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Valorization of Coffee Residue from Convenience Store and Retail Mass-Selling Store for Producing Highly Porous Carbon Materials and Taiwan Perspectives

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Abstract: In Taiwan, a considerable amount of coffee residue is produced from commercial activities without valuable utilization. To evaluate high-value valorization in the production of highly porous carbon materials, this study investigated the thermochemical properties of coffee residues and further pyrolysis for producing highly porous biochar products at an elevated temperature (i.e., 850 °C) and a moderate residence time of 30 min. Our findings indicate that this biomass has a relatively high calorific value (about 27 MJ/kg, dry basis) due to its low ash and high lignocellulose content. It can be also concluded that the non-activated biochar products are highly porous carbon materials with excellent pore properties (i.e., a BET surface area of about 800 m^2/g and a total pore volume of 0.4 cm^3/g), which are slightly lower than those of commercial activated carbon products. Based on the above-mentioned results and the high-value circular bio-economy promoted by regulatory policy in Taiwan, the prospects for the possible valorization of coffee residue from commercial shops are addressed here, focusing both on the reuse of plant-based residue (or agricultural waste) as a high-value bioresource in the production of biomass-based fuels and on carbon materials. The former includes solid recovered fuel (SRF) and biomass-to-biogas power. By contrast, the latter aims at the production of plant-based carbon as natural, edible colorants in accordance with the regulation of food safety and sanitation in Taiwan.

Keywords: coffee residue; valorization; thermochemical property; pyrolysis; energy use; porous biochar; promotion policy

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1. Introduction

In Taiwan, convenience stores and mass retail stores are known for satisfying people's needs in every aspect of daily life by providing a wide variety of services, including food, drink, paying, booking, and so on. By the end of 2022, there were more than 14,000 convenience stores and mass retail stores, which include Taiwan's largest restaurant chains [1]. With the commercial promotion by these stores and other local and multinational chain stores, Taiwan has become a region of coffee lovers in recent years. It should be noted that the coffee beans consumed in Taiwan are highly dependent on imports. Based on customs statistics [2], Table 1 lists the imported amounts of coffee since 2003, showing that Taiwan imported about 7800 metric tons of coffee (both raw and pre-roasted beans) over the past two decades (2003–2022). By 2022, that number had increased to over 4300 metric tons. As a consequence, large amounts of coffee residue (CR), accounting for approximately 60,000 metric tons based on 60 wt% moisture and a residual ratio of 90 wt%, were generated in the commercial and industrial sectors after steam and/or hot water extraction. In general, direct treatment by thermal combustion was often performed at municipal solid waste (MSW) incineration plants in Taiwan. However, this waste management process not only reduces the energy efficiency of power generation, but also generates air pollutants. Due to its richness in lignocellulosic constituents, CR-derived biomass or spent coffee grounds (SCG) pose the potential for a variety of valorization approaches, including their use as raw materials for biofuel, fertilizers, and feeds, their energetic use as auxiliary fuels, and their use as value-added materials/products for industrial, environmental, pharmaceutical, and food applications, which have been reviewed in recent years. Campos-Vega et al. reviewed the value-added by-products of coffee fruit and bean processing in the coffee agro-industry [3]. Kovalcik et al. focused on the compositions of SCG and isolation methods for functional ingredients within SCG [4]. Mata et al. presented a bio-refinery approach for valorizing SCG [5]. Atabani et al. aimed at producing biofuels from SCG [6]. The potential of SCG as a commercial feedstock for primary products (e.g., lipids) and secondary products (e.g., bioethanol) was surveyed by Massaya et al. [7], McNutt [8], and Zabaniotou & Kamaterou [9]. Bann et al. summarized the various biorefinery routes to SCG valorization and its technoeconomic aspects in the context of a circular bio-economy [10]. The production of carbon materials (e.g., biochar, charcoal, or activated carbon) by using pyrolysis/activation processes has been reviewed in the literature [11–13]. Gebreeyessus revealed that SCG can yield food ingredients, pharmaceutical bioproducts, organic fertilizer, and a variety of biofuels [14]. Johnson et al. updated the various ways of reusing SCG published after 2017, focusing on biochar development for pollutant removal in connection with sustainable development goals (SDGs) No. 12, No. 7, and No. 6 [15].

