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The By-products and Emissions from Manufacturing Torrefied Solid Fuel Using Waste Bamboo Chopsticks

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Abstract: Although the main purpose of the torrefaction of biomass is to produce high quality solid bio-fuel, the by-products, including liquid and gas products, are worth investigating to know their effects on the environment and the reusable possibility. Consequently, after torrefying waste bamboo chopsticks (WBCs) for producing solid bio-fuel, the liquid and gas products were examined in this study. The torrefaction target was set to produce torrefied waste bamboo chopsticks (WBC_T) retaining about 70 wt %. A proper torrefaction temperature (T_r) and torrefaction time (t_r) were found at 563 K and 40 min, respectively, for carrying out the torrefaction in a tubular furnace with carrier nitrogen. These conditions gave a solid yield (Y_S) of 69 wt % of WBC_T relative to the original WBC, and 31 wt % of by-products were produced. The liquid products were composed of water as high as 62 wt %, along with some organic acids. Some medicine components were also found in the liquid products, representing potential medicine applications. During torrefaction, CO, NO_x, SO_2, and CO_2 emissions were largely discharged from 10 to 20 min of torrefaction time. O_2, CO_2, and H_2O are the major compounds in the total gas products collected. Some combustible gases of C1 to C6 hydrocarbons were also produced. Moreover, the gas volume balances were computed and evaluated. The information obtained in this study is useful for the proper design, operation, pollution control, and utilization of the products.

Keywords: torrefaction; waste bamboo chopsticks; Moso bamboo; solid bio-fuel

1. Introduction

Torrefaction is a feasible method to convert biomass into high quality solid bio-fuel, and the advantages, application, and future trend of biomass torrefaction have been evidently presented by several review papers [1–4]. In the past, studies have mainly focused on the solid product after torrefaction. However, the liquid and gas products, as by-products, have the same important roles because of their potential reutilization and their effects on the environment.

After torrefaction, biomass is transformed into solid, liquid, and gas parts. The components of the products of torrefaction may be different when employing different biomasses, torrefaction temperatures (T_r), and torrefaction times (t_r), and typical components were reported by Bergman et al. [5]. The solid phase, regarded as bio-fuel, is comprised of a chaotic structure of the original sugar structures and modified sugar structures, newly formed polymeric structures including aromatic rings, and the ash. The liquid phase is composed of water, organics (sugars, polysugars, acids, alcohols, furans, ketones), and lipids (terpenes, phenols, fatty acids, waxes, tanins), and is collected by condensing in room temperature. On the basis of references [6,7], the liquid product produced by the pyrolysis of biomass is composed of acid components, aromatic hydrocarbons, phenols, and so on. However, as for a woody plant, the pyrolysis of a different construction of lignin results in different components being present in the liquid product [8]. Thus, analyzing the collected liquid product from torrefaction is a necessary step to figure out the composition for evaluating its usefulness and for maintaining a carbon balance. Detailed liquid product analyses from the torrefaction of biomass including lauan, bamboo, willow, straw, and larch, have been conducted in several studies [9–11]. For lauan, Chen et al. [9] found that monoaromatics are the major component accompanied with a small quantity of heterocyclic hydrocarbons. Concerning bamboo, Chen et al. [10] detected the presence of acid, alcohols, ketones, phenols, aldehydes, esters, and water. The pH value of the liquid was as low as 2.27–2.60. Moreover, the liquid was comprised of about 50% of water. As for willow, straw, and larch, Prins et al. [11] reported the following findings: (1) Acetic acid and water are the main components of the liquid, while methanol, formic acid, lactic acid, furfural, and hydroxyl acetone are present in a smaller amount, and traces of phenol occur for the case of willow; (2) Straw presented a comparable amount of liquid products similar to those of willow; and (3) Formic acid is the major acid generated by larch. Permanent gas like H_2, CO, CO_2, and CH_4 can be found in the gas phase. The gas phase also contains C_XH_Y, toluene, and benzene.

In our other study [12], torrefaction was used for reusing waste bamboo chopsticks (WBCs) which are made of Moso bamboo, in order to manufacture bio-fuel. Torrefaction temperatures T_r of 543, 563, and 583 K, with various torrefaction times t_r of 20, 40, and 60 min, were employed for carrying out the torrefaction in a tubular furnace with carrier nitrogen. Appropriate T_r and t_r values were found at 563 K and 40 min. The high heating value in dry basis (H_{HD}) of WBC was enhanced from 4615.86 to 5506.80 kcal kg^{-1}, while the energy densification factor (E_D) increased to 1.19 of torrefied WBC (WBC$_T$). The results thus deduced that the torrefaction process is advantageous to upgrade WBCs to high energy containing solid bio-fuel.

Materials similar to bamboo vinegar, which is useful for the medicine industry, can be expected to appear in the liquid product. The traditional method for manufacturing bamboo vinegar is to condense the emitted gas from the pyrolysis of bamboo charcoal at around 573–673 K [13]. Although the temperature and method for pyrolyzing the bamboo might make a difference to the composition of the liquid product compared with torrefying WBCs, the liquid product for the torrefaction of WBC at 563 K and 40 min might contain the components of bamboo vinegar, along with water and organic acids of a low carbon number, like acetic acid and carboxylic acid.

On the other hand, aromatic hydrocarbons produced from torrefaction can also be reused by employing a ring cleavage reaction such as hydrogenation, in order to form alkanes. After the ring cleavage reaction, long-chain alkanes can yield diesel fuel (C10–C40) and aviation fuel (C10–C20) by converting the liquid product in subsequent processes, including removing the acidity and other steps. As a result, it is beneficial to investigate the liquid product from the torrefaction of WBCs for finding an appropriate application for the liquid product.

As the preprocess of producing WBCs is carried out by immersing bamboo in strong oxidizers, including sulfur, which might ruin the construction of Moso bamboo [14], gaseous sulfides may be emitted, which is the evident difference for the torrefaction of WBCs. Moreover, CO and CO_2 are possible products from torrefaction. These pollutants should be controlled in case of a negative influence on the environment, and should be restricted to meet the air pollution standards.

Above all, although torrefying WBC can produce qualified solid biofuels, the by-products resulting from torrefaction need to be characterized, and are thus conducted in this study not only for examining their reusability, but also for controlling the pollutants emitted. This study also constructed a procedure for the analyses of the by-products, offering a reference for torrefaction industries.

2. Experimental Methods

2.1. Procedure of Collecting By-Products from the Torrefaction of WBC

The disposable bamboo chopsticks (DBC) (Songya Co., Taipei, Taiwan) were used to simulate the waste BC (WBC). They were cut into pieces with a dimension of 5 mm (D) × 10 mm (L) for manufacturing WBC_T with an upgraded quality. The WBC torrefaction was conducted employing a tubular furnace, which is the same as that used by Chen et al., with a carrier gas of nitrogen at a flow rate of 100 mL min^{-1} [12]. The furnace was pre-heated to the desired pre-set torrefaction temperature T_r. The sample was then introduced into the furnace and kept there for a certain torrefaction time t_r at constant T_r. As noticed in the previous section, the effects of T_r of 543, 563, and 583 K, with t_r of 20, 40, and 60 min, on the production of torrefied WBC have been examined in our previous work [12]. T_r and t_r values of 563 K and 40 min were found to be proper [12] and were thus chosen for further study on the characterization of the by-products and emissions produced from the torrefaction of WBC. During torrefaction, gas emissions were continually produced and were slowly transported to condensing containers by the nitrogen carrier gas. Following this, the liquid products were condensed in two containers with 273 K, and the remaining gas products were then separated.

