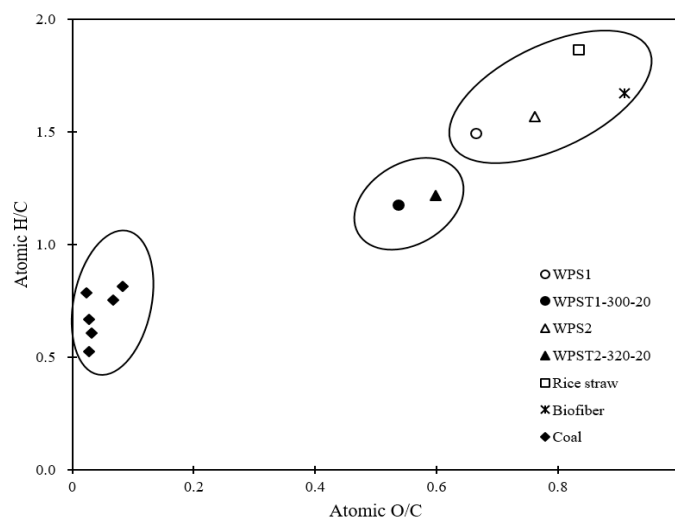
#### 2.4. Comparison of Results with Those of Others

The results of the proximate analysis, ultimate analysis, and equilibrium moisture content of WPS1, WPS2, WPST1-300-20, and WPST2-320-20 are listed in Table 1. After drying, the dried WPS1 and WPS2 possessed the equilibrium moisture contents,  $M_{WE}$ , of 12.75 and 3.77 wt %, respectively. By applying torrefaction, the  $M_{WE}$  of torrefied WPST1-300-20 and WPST2-320-20 decrease to 5.91 and 2.15 wt %, respectively. The  $M_{WE}$  of both torrefied samples are lower than those of WPS1 and WPS2, suggesting that torrefaction beneficially reduces the equilibrium moisture content.

The respective  $M_{VMD}$  values of WPS1 and WPS2, 74.41 and 61.55 wt %, were found to have decreased to those of torrefied WPST1-300-20 and WPST2-320-20, 48.67 and 53.75 wt %, respectively. On the other hand, the  $M_{FCD}$  values of WPS1 and WPS2 of 20.79 and 18.75 wt % increase to those of torrefied WPST1-300-20 and WPST2-320-20 at 42.74 and 20.86 wt %, respectively. This signifies the role of torrefaction in removing moisture and volatile matters at mild conditions while retaining most of the fixed carbon in biomass. The decrease in  $M_{CD}$  (the sum of  $M_{VMD}$  and  $M_{FCD}$ ) then results in the increase of  $M_{AD}$ .

The results of the ultimate analysis show an increase in the contents of carbon and nitrogen, while a decrease of hydrogen, oxygen, and sulfur were observed for torrefied WPST1-300-20 and WPST2-320-20. Since the WPS is hydrophilic, a decrease in the oxygen content makes the WPST comparatively more hydrophobic. From the results, it can be also inferred that the structure of the WPS is altered such that C-H, C-O, and C-S bonds are broken during torrefaction, releasing the H-, O-, and S-containing compounds. Thus, relatively larger amounts of carbon and nitrogen are retained. These findings suggest that the hygroscopic nature of the WPS can be destructed to yield hydrophobic products. Therefore, WPST would be easy to store and would not spoil easily. The characteristics of the relative contents of C, H, and O can be expressed in a Van Krevelen plot as atomic ratios of H/C vs. O/C as shown in Figure 5. A comparison with other carbon-containing materials is also plotted in Figure 5. The characteristics of H/C and O/C of coals are near the low left corner [40], while those of the raw WPS, rice straw, and bio-fiber are in the upper right region. After the torrefaction process, the said characteristics of WPST are close to those of coal. Moreover, both the WPST1-300-20 and WPST2-320-20 samples exhibit better heating values and atomic ratios of O/C and H/C when compared with torrefied rice straw at 553 K and 50 min [35], as shown in Table 1. Thus, the torrefaction of WPS is suitable for improving the combustion and co-firing quality of the torrefied products, WPST1-300-20 and WPST2-320-20, for use as solid-fuels.