Table 1. Variations in the imported amounts of coffee in Taiwan during the period of 2003–2022 [2].

Year	Imported Amount (Metric Tons)			
	Coffee (Not Roasted, Not Decaffeinated)	Coffee (Roasted, Not Decaffeinated)	Coffee (Not Roasted, Decaffeinated)	Coffee (Roasted, Decaffeinated)
2003	7602	1025	5	49
2004	9589	1195	21	73
2005	10,179	1220	12	66
2006	9423	1231	29	82
2007	12,298	1416	67	92
2008	9761	1673	66	99
2009	11,585	1686	24	100
2010	15,879	1843	48	117
2011	15,211	2258	88	129
2012	15,802	2509	56	77
2013	18,782	2846	108	65
2014	20,597	2997	103	76
2015	23,782	4433	199	128
2016	25,436	4656	122	141
2017	28,098	6666	104	637
2018	29,093	6519	155	41
2019	31,315	6306	74	24
2020	35,593	5787	105	22
2021	34,515	6251	77	23
2022	36,518	6345	83	32

Based on the literature survey, the production of porous biochar from CR has been reviewed in a previous report [11] and further studied in recent years [16–18]. Due to the lower carbonization temperatures, the pore properties of CR-based biochar products were not significant, resulting in less than 100 m^2/g based on the Brunauer–Emmett–Teller (BET) surface area [17,18]. In order to produce biochar from SCG for the construction of an electrode in the energy storage application, Andrade et al. set pyrolysis conditions to a high carbonization temperature of 850 °C and a long residence time of 60 min [16], yielding featured biochars with a high BET surface area and a micropore surface area of 492 m^2/g and 379 m^2/g, respectively. On the other hand, CR can be torrefied at lower pyrolysis temperatures (<360 °C) to produce a coal-like biochar [19–21], which is often used as an auxiliary fuel or alternative fuel due to its higher calorific value.

To evaluate the value-added valorization, previous studies described the pyrolyzation of exhausted coffee residue from the soluble coffee industry within a wide temperature range from 230 to 700 °C to prepare biochar fuels with different thermochemical properties and true densities [22,23]. Also, very little has been reported in the literature on the high pore properties of biochar products from coffee residue. More importantly, it was found from the literature review that CR was mostly obtained from food-processing plants and campus shops. Therefore, this study aimed at evaluating the thermochemical properties of coffee residues from commercial activities at convenience stores and mass retail stores and at producing highly porous biochar products at an elevated pyrolysis temperature (i.e., 850 °C) and a moderate residence time of 30 min. The pore properties and textural characteristics of the resulting biochar products were based on nitrogen (N_2) adsorption–desorption isotherms, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Furthermore, these results were discussed in connection with the prospects for high-value valorization of coffee residue from the commercial sector (convenience stores and mass retail stores) in Taiwan.

2. Materials and Methods

2.1. Materials

In this study, two starting materials (i.e., coffee residues) were produced on the same day and taken from local stores (Kaohsiung city, Taiwan), which included a well-known convenience store and a large mass retail store. As seen in Figure 1, the former was labeled CR-1, which seemed to contain less moisture. By contrast, the latter, which was labeled CR-2, seemed to be more viscous. Before performing the thermochemical property determinations and pyrolysis experiments, the as-received biomass samples were dried in the sun for about 6 h and then placed in an air-circulation oven for further drying at about 105 °C overnight. Finally, these dried samples were stored in the desiccator.

Figure 1. Starting materials (coffee residues) ((**left**): CR-1, from a convenience store; (**right**): CR-2, from a mass retail store).