2.2. Liquid Analysis

After measuring the volume and mass of the condensed liquid products, the composition of these products were analyzed using different equipment.

The total organic carbon (TOC) content was detected by Sievers InnovOx Laboratory TOC Analyzer of FIRMWARE VERSION 3.01 OR LATER (GE Analytical Instruments, Boulder, CO, USA). In this analysis, the liquid product diluted to 1/1000 was taken as the sample to be tested. By using the moisture titrator (model 851 Titrando, Karl Fischer Titrators, Coulometric, Metrohm, Riverview, FL, USA), the water content was detected with the method of Karl Fischer.

The equipment for simulated distillations of the liquid product from torrefaction and various oils to determine the carbon number of organic compounds, included gas chromatography with a flame ionization detector (FID) (Agilent 6890 Chemstation, Hewlett Packard Inc., Wilmington, DE, USA), equipped with a column (UA-1 (HT) with 15 m length × 0.53 mm ID × 0.25 µm thickness, Frontier Laboratories Ltd., Fukushima, Japan) and an integrator (HP 3395, Agilent Technologies Inc., Santa Clara, CA, USA).

As for identifying the organic component of the liquid product from torrefaction, a gas chromatography mass spectrophotometer, also called GC-MS (Thermo Scientific FOCUS GC Gas Chromatograph 1255080, Thermo Fisher Scientific Inc., Waltham, MA, USA), was used, adapting column Trace TR-1701 with a 30 m length, 0.25 mm ID, and 0.25 µm film thickness (Thermo Fisher Scientific Inc., Waltham, MA, USA). Helium was used as the carrier gas in this system.

2.3. Gas Analysis

The concentrations of the different components of gases were analyzed by both instant and accumulative analyses. The instant gas concentrations were detected every minute. Additionally, the

accumulative gas was collected in resident time using a sampling bag (Cat. No. 232-01, SKC Gulf Coast Inc., Houston, TX, USA) for analysis.

The equipment for analyzing the organic components of the gas product in the sampling bag included gas chromatography with a flame ionization detector (Agilent 6890 Chemstation, Hewlett Packard Inc., Wilmington, DE, USA), adopting a column (AB-5 with 30 m length, 0.32 mm ID, and 0.5 μm film thickness, Abel Industries, Dumfries, VA, USA) and an integrator (HP 3395). The main components detected were alkanes and other hydrocarbons. The relative humidity of the gas product was measured by Hygropalm (HP22-A, Rotronic, Bassersdorf, Switzerland). By measuring the temperature, pressure, and volume of the gas in the gas bag, the water content could be calculated.

Carbon monoxide, NO_x, SO_2 (ppmv), and O_2 (vol %) could be detected instantly (per min) using a gas analysis detector (Tempest 100, Telegan Gas Monitoring Ltd., Abingdon, Oxfordshire, UK). On the other hand, all emissions could also be collected in a gas bag through the whole torrefaction process, and the average content of CO, NO_x, SO_2, and O_2 could then be detected.

As for carbon dioxide, the emissions from the torrefaction process were collected in gas bags in two ways. Sequential samples collected every 10 min were used to examine the trend of CO_2 emission through torrefaction. Moreover, accumulated sampling until the end of torrefaction was employed to evaluate the average CO_2 content. The content of CO_2 was analyzed by a gas analyzer (HM5000, Infrared Industries Inc., Hayward, CA, USA). The unit of CO_2 concentration is vol %.

3. Results and Discussion

3.1. Composition of Solid, Liquid, and Gas Produts from the Torrefaction of WBC at 563 K and 40 min

After the process of torrefying WBC at 563 K (290 °C) and 40 min was finished, masses of the torrefied solid product WBC_T, liquid product, and gas product produced through the process were collected. A mass balance of three products was built to generate a detailed analysis, as presented in Table 1. A comparison of the mass, yield, and volume between the three products could deduce some information. Moreover, after analyzing the compositions of the solid, liquid, and gas, a more specific calculation and balance could be achieved by incorporating the information of the mass and volume of the liquid and gas, as well as the mass of the solid products.

Table 1. Solid, liquid, and gas products from the torrefaction of waste bamboo chopstick (WBC) at 563 K and 40 min.

T_r-t_r (K-min)	Mass [a] (g)			Mass Yield (-)			Volume (mL)	
	Solid [b1]	Liquid	Gas [c]	Solid [b1]	Liquid	Gas [c]	Liquid	Gas [c]
563-40	2.07 [b2]	0.43	0.51	0.69 [b2]	0.14	0.17	0.41 (0.03) [e]	183 [d] (27.1) [e]

[a] Initial mass of dried WBC = 3 g. [b1] Dry basis; [b2] Data of Chen et al. [12]. [c] Excluding nitrogen gas; flow rate of N_2 = 100 mL min^{-1} and calculation by balancing the solid and liquid. [d] Computed by (Q_{Ge} − Q_{Ni}) × 40 min, where Q_{Ge} and Q_{Ni} are the average flow rates of the exit gas and inlet N_2, respectively, which were 104.58 and 100 mL min^{-1}. Assume N_2 gas was not reacted. [e] Numbers in parentheses are standard deviations ó$_{n-1}$. T_r-t_r: Torrefaction temperature and time.

The main part of the products is the solid product, which consists of 69 wt % of the total products. Due to pyrolysis with a mild temperature at 563 K (290 °C), only moderate devolatilisation and carbonization occurred. In the end, the torrefied solid fuel was the main product after torrefaction. The mass yields of the liquid and gas products are 0.14 and 0.17, respectively. Notice that more gas is obtained than liquid, which is different to the findings of Prins et al. [11] and Le Thanh et al. [15]. This may be caused by the following: (1) The raw materials used were different, with WBC being employed in this study, and willow, straw, and larch being used by Prins et al. [11], and pine, ash wood, miscanthus, and wheat straw being used by Le Thanh et al. [15]; (2) Different condensation temperatures were employed at 273 K (0 °C), 268 K (−5 °C), and 253 K (−20 °C) by this work,

Prins et al. [11], and Le Thanh et al. [15], respectively; and (3) A small portion of liquid products may be condensed and trapped along the transmitting tube, but not in the condensate collector.

Because the mass and volume of the liquid are 0.425 g and 0.41 mL, respectively, the density of the liquid product is 1.04 g mL^{-1}, which is close to that of water, and this result also proves that the main component of the liquid product is water, which is discussed later in Section 3.2.1 with Figure 1. The volume of gas products without the carrier gas is 183 mL, while the mass is 0.505 g. The density of the gas products is about 2.76×10^{-3} g mL^{-1}, indicating the presence of light gases.
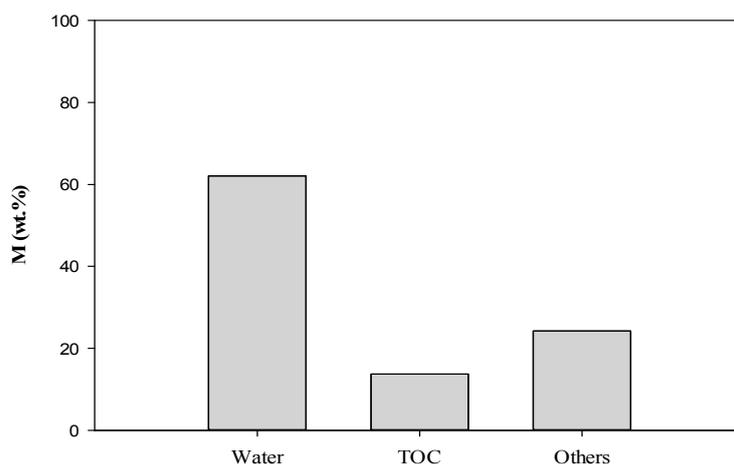

Figure 1. Mass percents (M) of water, total organic carbon (TOC), and others in the liquid products produced from the torrefaction of waste bamboo chopstick (WBC) at 563 K and 40 min. Concentration of TOC (C_{TOC}) = 137,000 mg L^{-1}. Mass of liquid products (m_L) = 0.43 g and volume of liquid products (V_L) = 0.41 mL.