**Figure 5.** Van Krevelen diagram for products of this study and some carbon-containing matters. Coal: data from Kurose et al. [40]; rice straw and bio-fiber: data from Yang [35].

### 3. Experimental Methods

The mixture of wood waste and the pulp sludge used in this study was a bio-waste obtained from a pulp factory, which is located in the eastern part of Taiwan and produces virgin pulp and fine quality papers. Two batches of WPS samples were received and tested, namely WPS1 and WPS2. Each sample has been prepared by open-air sun-drying over 3–4 days and then by oven treatment at 378 K over 24 h. It is noted that the open-air sun-drying method is usually used for the pre-treatment of waste sludge in wastewater treatment plants in Taiwan before further re-utilization. Otherwise, the dewatering of the waste sludge using other approaches (e.g., belt pressing) would still be required before disposal. Thus, the application of torrefaction to the dewatered waste sludge is feasible, in place of disposal, which is costly. In this study, the torrefaction process was applied to improve the qualities of WPS for use as a solid bio-fuel. The TGA was used to determine the optimal operation conditions of the torrefaction system in order to obtain the torrefied products fulfilling the quality specifications of coal.

#### 3.1. Property Analysis

Properties of the WPS and torrefied WPS (WPST) were determined and compared with the industrial quality specifications of coal, such as the Quality D coal specification of the TPC [39]. Triplicate experiments were performed to validate the torrefaction characteristics of the WPST samples. Heating values were measured according to the ASTM D2015 method via calorimeter (Oxygen bomb plain jacket calorimeter, model 1341, Parr Instrument, Moline, IL, USA). These included  $HHV_D$  (or  $H_{HD}$ ),  $HHV_{WE}$ , and  $LHV_{WE}$ . The proximate analyses determine the contents of the main components, such as  $M_W$ ,  $M_{VM}$ ,  $M_{FC}$ , and  $M_A$ . The sum of  $M_{VM}$  and  $M_{FC}$  is noted as  $M_C$ . A drying oven (YF-OVP60, Yi Feng, Taipei, Taiwan) and muffle furnace (DF-40, Deng Yng, Taipei, Taiwan) were used. Ultimate analysis was conducted using a Flash 2000 (Thermo Scientific, Fisher Scientific, Milan, Italy) for C, H, N, and S, Vario III-NCSH (Heraeus, Postfach, Hanau, Germany) for O, and Ion Chromatography (792 basic IC, Metrdm, Herisau, Switzerland) for Cl. Metal compositions were measured using an inductively coupled plasma-mass spectrometer (Agilent 725-ICP-OES, Agilent Technologies, Santa Clara, CA, USA).

#### 3.2. Thermal Gravimetric Analysis

A TGA analyzer (TGA-51, Shimadzu, Kyoto, Japan) was used to simulate the pyrolysis and torrefaction of the WPS. For each test, 20 g of pre-dried WPS was placed into the furnace in a container. During pyrolysis or torrefaction,  $N_2$  working gas was purged into the furnace at 50 mL/min, which was

controlled by a mass flow controller (Manufacturer, Brooks, Hatfield, PA, USA). The final temperature of the pyrolysis was set at 1073 K with an HR of 10 K/min. Various  $T_T$  values were set from 573 to 593 K (260 to 320 °C) with 10 K intervals. Detailed temperature control parameters of the TGA are listed in Table 4. All the samples were pre-heated at 378 K (105 °C) for 20 min in order to avoid the interference of moisture.