2.2. Thermochemical Analyses of Coffee Residues

The proximate analysis, calorific value, and thermogravimetric analysis (TGA) of the biomass samples were determined by the standard methods of the American Society for Testing and Materials (ASTM). The calorific value (also referred to as the higher heating value) was obtained using an adiabatic bomb calorimeter (Parr Co., Moline, IL, USA). These thermochemical properties of the dried CR samples were relevant to the potential for reusing them as auxiliary or alternative fuels and producing biochar products properly. In this study, the TGA analysis was performed using a precision instrument (Shimadzu Co., Kyoto, Japan) at temperatures ranging from 25 °C (room temperature) to 900 °C at a heating rate of 10 °C/min, which was close to the operating conditions in the pyrolysis experiments. The elemental compositions were preliminarily determined using the EDS instrument (HORIBA Co., Osaka, Japan).

2.3. Pyrolysis Experiments

As mentioned above, other previous research mostly focused on the production of biochar (BC) fuels and soil amendments under mild pyrolysis conditions, thus yielding poor pore properties. In addition, the plant-based char products, which are used as natural edible colorants, must be produced at 800 °C and above according to regulatory requirements in Taiwan (further discussed in Section 4). According to the review results [24], the higher pore properties of the resulting biochar were generally produced at elevated pyrolysis temperatures of up to 800 °C. Therefore, the pyrolysis experiments in this study were specifically performed at an elevated temperature (i.e., 850 °C) and a moderate residence time of 30 min by using a vertical fixed-bed reactor. About 5 g of the dried CR biomass was used in each pyrolysis experiment, where the heating rate was set to about 10 °C/min. This resulted in a significant difference between the mass yields of BC/CR-1 (about 30 wt%) and BC/CR-2 (about 10 wt%). The resulting biochar products were further used to determine their pore properties and textural characteristics by using precision instruments.

2.4. Pore and Textural Analyses of Resulting Biochar Products

In order to determine the pore properties (i.e., the specific surface area, pore volume, and pore size) of the resulting biochar products, an accelerated porosimeter (Micromeritics Co., Norcross, GA, USA) was operated at 77 K (i.e., −196 °C). During this property analysis, the biochar sample of about 0.25 g was first degassed under a vacuum pressure of 1.33 Pa while heating to 200 °C for about 10 h. The data on the specific surface area included the calculation models of single-point, Brunauer–Emmett–Teller (BET), Langmuir, and *t*-plot micropore [25,26], which were based on a relative pressure (P/P_0) range between 0.05 and 0.30. However, the calculation of the BET surface area was adopted in the P/P_0 range from 0.05 to 0.10, with the aim of ensuring a parameter C value larger than zero in the linear correlation region (i.e., positive intercept of the y-axis). The total pore volume was generally given by the ratio of the volume of liquid nitrogen at saturation (i.e., P/P_0 of 0.995) per gram to liquid nitrogen density at 77 K (i.e., 0.808 g/cm^3). Concerning the micropore (a pore diameter or width less than 2.0 nm) properties, the micropore surface area and micropore volume were based on the *t*-plot method, using the Harkins & Jura equation for the evaluation of the multilayer thickness [26].

The microscopic structure on the surface of the resulting biochar products was observed by scanning electron microscopy (SEM) applying a 15 kV acceleration potential. In order to make the sample surfaces conductive, the dried CR and resulting biochar samples were coated with a gold (Au) film before scattering during the SEM observation. In addition, the elemental compositions of dried CR samples and CR-based biochar products on the surface were roughly determined by using energy dispersive X-ray spectroscopy (EDS) when observing the surface morphology by SEM.