3.2. Liquid Products from the Torrefaction of WBC at 563 K and 40 min

3.2.1. TOC and Water

A liquid product with a moderate brown color was condensed and collected in a glass container. Analyses of the water content, total organic content (TOC), and the characteristics of the organic components in the liquid product were conducted.

Figure 1 shows the mass percentages (M) of TOC, water, and others (the residual mass excluding water and TOC) in the liquid product. The water content (62 wt %) in the liquid product might result from the reaction of pyrolyzing WBCs and water in cells of WBCs which couldn't be removed from drying at 378 K (105 °C). Moreover, the moisture in the air sliding in would bring in some water during the loading of WBCs in torrefaction. The moisture can be easily condensed in a glass container surrounded by 273 K (0 °C) of water and contributed to the water content in the liquid product. In comparison, 51% of the moisture content in the liquid product from bamboo torrefaction at 573 K for 60 min can be found in Chen's study [10], which also indicates that water is the major component in the liquid product after torrefaction.

Using a TOC analyzer, the concentration of TOC (C_{TOC}) of the liquid product can be measured with 137,000 mg L^{-1}. Consequently, with a volume of liquid product (V_L) of 0.41 mL and a mass of liquid product (m_L) of 0.43 g, the mass percentage of TOC (M_{TOC}) can be calculated by the formula listed below:

$$M_{TOC} = (C_{TOC} \times V_L / m_L) \times 100 \text{ wt \%} \tag{1}$$

Roughly, an M_{TOC} value of 13 wt % was obtained. The content of the others, excluding water, was 25 wt %. The compounds of TOC can be further identified by GC-MS.

3.2.2. pH Value

Using a pH meter, the diluted liquid of 1/100 from the original liquid product was measured with pH = 2.96, indicating that the components in the liquid contain acid matters. The pH value of the un-diluted liquid is 0.96, assuming that the H^+ of the acid matters can be totally dissociated. The acidity can be inferred to be caused by the organic acids from the pyrolysis of WBCs, supported by the reference mentioned previously. Another source of acidity comes from the inorganic acids, which are probably generated by the reactions between the gaseous emissions in the furnace of CO_2 and H_2O, and SO_2 and H_2O (the gas products discussed in Section 3.3.2), which would form acid materials like H_2CO_3 and H_2SO_3. The formation of SO_2 is due to the sulfur-treated preprocess of the bamboo chopsticks described in the introduction. As a result, the pH value of the liquid product in this study is much lower than that of 2.27 to 2.60 from bamboo torrefaction [10].

3.2.3. Simulated Distillation

For the sake of determining the distribution of organic compounds of different boiling points (bps) in the liquid product, simulated distillation gives an index to compare the liquid product with different oils. From the simulated distillation in Figure 2, the major compositions, excluding the water of the liquid products, are low bp organic compounds (bp < 341 K) which have a carbon number below C6. The results of the liquid products are more similar with gasolines 92, 95, and 98, which are comprised of isooctane (C8) and heptane (C7) with a low carbon number [16].
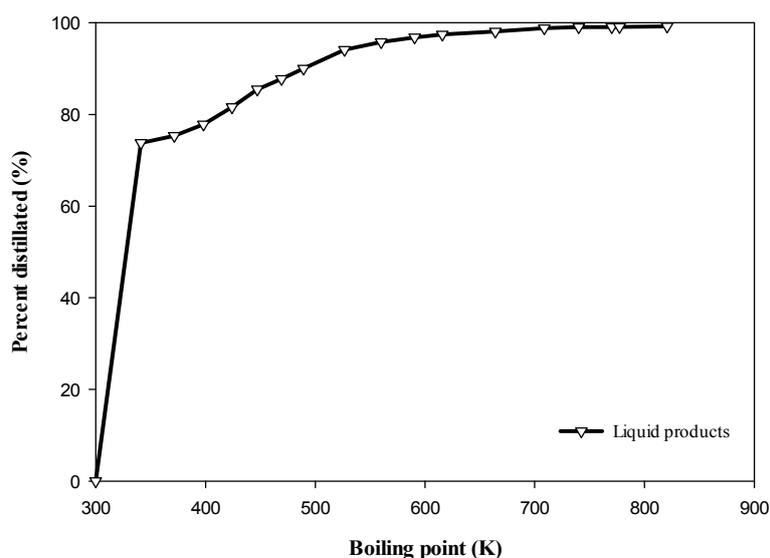

Figure 2. Simulated distillation of liquid products from the torrefaction of WBC at 563 K and 40 min.

The traditional way to produce bamboo vinegar is to condense the gas products obtained from the pyrolysis of bamboo charcoal at about 573–673 K [13]. Although the temperature and method for pyrolyzing the bamboo might make a difference to the composition of the liquid product compared with torrefying WBCs, the liquid product from the torrefaction of WBC at 563 K and 40 min might contain the components of bamboo vinegar. Noting the acidity of the liquid products, it can be deduced that organic acids of a low carbon number probably include acetic acid and carboxylic acid, which are the primary chemicals in bamboo vinegar. The stationary phase in a column of GC-FID is 100% dimethylpolysiloxane, which is nonpolar. Van der Waals' force is the main factor of the mechanism used to separate compounds of liquids. Materials exhibit different detention times in a column because of the different degree of interacting with the stationary phase by Van der Waals' force. As a result, polar materials will appear prior to nonpolar materials, due to the stronger attraction between the nonpolar materials and stationary phase.