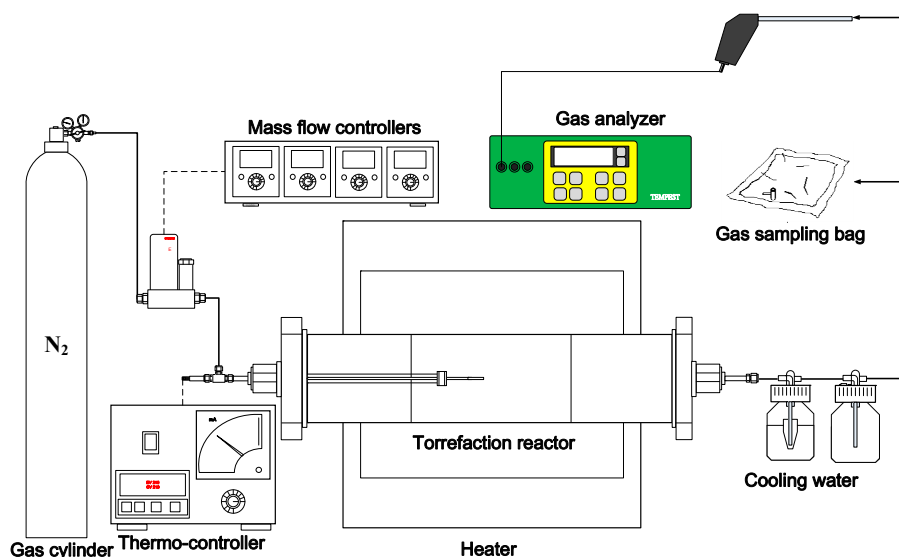
**Table 4.** Temperature control of thermal gravimetric analysis (TGA).

Process	TGA	Simulated Torrefaction
1. Drying from 303 to 378 K		
Heating rate, HR (K/min)	30	30
2. Drying at 378 K		
Constant drying time (min)	20	20
3. Pyrolysis from 378 to 1073 K		
HR (K/min)	10	NA
4. Pyrolysis from 378 K to $T_T$		
Torrefaction temperature, $T_T$ (K)	NA	533, 543, 553, 563, 573, 583, 593
HR (K/min)	NA	10
Time of torrefaction, $t_T$ (min)	NA	80

NA: Not applicable.

### 3.3. Torrefaction System

A lab-scale torrefaction system with a tube furnace (TF-35, Cheng Huei Co., New Taipei City, Taiwan) used in this study is illustrated in Figure 6. The tube is made of 314 stainless steel with an inner diameter of 6.2 cm and a length of 15 cm. For an experiment, it was firstly purged by nitrogen gas controlled via mass flow controller (Brooks Co., Charlotte, NC, USA) at 500 mL/min for 10 min before loading the sample. Then, 5 g of WPS that was loaded in a sample boat was pushed and charged into the reactor at the pre-set  $T_T$ . The flow rate of nitrogen was then reduced to 165 mL/min during the torrefaction. The  $T_T$  values were set at 533, 553, and 573 K for WPS1 and 553, 573, and 593 K for WPS2. The  $t_T$  tested for each  $T_T$  were 20, 40, and 60 min. After reaching the set  $T_T$  and  $t_T$ , a cooling fan was employed to quickly reduce the temperature of the tube. When the tube temperature was below 378 K, the torrefied samples were taken out from the tube and then kept in sealed glass jars with desiccants before further analysis. All gaseous products with boiling points above 298 K were condensed and collected by a condenser. Other non-condensable gases were then discharged.



**Figure 6.** Schematic diagram of torrefaction system.

#### 4. Conclusions

Wood waste with pulp sludge (WPS) can be used as a raw bio-mass material to produce solid bio-fuel for use in co-firing with coal and can therefore reduce coal consumption and waste discharges. The torrefaction process can be applied to effectively improve the properties of WPS such that they become close to those of coal. The energy densification ratios of the torrefied products of WPS, e.g., WPST1-300-20 (at 300 °C with 20 min) and WPST2-320-20 (at 320 °C with 20 min), were enhanced as high as 1.50 and 1.26, respectively. The corresponding dry-basis heating values increased to high values of 27.49 and 19.74 MJ/kg. The respective wet-basis high heating values are 25.87 and 19.31 MJ/kg, with WPST1-300-20 satisfying the Quality D coal specification of the Taiwan Power Co. of above 20.92 MJ/kg.

**Acknowledgments:** The authors would like to thank the Ministry of Science and Technology (formerly, National Science Council) of Taiwan for the financial support of this study (NSC 102-3113-P-002-038).