3. Results

3.1. Thermochemical Properties of Coffee Residues

Prior to the determinations of the thermochemical properties of the dried CR samples, the moisture content of the raw samples was found to be 56.7 wt% and 67.7 wt% for CR-1 and CR-2, respectively. Table 2 lists the data on the proximate analysis and calorific value of the dried CR samples in triplicate. The CR biomass featured very low ash content (less than 2.0 wt%), thus yielding higher calorific values (about 27 MJ/kg). Therefore, this dried biomass can be used as an auxiliary/alternative fuel in biomass-derived fuel combustion systems. This result was consistent with elemental compositions having a high carbon content of 62–64 wt% and an oxygen content of 30–40 wt% according to the EDS analysis (not shown here). Figure 2 shows the thermal decomposition behaviors by thermogravimetric analysis (TGA) at 10 °C/min. The two CR samples clearly exhibited similar patterns. As with other lignocellulosic residues, the most significant peaks occurred in the pyrolysis temperature range of 250–450 °C, which should be indicative of the near devolatilization of lignocellulosic components at temperatures above 450 °C. In this regard, the resulting biochar products from the coffee residues in the pyrolysis experiments (850 °C) in this study should be fully carbonized and charred.

Table 2. Proximate analysis and calorific value of dried coffee residue (CR).

Property	Value [c]	
	CR-1	**CR-2**
Proximate analysis [a]		
Volatile matter (wt%)	81.73 ± 0.13	80.72 ± 0.11
Ash (wt%)	1.34 ± 0.08	1.93 ± 0.19
Fixed carbon [b] (wt%)	16.93	17.36
Calorific value (MJ/kg) [a]	27.00 ± 0.11	26.61 ± 0.57

[a] Mean ± standard deviation for three determinations. [b] By difference. [c] Dry basis.

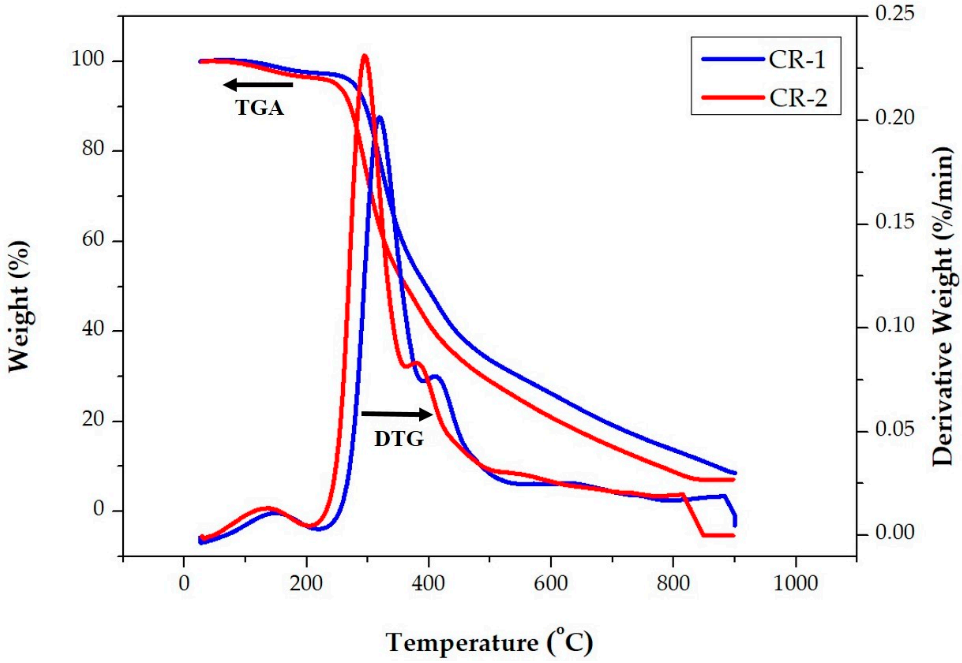

Figure 2. Thermogravimetric analysis/derivative thermogravimetry (TGA/DTG) curves of dried coffee samples (CF-1 and CF-2) at a heating rate of 10 °C/min.