In Figure 2, the bp is seen to increase with the detention time. The standard oils are primarily nonpolar, so the molecular weight is the factor of the separation temperature. As to the liquid product, 74 area % at 341 K indicates that acidic organic compounds with a polar property have a short detention time and occur at a low temperature, before the nonpolar materials. Consequently, the compounds contributing to the peaks within 74 area % might contain organic acids with a carbon number up to C6. Notice that it is not easy to separate useful compounds from pyroligneous liquor. However, the study of Wang et al. [17] was dedicated to extracting useful materials from wood vinegar. The study reported the concentrating of acetol from wood vinegar by distillation and solvent extraction, which successfully concentrated acetol from 1% to 40%. Accordingly, medicine materials in pyroligneous liquor might be separated by different boiling points and proper extracting solvent. Further studies would certainly be helpful to verify the validity of the distillation-extraction process.
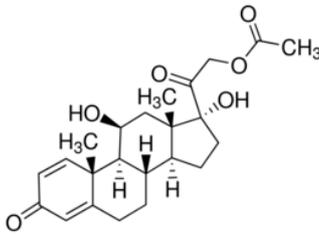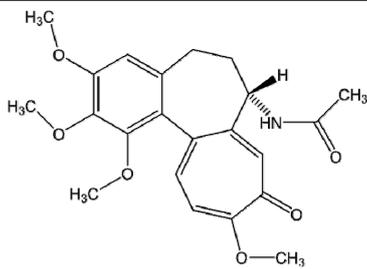
3.2.4. Probable Organic Compounds

In order to understand the detail composition of the liquid product, the probable organic compounds were determined by GC-MS. From the GC-MS spectrum in Figure 3, some evident signal peaks were identified and sophisticated analyses for the components of the liquid products were carried out using those peaks by GC-MS. From the data base, the probability of every compound in each signal with a specific appearing time and temperature can be listed and three of the most probable compounds of every peak were then selected, as shown in Table 2. GC-MS only detects compounds with a high carbon number > C14, which are a minor part in the liquid products. Among those compounds chosen for each peak, some compounds are useful and are re-listed in Table 3. These include organic components of long-chain alkanes, such as C16 hexadecane, C18 octadecane, and C21 heneicosane, which can produce diesel fuel or aviation fuel. Others include C22 colchicine, C23 prednisolone acetate, and C28 beclomethasone which have bonds with oxygen, chlorine, and nitrogen, respectively. Thus, a lot of useful compounds can be detected in the liquid products. However, torrefaction is mild pyrolysis. The temperature is still too low to break the structure of the complicated organic compounds in WBC. The detected signal of long-chain alkanes might be the cycloalkanes which still have to go through a ring cleavage reaction by hydrogenation to form alkanes. After the ring cleavage reaction, long-chain alkanes can yield diesel fuel (C10–C40) and aviation fuel (C10–C20) by converting the liquid product in subsequent processes, including removing the acidity and other steps. Moreover, C23 prednisolone acetate, C22 colchicine, and C28 beclomethasone are useful in medical science. C23 prednisolone acetate is purposed to diminish inflammation and relieve the symptoms of an allergy, and C22 colchicine can be used to treat gout and Familial Mediterranean fever. C28 beclomethasone is a steroid. It can prevent the release of substances in the body that cause inflammation. However, because of its high acidity, the application of the liquid product may be restricted in industries. The corrosivity of the liquid would lead to destroying the container or equipment. Fortunately, a hydrothermal process can be introduced to decrease the acidity and oxygen content in the liquid products for the sake of improving the quality of the liquid products which can be converted to biodiesel [16,18].

The major components in the liquid products, except water, are organic compounds with carbon. Above all, the liquid products from the torrefaction of WBC can be regarded as pyroligneous liquor, which has an economical value in industries and medicine.

Table 2. GC-MS results of liquid products from the torrefaction of WBC at 563 K and 40 min.

Time (min)	Temperature (°C)	Possible Compound	Probability (%)	Formula
51.1	142.1	Tetradecane	51.34	$C_{14}H_{30}$
		Hexadecane	13.16	$C_{16}H_{34}$
		Pentadecane	12.65	$C_{15}H_{32}$
57.5	155.0	Pentadecane	46.03	$C_{15}H_{32}$
		Hexadecane	13.29	$C_{16}H_{34}$
		Eicosane	9.91	$C_{20}H_{42}$
63.6	167.1	Hexadecane	46.33	$C_{16}H_{34}$
		Heptadecane	10.22	$C_{17}H_{36}$
		Eicosane	8.03	$C_{20}H_{42}$
69.3	178.6	Heptadecane	45.90	$C_{17}H_{36}$
		Hexadecane	11.34	$C_{16}H_{34}$
		Pentadecane, 2-methyl-	9.14	$C_{16}H_{34}$
74.8	189.6	Octadecane	26.91	$C_{18}H_{38}$
		Heneicosane	13.88	$C_{21}H_{44}$
		Eicosane	12.08	$C_{20}H_{42}$
80.0	200.0	Nonadecane	19.17	$C_{19}H_{40}$
		Tetracosane	16.94	$C_{24}H_{50}$
		Heneicosane	12.63	$C_{21}H_{44}$
85.0	209.9	Heneicosane	27.05	$C_{21}H_{44}$
		Tetracosane	26.00	$C_{24}H_{50}$
		Eicosane	7.08	$C_{20}H_{42}$
89.7	219.4	Heneicosane	32.52	$C_{21}H_{44}$
		Pentadecane, 2-methyl-	9.91	$C_{16}H_{34}$
		Octacosane	8.37	$C_{28}H_{58}$
94.3	228.6	Hydrocortisone acetone	14.96	$C_{23}H_{32}O_6$
		Digitoxin	14.38	$C_{41}H_{64}O_{13}$
		Docosane	9.00	$C_{22}H_{46}$
102.1	244.2	Prednisolone acetate	20.37	$C_{23}H_{30}O_6$
		Beclomethasone	16.41	$C_{28}H_{37}ClO_7$
		Colchicine	15.78	$C_{22}H_{25}NO_6$
107.5	255.0	Prednisolone acetate	18.65	$C_{23}H_{30}O_6$
		Colchicine	17.92	$C_{22}H_{25}NO_6$
		Beclomethasone	11.22	$C_{28}H_{37}ClO_7$
112.6	265.2	Colchicine	23.89	$C_{22}H_{25}NO_6$
		Prednisolone acetate	12.32	$C_{23}H_{30}O_6$
		Beclomethasone	11.34	$C_{28}H_{37}ClO_7$
117.4	274.7	Prednisolone acetate	22.65	$C_{23}H_{30}O_6$
		Beclomethasone	18.25	$C_{28}H_{37}ClO_7$
		Colchicine	12.16	$C_{22}H_{25}NO_6$
121.8	280.0	Colchicine	47.95	$C_{22}H_{25}NO_6$
		Colchicine, (+)-	12.81	$C_{22}H_{25}NO_6$
		Pregn-4-ene-3,20-dione, 11-hydroxy-, (11α)-	8.02	$C_{21}H_{30}O_3$
125.9	281.9	Prednisolone acetate	27.13	$C_{23}H_{30}O_6$
		Gamabufotalin	18.07	$C_{24}H_{34}O_5$
		Beclomethasone	13.84	$C_{28}H_{37}ClO_7$
134.0	298.0	Prednisolone acetate	48.90	$C_{23}H_{30}O_6$
		Colchicine	17.86	$C_{22}H_{25}NO_6$
		Colchicine, (+)-	4.27	$C_{22}H_{25}NO_6$

Table 3. Structure of useful and possible compounds of liquid products for producing WBC_T.