**Author Contributions:** Michael Huang, Chia-Chi Chang and Ching-Yuan Chang conceived and designed the experiments; Michael Huang, Yen-Hau Chen, Wei-Ren Chang and Tzu-Yi Yang performed the experiments; Michael Huang, Chia-Chi Chang and Ching-Yuan Chang analyzed the data; Chao-Hsiung Wu, Je-Lueng Shie, Yi-Hung Chen, Chungfang Ho and Far-Ching Lin contributed reagents/materials/analysis tools; Michael Huang, Chia-Chi Chang, and Min-Hao Yuan and Ching-Yuan Chang wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### Nomenclature

$dM_R/dT$	Differential temperature variation of $M_R$ (wt %/K or wt %/°C)
$dM_R/dt$	Instantaneous reaction rate, =HR ( $dM_R/dT$ ) (wt %/min)
$E_D$	Energy densification ratio (-)
$H_{HD}$ or $HHV_D$	Dry-basis HHV (MJ/kg or kcal/kg, 1 kcal = $4.184 \times 10^{-3}$ MJ)
$H_{HDDR}$ , $H_{HDDT}$	$H_{HD}$ of dried raw and torrefied samples (MJ/kg or kcal/kg)
HHV	High heating value (MJ/kg or kcal/kg)
$HHV_{WE}$	Wet-basis HHV of sample with equilibrium moisture (MJ/kg or kcal/kg)
HR	Heating rate (K/min or °C/min)
$LHV_{WE}$	Wet-basis low heating value of sample with equilibrium moisture (MJ/kg or kcal/kg)
$M_A$ , $M_{AD}$	Ash contents of sample by proximate analyses in wet and dry bases (wt %)
$M_C$ , $M_{CD}$	Combustibles contents of sample by proximate analyses in wet and dry bases (wt %)
$M_{FC}$ , $M_{FCD}$	Fixed carbon contents of sample by proximate analyses wet and dry bases (wt %)
$M_R$	Residual mass fraction (wt %)
$M_{VM}$ , $M_{VMD}$	Volatile matters contents of sample by proximate analysis wet and dry bases (wt %)
$M_W$	Moisture content of sample as received by proximate analysis (wt %)
$M_{WE}$	Equilibrium moisture content of sample in air by proximate analysis (wt %)
$m_{RD}$ , $m_{TD}$	m of dried raw and torrefied samples(g)
T	Temperature (K or °C)
$T_T$	Torrefaction temperature (K or °C)
t	Time (min)
$t_T$	Time of torrefaction (min)
WPS-T-t (e.g., WPST1-300-20)	T and t denote temperature (°C) and time (min), respectively
$Y_E$	Energy yield (-)
$Y_M$	Mass yield (-)

#### Abbreviations

DTG	Differential thermogravimetric
NA	Not applicable
ND	Not detected
TGA	Thermal gravimetric analysis
TPC	Taiwan Power Co.
WPS	Wood waste with pulp sludge
WPST	Torrefied WPS