3.2. Textural Characteristics of Resulting Biochar Products

Table 3 lists the main pore properties of the resulting biochar products (i.e., BC/CR-1 and BC/CR-2) in comparison with the study by Andrade et al. [16]. Clearly, the pore property values of the resulting biochar products were significantly larger than those in the literature [16–18]. For example, the values for the BET surface area and total pore volume in the BC/CR-1 sample were 783.60 m^2/g and 0.404 cm^3/g, respectively. Based on the literature survey, the largest pore properties of biochar from spent coffee grounds were 492 m^2/g and 0.238 cm^3/g [16]. Furthermore, these biochar materials are typical of microporous solids, in that significant micropore filling occurred at very low relative pressure ($P/P_0 < 0.05$, not shown here). The nitrogen adsorption process was complete at a P/P_0 of about 0.40. According to the isotherm classification by the International Union of Pure and Applied Chemistry (IUPAC), these materials should be classified as Type I isotherms [25,26]. On the other hand, the hysteresis loop can be seen from a P/P_0 of about 0.45 in the nitrogen adsorption–desorption isotherms. This was characteristic of mesoporous solids with Type IV isotherms, where capillary condensation occurred.

Table 3. Pore properties of the resulting CR-based biochar products compared to the study by Andrade et al. [16].

Pore Property	This Study		Andrade et al. [16]
	BC/CR-1	BC/CR-2	
Single point surface area (m^2/g, at P/P_0 of about 0.1 for BC/CF-1 and 0.3 for BC/CF-2)	799.00	688.92	- [d]
Langmuir surface area (m^2/g)	968.96	1066.45	-
BET surface area (m^2/g) [a]	783.60	825.13	492
t-plot micropore area (m^2/g) [b]	608.10	568.11	379
t-plot external surface area (m^2/g)	175.50	257.02	113
Single point adsorption total pore volume (cm^3/g, at P/Po of about 0.995)	0.404	0.386	0.238
t-plot micropore volume (cm^3/g) [b]	0.250	0.227	0.117
Average pore diameter (nm) [c]	2.060	1.870	-

[a] Based on a relative pressure range of 0.05–0.10 (4–5 points). [b] Obtained by using the *t*-plot method. [c] Roughly calculated from the ratio of the total pore volume to the BET surface area and multiplying by 4. [d] Not provided.

In order to observe the highly porous surface textures of the resulting biochar products, this study used scanning electron microscopy (SEM) at two different magnifications (i.e., ×500 and ×3000), as shown in Figure 3. The products exhibited a rigid, smooth surface at higher magnification (i.e., ×3000) due to the high degree of carbonization under severe pyrolysis conditions (850 °C and 30 min). When the SEM image was viewed at lower magnification (i.e., ×500), the biochar products displayed a highly porous surface texture similar to that of a honeycomb structure. On the other hand, the elemental compositions of the resulting biochar products on the surface were preliminarily determined by energy dispersive X-ray spectroscopy (EDS). Table 4 listed the average contents of the main elements, including carbon (C), oxygen (O), potassium (K), magnesium (Mg), and calcium (Ca). Compared to the contents of C and O (62–64 wt% and 30–40 wt%, respectively) in the starting biomass samples (Section 3.1), significant variations in the content of carbon and oxygen were observed in the resulting biochar products. This can be attributed to the release of oxygen-containing gases (e.g., CO_2, CO, H_2O) from the coffee residues during the carbonization process, thus causing a significant decrease in oxygen content and a moderate increase in carbon content. However, the content of potassium (K) in BC/CR-2 indicated an abnormal value, as seen in Table 4. It would be better to determine their real values by elemental analyzer (EA) and inductively coupled plasma optical emission spectrometry (ICP-OES).