Compound	Formula	Structure
Hexadecane	$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$
Octadecane	$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$
Heneicosane	$C_{21}H_{44}$	$CH_3(CH_2)_{19}CH_3$
Prednisolone acetate	$C_{23}H_{30}O_6$	
Colchicine	$C_{22}H_{25}NO_6$	
Beclomethasone	$C_{28}H_{37}ClO_7$	
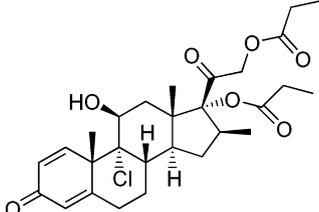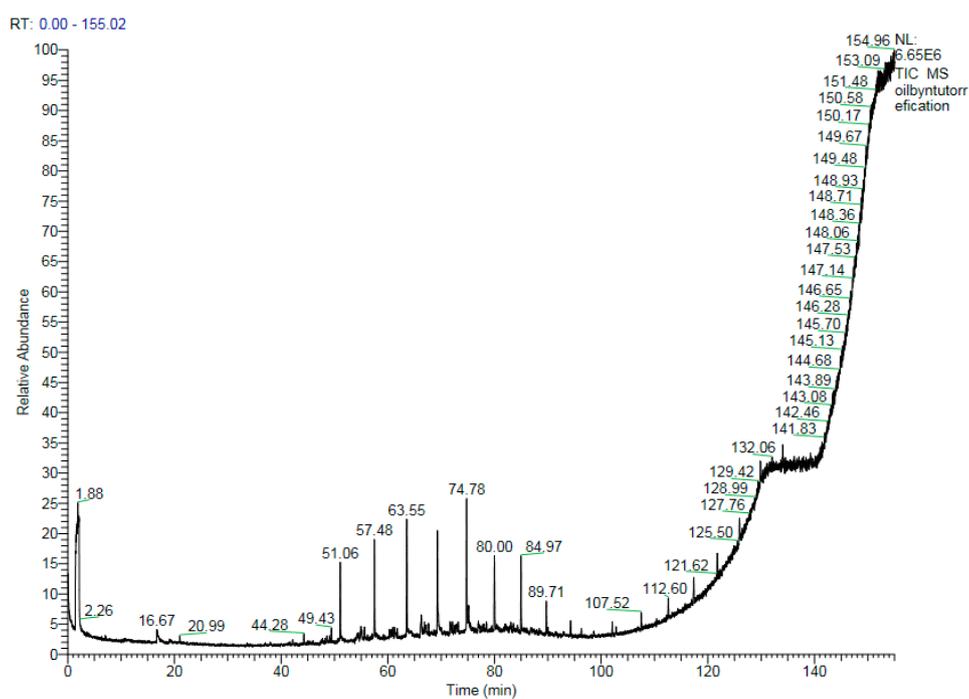
Figure 3. GC-MS spectrum of liquid products from the torrefaction of WBC at 563 K and 40 min.

3.3. Gas Products from the Torrefaction of WBC at 563 K and 40 min

3.3.1. Hydrocarbons

　　The emissions from the torrefaction process contain hydrocarbons (HCs) of a lower carbon number (Cn). When analyzing the emitted gas of the whole process through GC-FID, the basic composition of the hydrocarbons in the gas could be determined. By different volumes (10, 15, 20, 25, 30 μL) of a standard sample of alkanes which contains CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, and C_6H_{14} with a concentration of 1000 ppmv, the calibration line of each alkane was established for the relationship between the area of the signal and the amount of standard sample injected. The peaks of the signal from the standard sample stand for the hydrocarbons which appear at different times, and the sequence of their appearance is decided by the carbon number. The lower the carbon number is, the sooner the peak appears.

　　Through GC-FID, the spectrum of the gaseous products from the torrefaction of WBC_T is illustrated in Figure 4. Many peaks can be seen, representing different appearance times. Compared with the GC-FID spectrum of the standard gases of hydrocarbons, the peaks could be sorted according to the similar chemical polarity of the alkanes.
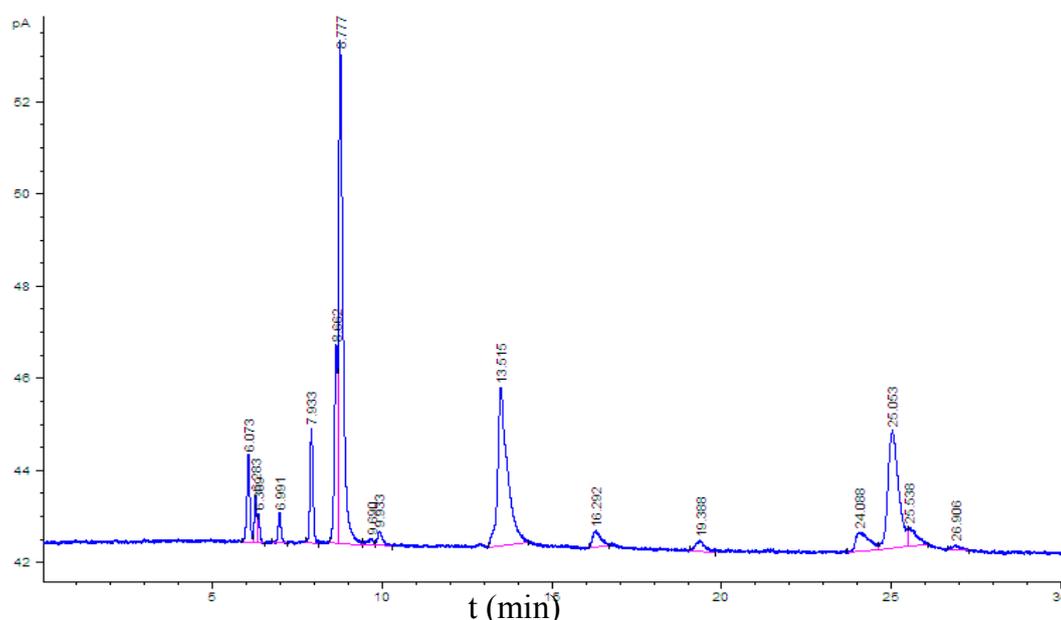

Figure 4. GC-FID spectrum of gaseous products from the torrefaction of WBC at 563 K and 40 min. Volume of gas sample = 200 μL.

　　Using the calibration curve, the individual volume of Cn HC (V_{Cn-HC}) in the injected gas products can be obtained. Notice that HCs with a Cn value higher than seven are trace components and are thus assumed to be negligible. The volume percentage of each hydrocarbon of C1–C6 in gaseous HCs with a sum of 100% is shown in Figure 5. The C4 HC expressed, equivalent to butane, is the major compound of the gaseous hydrocarbons. Hydrocarbons other than C4 HC are also obviously present.

　　Knowing that the volume of the gas products injected into GC-FID (V_I) is 200 μL and that the total gas products with the carrier gas (V_T) is 4183 mL, the total volume of all Cn HCs with n = 1 to 6 (V_{THC}) in the gas products could be calculated by assuming that all of the gas products are ideal gas. The applicable equation can be seen below.

$$V_{THC} = ((\text{Sum of } V_{Cn-HC})/V_I) \times V_T \tag{2}$$

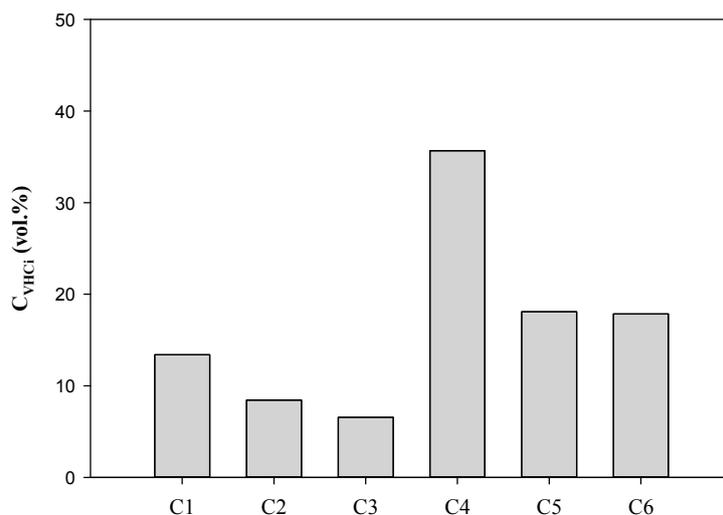Using this equation, the total volume of hydrocarbons when concerning only C1–C6 HCs is 1.74 mL.