## References

- Intergovernmental Panel on Climate Change (IPCC). *Fifth Assessment Report: Synthesis Report*; IPCC: Geneva, Switzerland, 2014.
- Betts, R.A.; Jones, C.D.; Knight, J.R.; Keeling, R.F.; Kennedy, J.J. El Niño and a record CO<sub>2</sub> rise. *Nat. Clim. Chang.* **2017**, *6*, 806–810. [[CrossRef](#)]
- Boyle, G. *Renewable Energy-Power for a Sustainable Future*, 2nd ed.; Oxford University Express: Glasgow, UK, 2004.
- International Energy Agency (IEA). *World Energy Outlook 2016*; IEA: Paris, France, 2016.
- Huang, Y.F.; Chiueh, P.T.; Lo, S.L. A review on microwave pyrolysis of lignocellulosic biomass. *Sustain. Environ. Res.* **2016**, *26*, 103–109. [[CrossRef](#)]
- Wang, Y.Y.; Chang, C.C.; Chang, C.Y.; Chen, Y.H.; Shie, J.L.; Yuan, M.H.; Chen, Y.H.; Huang, L.X.; Andrade-Tacca, C.; Manh, D.V.; et al. Thermal cracking of jatropha oil with hydrogen to produce bio-fuel oil. *Energies* **2016**, *9*, 910. [[CrossRef](#)]
- Chang, C.C.; Chen, C.P.; Yang, C.S.; Chen, Y.H.; Huang, M.; Chang, C.Y.; Shie, J.L.; Yuan, M.H.; Chen, Y.H.; Ho, C.F.; et al. Conversion of waste bamboo chopsticks to bio-oil via catalytic hydrothermal liquefaction using K<sub>2</sub>CO<sub>3</sub>. *Sustain. Environ. Res.* **2016**, *26*, 262–267. [[CrossRef](#)]
- Şensöz, S. Slow pyrolysis of wood barks from *Pinus brutia* Ten. and product compositions. *Bioresour. Technol.* **2003**, *89*, 307–311. [[CrossRef](#)]
- Thi, N.B.D.; Lin, C.Y.; Kumar, G. Electricity generation comparison of food waste-based bioenergy with wind and solar powers: A mini review. *Sustain. Environ. Res.* **2016**, *26*, 197–202. [[CrossRef](#)]
- Hernandez-Atonal, F.D.; Ryu, C.; Sharifi, V.N.; Swithenbank, J. Combustion of refuse-derived fuel in a fluidised bed. *Chem. Eng. Sci.* **2007**, *62*, 627–635. [[CrossRef](#)]
- Zhao, L.; Giannis, A.; Lam, W.Y.; Lin, S.X.; Yin, K.; Yuan, G.A.; Wang, J.Y. Characterization of Singapore RDF resources and analysis of their heating value. *Sustain. Environ. Res.* **2016**, *26*, 51–54. [[CrossRef](#)]
- Robinson, T.; Bronson, B.; Gogolek, P.; Mehrani, P. Sample preparation for thermo-gravimetric determination and thermo-gravimetric characterization of refuse derived fuel. *Waste Manag.* **2016**, *48*, 265–274. [[CrossRef](#)] [[PubMed](#)]
- Sadaka, S.; Negi, S. Improvements of biomass physical and thermochemical characteristics via torrefaction process. *Environ. Prog. Sustain. Energy* **2009**, *28*, 427–434. [[CrossRef](#)]
- Tumuluru, J.S.; Sokhansanj, S.; Hess, J.R.; Wright, C.T.; Boardman, R.D. A review on biomass torrefaction process and product properties for energy applications. *Ind. Biotechnol.* **2011**, *7*, 384–401. [[CrossRef](#)]
- Van der Stelt, M.; Gerhauser, H.; Kiel, J.; Ptasinski, K. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass Bioenergy* **2011**, *35*, 3748–3762. [[CrossRef](#)]
- Azhakesan, M.; Bartle, K.D.; Murdoch, P.L.; Taylor, J.M.; Williams, A. Rapid pyrolysis as a method of characterizing coals for combustion. *Fuel* **1990**, *70*, 322–328. [[CrossRef](#)]
- Balat, M.; Balat, M.; Kırtay, E.; Balat, H. Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Convers. Manag.* **2009**, *50*, 3147–3157. [[CrossRef](#)]
- Sáiz-Jiménez, C.; De Leeuw, J. Lignin pyrolysis products: Their structures and their significance as biomarkers. *Org. Geochem.* **1986**, *10*, 869–876. [[CrossRef](#)]
- Wanzl, W. Chemical reactions in thermal decomposition of coal. *Fuel Process. Technol.* **1988**, *20*, 317–336. [[CrossRef](#)]
- Bergman, P.C.A.; Boersma, A.R.; Zwart, R.W.R.; Kiel, J.H.A. *Torrefaction for Biomass Co-Firing in Existing Coal-Fired Power Stations*; ECN-C-05-013, BIOCOAL; Energy Research Centre of The Netherlands: Utrecht, The Netherlands, 2005.
- Chen, W.H.; Wu, J.S. An evaluation on rice husks and pulverized coal blends using a drop tube furnace and a thermogravimetric analyzer for application to a blast furnace. *Energy* **2009**, *34*, 1458–1466. [[CrossRef](#)]
- Deng, J.; Wang, G.J.; Kuang, J.H.; Zhang, Y.L.; Luo, Y.H. Pretreatment of agricultural residues for co-gasification via torrefaction. *J. Anal. Appl. Pyrolysis* **2009**, *86*, 331–337. [[CrossRef](#)]
- Mohan, D.; Pittman, C.U.; Steele, P.H. Pyrolysis of wood/biomass for bio-oil: A critical review. *Energy Fuel* **2006**, *20*, 848–889. [[CrossRef](#)]
- Bourgois, J.; Guyonnet, R. Characterization and analysis of torrefied wood. *Wood Sci. Technol.* **1988**, *22*, 143–155. [[CrossRef](#)]