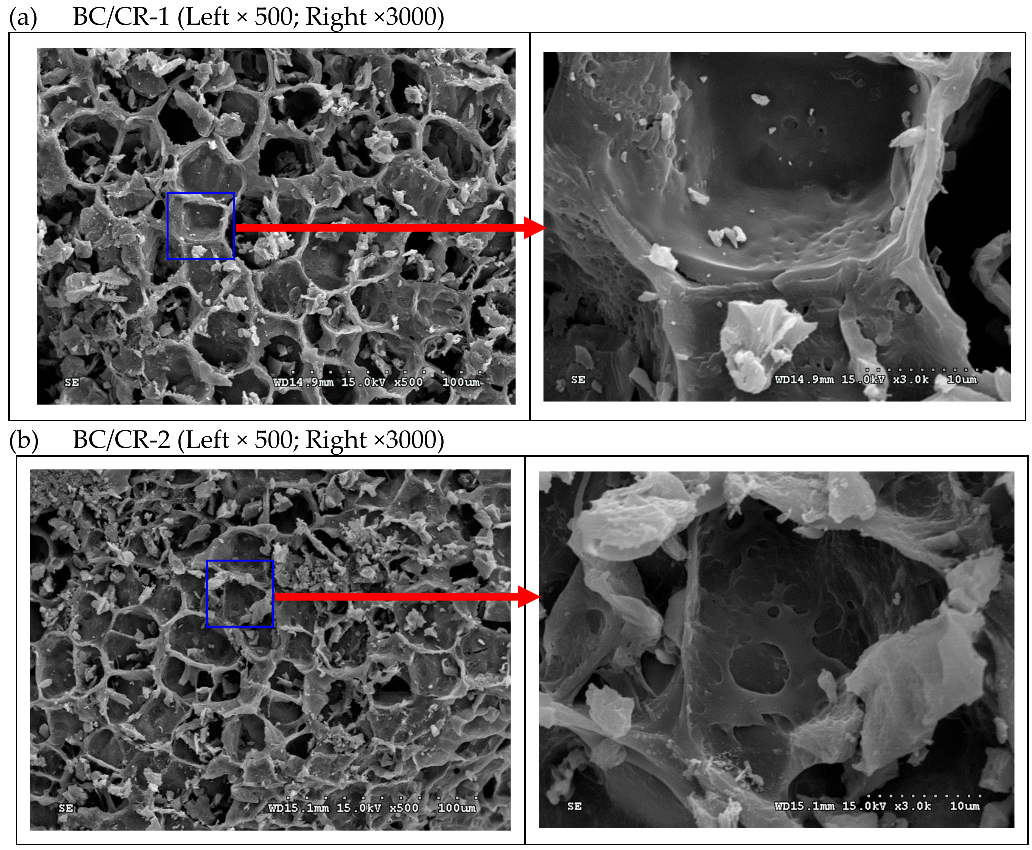

Figure 3. SEM images of biochar products; (**a**) BC/CR-1 and (**b**) BC/CR-2.

Table 4. Elemental contents of the resulting biochar products determined from EDS spectra.

Elemental Content (wt%)	BC/CR-1	BC/CR-2
Carbon (C)	84.77	64.77
Oxygen (O)	8.99	16.55
Potassium (K)	2.48	14.29
Magnesium (Mg)	1.67	2.52
Calcium (Ca)	2.09	1.87

4. Discussion

As mentioned above, a variety of valorization options of coffee residue or spent coffee grounds using physical, chemical, and biological methods have been reviewed in recent years. Among these approaches, reusing these materials as a renewable fuel and carbon material by pyrolysis could be the most promising option for application in a circular bio-economy (CBE) [12]. However, its economic success must be incorporated into current solid waste management strategies and policies. In Taiwan, the government recently focused on the reuse of plant-based residue and agricultural waste as a high-value bioresource in the production of biomass-based fuels and carbon materials. The subsequent sections will discuss prospects for possible valorization of coffee residue from the commercial sector in Taiwan based on the above-mentioned results and the high-value CBE principle.