Figure 5. Volume concentration of compounds of hydrocarbons (HCs) in gaseous HCs from the torrefaction of WBC at 563 K and 40 min. C1–C6: HC with 1 to 6 carbons. Hydrocarbons other than C1–C6 HC are negligible.

3.3.2. CO, NO_x, SO_2, and CO_2

By using a gas detector, CO, NO_x, and SO_2 from the gas products are continually detected per minute from the 40 min torrefaction process. The diagrams which illustrate the relationship between the concentration of emissions and the residence time of torrefaction are established. Taking an example in Figure 6 for the CO emission from the torrefaction of WBC_T, average gas concentrations with the error bars standing for the standard deviation from repetitive analyses are shown.
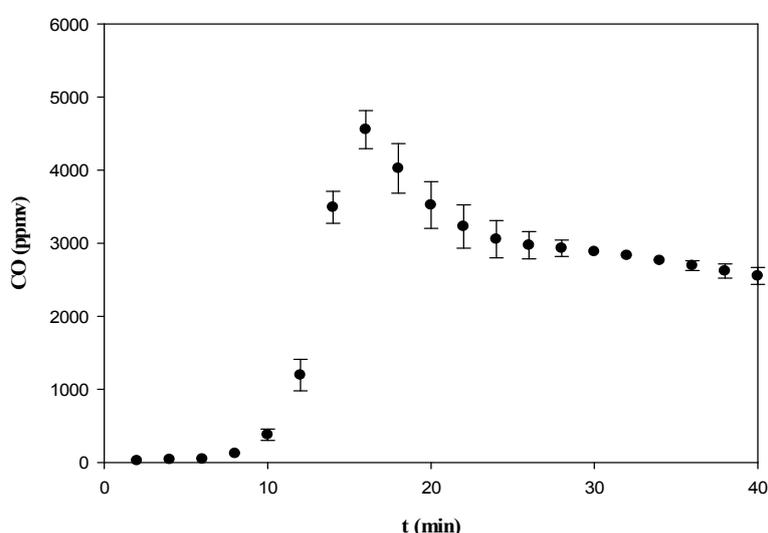

Figure 6. Emissions of CO from the torrefaction of WBC at 563 K and 40 min.

According to continual emissions analysis, the trend of emission can be observed. In Figures 6–8, CO, NO_x, and SO_2 all start to appear at around 8 min, so it is an indisputable fact that pyrolysis occurs after 8 min of torrefaction. When the time reaches 16 min, the maximal peak of CO appears and the value arrives at 4500 ppmv in total gas, including the carrier gas nitrogen (Figure 6). As for NO_x, there is no explicit peak and the concentration of NO_x is maintained at around 60 ppmv until the end of process (Figure 7). Besides, SO_2 had a maximum concentration of 58 ppmv at around 12 min (Figure 8). The reason for the emission of SO_2 is that disposable chopsticks are pretreated by an oxidizer such as

bleach, which includes the component of sulfur, and the amount of bleach used for each chopstick has an influence on the results.
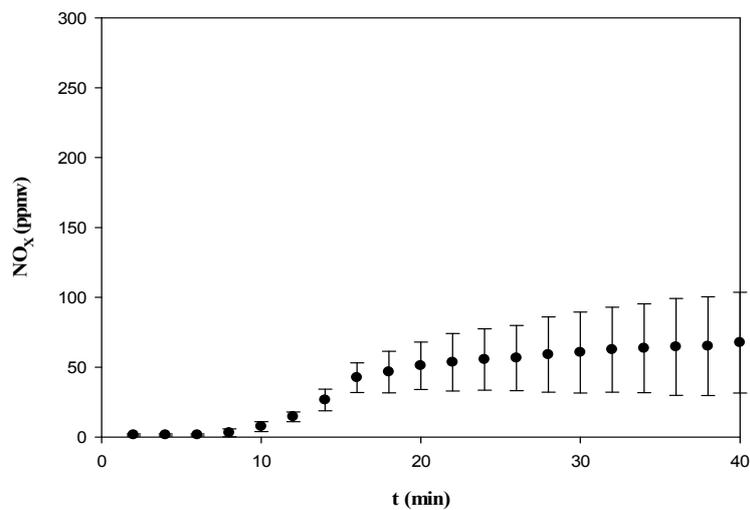

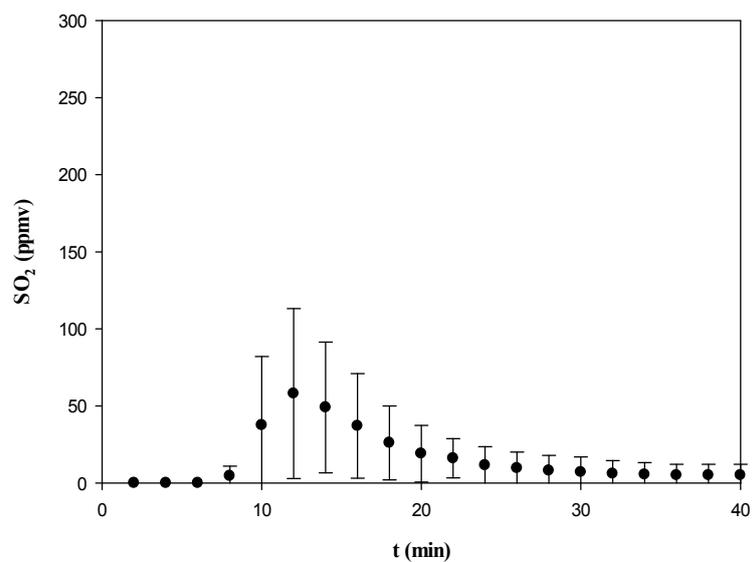**Figure 7.** Emissions of NO_x from the torrefaction of WBC at 563 K and 40 min.

Figure 8. Emissions of SO_2 from the torrefaction of WBC at 563 K and 40 min.

By sampling gas products every 10 min with a gas bag, the trend of CO_2 emission through torrefaction could be constructed. The concentrations of CO_2 in the gas bags represent the instant concentrations of 5, 15, 25, and 35 min through the 40 min torrefaction process. In Figure 9, the maximum value appears at around 15 min with a CO_2 measurement of 1.94 vol %.