25. Antal, M.J.; Grønli, M. The art, science, and technology of charcoal production. *Ind. Eng. Chem. Res.* **2003**, *42*, 1619–1640. [[CrossRef](#)]
26. Arias, B.; Pevida, C.; Feroso, J.; Plaza, M.G.; Rubiera, F.; Pis, J.J. Influence of torrefaction on the grindability and reactivity of woody biomass. *Fuel Process. Technol.* **2008**, *89*, 169–175. [[CrossRef](#)]
27. Chen, W.H.; Hsu, H.C.; Lu, K.M.; Lee, W.J.; Lin, T.C. Thermal pretreatment of wood (Lauan) block by torrefaction and its influence on the properties of the biomass. *Energy* **2011**, *36*, 3012–3021. [[CrossRef](#)]
28. Bridgeman, T.; Jones, J.; Williams, A.; Waldron, D. An investigation of the grindability of two torrefied energy crops. *Fuel* **2010**, *89*, 3911–3918. [[CrossRef](#)]
29. Phanphanich, M.; Mani, S. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. *Bioresour. Technol.* **2011**, *102*, 1246–1253. [[CrossRef](#)] [[PubMed](#)]
30. Williams, A.; Pourkashanian, M.; Jones, J.M. Combustion of pulverised coal and biomass. *Prog. Energy Combust. Sci.* **2001**, *27*, 587–610. [[CrossRef](#)]
31. Baxter, L. Biomass-coal co-combustion: Opportunity for affordable renewable energy. *Fuel* **2005**, *84*, 1295–1302. [[CrossRef](#)]
32. Pentananunt, R.; Rahman, A.N.M.M.; Bhattacharya, S.C. Upgrading of biomass by means of torrefaction. *Energy* **1990**, *15*, 1175–1179. [[CrossRef](#)]
33. Pimchui, A.; Dutta, A.; Basu, P. Torrefaction of agriculture residue to enhance combustible properties. *Energy Fuel* **2010**, *24*, 4638–4645. [[CrossRef](#)]
34. Sondreal, E.A.; Benson, S.A.; Hurley, J.P.; Mann, M.D.; Pavlish, J.H.; Swanson, M.L.; Weber, G.F.; Zygarlicke, C.J. Review of advances in combustion technology and biomass cofiring. *Fuel Process. Technol.* **2001**, *71*, 7–38. [[CrossRef](#)]
35. Yang, T.Y. Torrefaction of Rice Straw and Biofiber. Master's Thesis, Graduate Institute of Environment Engineering, National Taiwan University, Taipei, Taiwan, 2012. (In Chinese)
36. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788. [[CrossRef](#)]
37. Coimbra, R.N.; Paniagua, S.; Escapa, C.; Calvo, L.F.; Otero, M. Combustion of primary and secondary pulp mill sludge and their respective blends with coal: A thermogravimetric assessment. *Renew. Energy* **2015**, *83*, 1050–1058. [[CrossRef](#)]
38. McKendry, P. Energy production from biomass (Part 1): Overview of biomass. *Bioresour. Technol.* **2002**, *81*, 37–46. [[CrossRef](#)]
39. Taiwan Power Co. (TPC). *Coal Standard of Taiwan Power Co.*; TPC: Taipei, Taiwan, 2010. (In Chinese)
40. Kurose, R.; Ikeda, M.; Makino, H.; Kimoto, M.; Miyazaki, T. Pulverized coal combustion characteristics of high-fuel-ratio coals. *Fuel* **2004**, *83*, 1777–1785. [[CrossRef](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).