4.1. Energy Use

In a previous report [27], Tsai et al. summarized the regulatory policies for promoting biomass-to-energy and solid recovered fuel (SRF). These sustainable waste management strategies aimed at achieving sustainable development goals (SDGs) and mitigating greenhouse gas (GHG) emissions. As listed in Table 3, the dried coffee residues from commercial shops had relatively high calorific values (about 27 MJ/kg), which were close to that of coal (e.g., lignite, anthracite) [28] and obviously larger than those of wood, herbaceous plants, and crop residues [29,30]. This result can be due to its residual oily fraction and the low ash and high lignocellulose content in the dried CR samples. However, high costs are likely to be associated with the collection of coffee residues from commercial shops and from thermal pretreatment for moisture removal before their direct energy use to produce SRF as an additive. To ensure the quality of SRF for reducing both fossil fuel consumption in industrial boilers as well as the resulting air pollutants, the central competent authority (i.e., the Ministry of Environment, MOENV) promoted the use of lignocellulosic residues (e.g., woody and crop residues) in the production of SRF. In this regard, coffee residue can be considered an excellent biomass energy source in accordance with the quality standards for SRF in Taiwan [27]. On the other hand, this biomass is a food waste with a high moisture and lignocellulose content. Therefore, it can be alternatively processed by anaerobic digestion (AD) for producing biogas and organic fertilizer under the regulatory policies of biomass-to-energy (or waste-to-power) and organic farming. The former was a joint venture by the MOENV and the Ministry of Economic Affairs (MOEA) under the feed-in-tariff (FIT) promotion. The latter was promulgated by the Ministry of Agriculture.

4.2. Precursor for Highly Porous Carbon Material

Concerning the high-value valorization of plant-based residue, the central competent authorities (i.e., Ministry of Agriculture and Ministry of Health and Welfare) jointly announced a regulation ("Sanitation Standards for Natural Edible Colorants") under the authorization of the Food Safety and Sanitation Act. Plant-based carbon has been listed as one of these natural edible colorants, which must be derived from lignocellulosic materials such as wood, cellulose, peat, coconut shell, and other fruit/crop husks. In addition, the production process must be performed at a carbonization temperature of 800 to 1000 °C. The specification limits (or standards) of mercury (Hg) and cadmium (Cd) in the plant-based carbon must be below 1 mg/kg. As listed in Table 3, the values of BET surface area in the resulting biochar products from coffee residue produced at 850 °C were significantly higher than those of biochar products in the literature [24], but slightly lower than those of commercial activated carbon products [31]. Therefore, the CR-based biochar products can be used as a natural edible colorant in the food industry and also as an excellent adsorbent and highly porous carbon material with high pore properties (i.e., BET surface area of about 800 m^2/g and total pore volume of about 0.4 cm^3/g).

5. Conclusions

A considerable amount of coffee residue is produced from commercial activities without valuable valorization, thus posing potential value for the production of carbon materials. Therefore, this study determined the thermochemical properties of two types of coffee residue from commercial activities and analyzed the pore properties of the resulting biochar products under severe pyrolysis conditions (i.e., 850 °C for 30 min). It was found that this biomass has a relatively high calorific value (about 27 MJ/kg, dry basis), which is close to the fuel properties of coal, but without the harmful contaminants (i.e., sulfur and mercury). Our findings also demonstrated that the resulting biochar products are highly porous carbon materials with excellent pore properties (i.e., a BET surface area of about 800 m^2/g and a total pore volume of 0.4 cm^3/g).

Based on the above-mentioned results and the high-value circular bio-economy promoted by the regulatory policies of Taiwan, the prospects for possible valorization of coffee residue from commercial shops were further addressed with an emphasis on the reuse of plant-based residue both as a high-value bioresource in the production of biomass-based fuels and as carbon materials. The former included solid recovered fuel (direct energy use by a combustion process) and biomass-to-power (indirect energy use by an anaerobic digestion process) under regulatory promotions such as feed-in-tariff (FIT). By contrast, the aim of the latter is to produce plant-based carbon (as natural edible colorants) based on the regulation of food safety and sanitation in Taiwan.

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

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