In summary, the most intense pyrolysis of torrection takes place between the retention time of 10 min to 20 min, which has a maximum of instant concentration of each gas except NO_x. During 40 min of torrefaction, except SO_x, the instant concentrations of gases are still maintained at a considerable amount at the last minute of torrefaction. As a result, the pyrolysis could continue after 40 min of torrefaction and it still takes time to reach the levelling off of the concentration values of emitted gases such as CO.
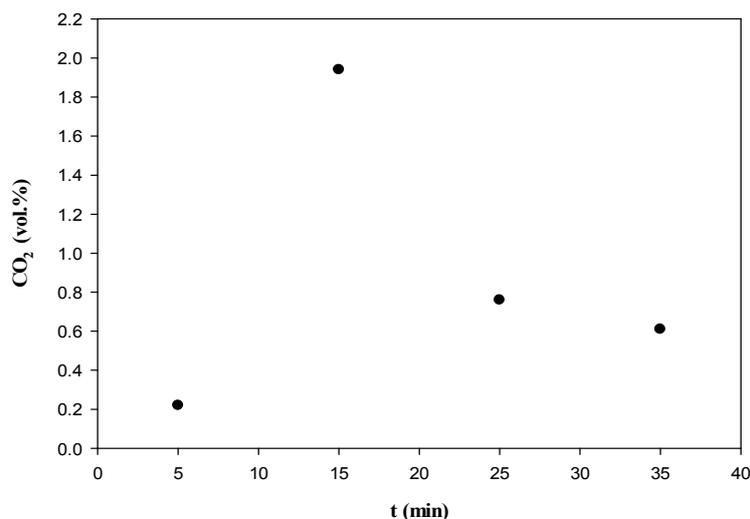
Figure 9. Emissions of CO_2 from the torrefaction of WBC at 563 K and 40 min.

3.3.3. Gas Balance

After collecting all of the gas products from 40 min of the process of torrefaction, the average concentration of each kind of gas could be measured by a gas analyzer. SO_2 and NO_x only occupy a small part of the gas products. The average concentrations of SO_2 and NO_x are 37.7 and 75.3 ppmv, respectively. The SO_2 and NO_x of a low amount are neglected to create a volume data of each gas, as shown in Table 4. By using the total volume of the output gas including N_2 (V_{G+N}) and the volume concentration (C_{VGNi}) of each component in V_{G+N}, the individual gas volume (V_{Gi}) could be counted. The equation is listed below:

$$V_{Gi} = C_{VGNi} \times V_{G+N} \tag{3}$$

Summing V_{Gi} for all i components then gives a total volume of gases excluding N_2.

Table 4. Volume of different compounds in the gas products from the torrefaction of WBC at 563 K and 40 min.

Compound	Volume (mL)
O_2 [a]	79.5
CO [b]	16.2
C1–C6 HCs	1.74
C1 HC	0.19
C2–C6 HCs	1.55
CO_2 [c]	41.4
H_2O [d]	51.2
Total	190
Total gases measured from flowmeter [e]	183

[a] Volume concentration of O_2 in total output gas including N_2 (V_{G+N} = 4183 mL) = 1.9%. [b] Volume concentration of CO in V_{G+N} = 3863.7 ppmv. [c] Volume concentration of CO_2 in V_{G+N} = 0.99%. [d] Relative humidity in gas = 40.7% at 24.3°C, assuming 1 atm. Humidity is 9.00 g m^{-3}. From ideal gas equation, volume of H_2O can be obtained. [e] Estimated as difference of V_{G+N} and V_N (volume of inlet N_2) with V_N = 4000 mL.

According to Table 4, oxygen, carbon dioxide, and moisture are the major gases emitted. It is noted that, although the reactor was pre-purged by nitrogen to remove the air, during the charging of the sample into the reactor, some air with moisture was able to flow in. Moreover, the leakages of the torrefaction equipment could cause errors in the measurement of the collected gas products. Accordingly, these causes would affect the measurements of the components of atmosphere like the O_2, CO_2, and H_2O in the gas products. Detailed procedures of pre-purging of air by nitrogen before

torrefaction are as follows. The torrefaction of WBC was conducted by employing a tubular furnace with a volume of 3393 mL (30 cm in length and 12 cm in inside diameter). Every time before conducting torrefaction, nitrogen with a flow rate of 300 mL min^{-1} (three times the flow rate used for torrefaction) was introduced continuously into the furnace for 30 min (9000 mL of nitrogen), until a stable pre-set torrefaction temperature was reached. As a result, by assuming an ideal reactor, the hydraulic retention time (τ) is 11.3 min (= 3393/300), while the purging time of nitrogen (t_N) is 2.6 (= 30/11.3) times the τ value. The fractional concentration of residual oxygen (C/C_0) is 0.074 (= $\exp(-t_N/\tau)$ = $\exp(-2.6)$). For $C/C_0 = 0.5$, $t_N = 3\tau = 33.9$ min, which is comparable to a torrefaction time t_r of 20, 40, and 60 min tested, and close to the purging time t_N of 30 min. Thus, oxygen would be mostly removed by a great amount of nitrogen with 2.6τ through the outlet in the end tail in the air purged procedure using nitrogen.

It is worth comparing the sum of volumes of gases excluding N_2 in Table 4 (190 mL), which were directly measured by a gas analyzer with the volume of non- N_2 gas products in Table 1 (183 mL), which is estimated from the flowrates via a flowmeter during the experiment. The comparison shows that the two values determined by the different methods are close. Therefore, the volume of the gas product is about 183–190 mL.

According to the gas analyses of Table 4, the volume fractions of the component gases can be presented, as in Figure 10. The results indicate that non-hydrocarbons (NHC) are the main compounds in the gas products, excluding the carrier nitrogen. CH_4 (C1 HC) and other HCs of C2–C6 HCs only occupy 0.11 vol % and 0.91 vol %, respectively, of the total emissions, excluding the carrier nitrogen. The essential HCs contain C1–C6 HCs.
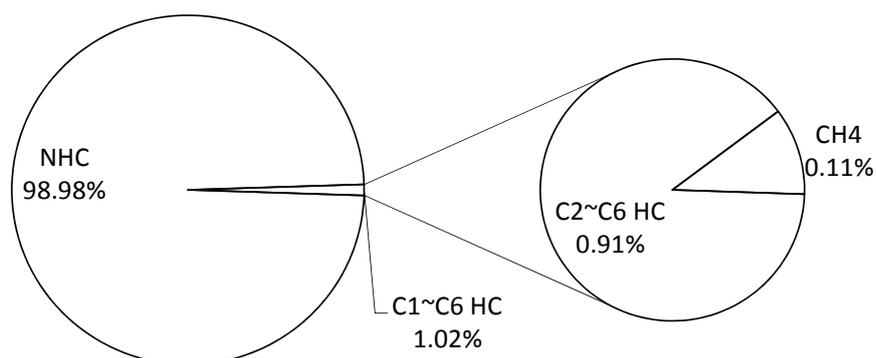

Figure 10. Volume percentage of non-hydrocarbons (NHC), C1–C6 HC, C2–C6 HC, and CH_4 in the gaseous products from the torrefaction of WBC at 563 K and 40 min, excluding the carrier nitrogen. Hydrocarbons other than C1–C6 HC are negligible.

The possible application of gas products may be assessed by considering their fuel components in a gas mixture which consists of carbon monoxide, hydrogen, methane, and C2–C6 HCs. As seen in Table 3 and Figure 10, the gas products entail 0.11 vol % of CH_4, 0.91 vol % of C2–C6 HCs, and 8.85 vol % of CO in 183 mL of gas product from torrefaction, excluding the carrier nitrogen. After proper purification and concentrating, these enriched combustible gases can be used as gas fuel.

3.3.4. Comparison of Gas Emissions with Air Pollution Standards

Table 5 compares the maximum gas emissions from torrefaction with emission standards of stationary sources (ESSS) of Taiwan Environmental Protection Administration (TEPA) [19]. Although the emissions of SO_2 and NO_2 meet the regulations, that of CO exceeds the ESSS of TEPA. Thus, proper air pollution control measures are needed.

Table 5. Comparison of gas emissions with air pollution standards.

Item	Emission Standards [a] (ppmv)	Maximum Concentration through Torrefaction (ppmv)
SO_2	650	58.0
NO_2	250	67.5 [b]
CO	2000	4555.5

[a] Emission standards of stationary sources in Taiwan [19]. Velocity of wind: 3.5 m s^{-1}; SO_2 and NO_2: Standards of processes excluding combustion. [b] Actually concentration of NO_x.

4. Conclusions

1. The pH value of the liquid products is about 0.96, which demonstrates that some preprocesses used for removing acidic components are necessary to more usefully reuse these products.

2. With the exception of the water content, the major components of the liquid products are organic matters with a low carbon number below C6.

3. There are some useful compounds appearing in the liquid. The main components can be reformed to produced long-chain alkanes, forming diesel fuel (C10–C40) and aviation fuel (C10–C20).

4. The liquid contains some useful medicinal components like C23 prednisolone acetate and C22 colchicine.

5. Proper air pollution control measures are needed for avoiding air pollution resulting from the torrefaction of WBC.

6. Gas products from the large scale torrefaction of WBC represent chance to develop the utilization of biogas (alkanes).

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

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

Nomenclature

bp	Boiling point (K)
Cn	Number of carbons (-)
C_{TOC}	Concentration of TOC (mg L^{-1})
C_{VGNi}	Volume concentration of component i in total gas including N_2 (vol %)
C_{VHCi}	Volume concentration of individual hydrocarbon i in total HCs (vol %)
E_D	Energy densification factor (-)
H_{HD}	High heating value in dry basis (kcal kg^{-1})
M	Mass content (wt %)
M_{TOC}	Mass percent of TOC (wt %)
m_L	Mass of liquid product (g)
Q_{Ge}	Average flow rate of exist gas (mL min^{-1})
Q_{Ni}	Average flow rate of inlet N_2 (mL min^{-1}), 100 mL min^{-1}
T_r or T_{tor}	Torrefaction temperature (K)
t_r or $t_{reaction}$	Torrefaction time (min)
V_{Cn-HC}	Volume of Cn HC (mL)
V_{G+N} or V_T	Volume of total output gas including carrier gas N_2 (mL), 4183 mL
V_{Gi}	Gas volume of component i (mL)
V_I	Volume of gas products injected into GC-FID (μL), 200 μL
V_L	Volume of liquid product (mL)

V_N	Volume of nitrogen (mL)
V_{THC}	Volume of all Cn HC with n = 1 to 6 (mL)
Y_S	Solid yield (wt % or -)

Abbreviation

AAQS	Ambient air quality standards
DBCs	Disposable bamboo chopsticks
DCs	Disposable chopsticks
ESSS	Emission standards of stationary sources
FID	Flame ionization detector
GC	Gas chromatography
GC-MS	GC with mass spectrum
HCs	Hydrocarbons
TEPA	Taiwan Environmental Protection Administration
TOC	Total organic carbon
WBCs	Waste bamboo chopsticks
WBC_T	Torrefied waste bamboo chopsticks

References

1. Arcate, J. New process for torrefied wood manufacturing. *Bioenergy Update* **2000**, *4*, 1–4.
2. Arias, B.; Pevida, C.; Fermoso, J.; Plaza, M.G.; Rubiera, F. Influence of torrefaction on the grindability and reactivity of wood biomass. *Fuel Process. Technol.* **2008**, *89*, 169–175. [CrossRef]
3. Chen, W.H.; Peng, J.H.; Bi, X.T.T. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew. Sustain. Energy Reviews* **2015**, *44*, 847–866. [CrossRef]
4. Eseyin, A.E.; Steele, P.H.; Pittman, C.U. Current trends in the production and applications of torrefied wood/biomass—A review. *BioResources* **2015**, *10*, 8812–8858. [CrossRef]
5. 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, in "Biocoal"*; Report ECN-C-05–013; Energy Research Center of the Netherlands: Petten, The Netherlands, 2005.
6. Şensöz, S. Slow pyrolysis of wood barks from Pinus brutia Ten and product compositions. *Bioresource Technol.* **2003**, *89*, 307–311. [CrossRef]
7. Zhang, S.; Yan, Y.; Li, T.; Ren, Z. Upgrading of liquid fuel from the pyrolysis of biomass. *Bioresource Technol.* **2005**, *96*, 545–550. [CrossRef] [PubMed]
8. Saizjimenez, C.; Deleeuw, J.W. Lignin pyrolysis products: Their structures and their significance as biomarkers. *Organic Geochem.* **1986**, *10*, 869–876. [CrossRef]
9. 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]
10. Chen, W.H.; Liu, S.H.; Juang, T.T.; Tsai, C.M.; Zhuang, Y.Q. Characterization of solid and liquid products from bamboo torrefaction. *Appl. Energ.* **2015**, *160*, 829–835. [CrossRef]
11. Prins, M.J.; Ptasinski, K.J.; Janssen, F.J.J.G. Torrefaction of wood—Part 2. Analysis of products. *J. Anal. Appl. Pyrol.* **2006**, *77*, 35–40. [CrossRef]
12. Chen, Y.H.; Chang, C.C.; Chang, C.Y.; Yuan, M.H.; Ji, D.R.; Shie, J.L.; Chen, Y.H.; Chang, W.R.; Yang, T.Y.; Lee, C.H.; et al. Production of Solid Bio-fuel from Waste Bamboo Chopsticks by Torrefaction. *J. Anal. Appl. Pyrol.* **2017**. (Under review).
13. Biswas, A.; Mahanta, P. Design and experimental analysis of condenser for the production of bamboo vinegar. *Int. J. Appl. Res. Mech. Eng.* **2012**, *2*, 79–86.
14. Hung, Z.S.; Chang, C.C.; Chang, C.F.H.; Lin, Y.S.; Ji, D.R.; Chang, C.Y.; Tseng, J.Y.; Chiang, S.W.; Shie, J.S.; Chen, Y.H.; et al. Autoclaving treatment of wasted disposable bamboo chopsticks. *J. Taiwan Inst. Chem. Eng.* **2013**, *44*, 1010–1015. [CrossRef]
15. Lê Thành, K.; Commandréa, J.M.; Valettea, J.; Vollea, G.; Meyerb, M. Detailed identification and quantification of the condensable species released during torrefaction of lignocellulosic biomasses. *Fuel Process. Technol.* **2015**, *139*, 226–235. [CrossRef]

16. 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.; et al. Conversion of waste bamboo chopsticks to bio-oil via catalytic hydrothermal liquefaction using K_2CO_3. *Sustain. Environ. Res.* **2016**, *26*, 262–267. [CrossRef]
17. Wang, Z.; Lin, W.; Song, W.; Yao, J. Preliminary investigation on concentrating of acetol from wood vinegar. *Energy Convers. Manag.* **2010**, *51*, 346–349. [CrossRef]
18. Sanders, J.; Scott, E.; Weusthuis, R.A.; Mooibroek, H. Bio-refinery as the bio-inspired process to bulk chemicals. *Macromol. Biosci.* **2007**, *7*, 105–117. [CrossRef] [PubMed]
19. TEPA (Taiwan Environmental Protection Administration). Emission Standards of Stationary Sources (ESSS). Available online: http://ivy5.epa.gov.tw/docfile/040070.pdf (accessed on 24 June 2016).