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Thermochemical Characterization of Rice-Derived Residues for Fuel Use and Its Potential for Slagging Tendency

Chi-Hung Tsai [1], Yun-Hwei Shen [1,*] and Wen-Tien Tsai [2,*]

[1] Department of Resources Engineering, National Cheng Kung University, Tainan 701, Taiwan; n48091089@gs.ncku.edu.tw

[2] Graduate Institute of Bioresources, National Pingtung University of Science and Technology, Pingtung 912, Taiwan

* Correspondence: yhshen@mail.ncku.edu.tw (Y.-H.S.); wttsai@mail.npust.edu.tw (W.-T.T.); Tel.: +886-6-2757575 (Y.-H.S.); +886-8-7703202 (W.-T.T.)

Abstract: Rice is the most important cereal in Asia. However, it also results in the generation of large quantities of rice-derived residues (i.e., rice straw and rice husk). Due to the residues richness in lignocellulosic components, they potentially have considerable value in material and/or energy production without illegal burning in open fields. This work focused on investigating the thermochemical properties and inorganic/metal element contents of rice straw and rice husk. The former included proximate analysis, calorific value, thermogravimetric analysis (TGA) and energy dispersive X-ray spectroscopy (EDS). The latter covered the ten elements most relevant to their slagging/fouling indices. The results showed that they are suitable for energy use as biomass fuels, but rice husk was superior to rice straw because of the high silica content in the rice husk and the significant contents of potassium, sulfur and phosphorus in the rice straw. Using several slagging and fouling indices, the evaluation results were also consistent with their contents of inorganic elements or oxides. To increase the fuel properties of rice-derived residues, they could be pretreated with alkaline leaching, thus causing lower emissions of particulates and reduced slagging tendency when co-firing them with coal in industrial boilers.

Keywords: rice straw; rice husk; thermochemical property; slagging evaluation

1. Introduction

It is well known that crop residue is a lignocellulosic biomass due to its richness in natural constituents, such as cellulose, hemicellulose and lignin [1]. It is the most important renewable feedstock (e.g., rice straw, rice husk), thus indicating considerably cheap, clean and environment-friendly (carbon-neutral) features as compared to fossil fuels such as coal [2]. As a result, there is increased interest in developing biomass-derived fuels for direct energy use [3–7] or converting them into higher energy density biofuels via thermochemical processes [8–11], including torrefaction [1,12,13], pyrolysis [1,14,15] and gasification [1,16,17]. Although the contents of sulfur and ash in lignocellulosic biomass are relatively lower than those of coal [1], the so-called slagging, fouling or agglomeration often causes challenges during direct energy use (i.e., combustion) and/or co-firing with coal in boilers and power plants [5–7].

Rice is the most abundant crop residue in Asia. It was estimated that the mass ratios of rice straw and rice husk to rice production were approximately 100% and 20%, respectively [10]. Due to its richness in lignocellulosic constituents and other nutrients, the biomass is currently reused as a variety of by-products or application fields [4,7,8,10,18–21]. Their industrial/agricultural reuses include surface retention (as mulch), soil amendment, poultry/livestock feed, composting, biofuel and so on. Undeniably, the open burning of rice residues (especially in rice straw) in fields is a common practice in China and India [22]. This traditional practice not only emits large amounts of greenhouse gases, such

as carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), but also generates other air pollutants, such as particulates (e.g., soot), halides (e.g., hydrogen chloride) and air toxics (e.g., dioxins/furans), thus causing deteriorating air quality [23]. Furthermore, the fire incidents from open burning have been a concern for public security and occupational safety [24]. In recent years, rice residues (especially in rice husk) for energy use (reused as solid fuels or for electricity generation) and/or carbon material (e.g., biochar) production have become more and more noted due to the fuel cost and climate change [25–29].

In Taiwan, the most abundant crop residues are rice straw and rice husk, accounting for an annual average value of approximately two million metric tons [30]. To understand their slagging tendencies for fuel use in boilers or gasifiers, this work aimed at characterizing their thermochemical properties, including proximate analysis, calorific value, thermogravimetric analysis (TGA), inorganic element content and scanning electron microscopy—energy dispersive X-ray spectroscopy (SEM–EDS) analysis. In addition, several commonly used indices were adopted to evaluate the slagging and fouling tendencies based on the contents of inorganic elements [31–34].

2. Materials and Methods

In this work, rice residues (i.e., rice straw and rice husk) were obtained from a local place rich in rice production (Puzi Township, Chiayi County, Taiwan), which is located in Southern Taiwan. Prior to the thermochemical characterization, these biomass samples were dried at approximately 100 °C for 24 h to achieve a stable weight on a dry basis within 0.5% of water loss. Figure 1 shows the different textures (a magnification of 500) on the surface of rice straw and rice husk using scanning electron microscopy (SEM). It shows that the morphological structure of the outer rice husk surface is well organized and corrugated in some places. However, it can be observed from the SEM micrograph ($\times$500) that many small and round bodies are randomly distributed in the epidermis.
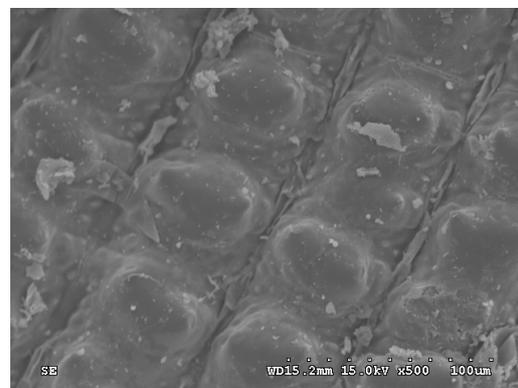
(**a**) Rice straw (RS)
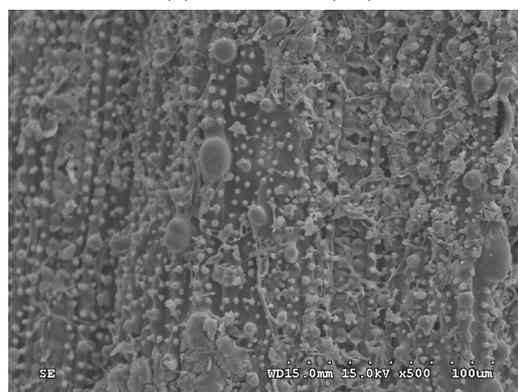
(**b**) Rice husk (RH)

Figure 1. SEM images ($\times$500) of (**a**) rice straw (RS) and (**b**) rice husk (RH).

The procedures, instruments and methods for determining the thermochemical properties of the rice straw and rice husk were identical to the previous studies [35,36]. In this work, the thermochemical characterization covered proximate analysis, calorific value, inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis for inorganic elements (i.e., silicon, potassium, sodium, magnesium, calcium, titanium, iron, aluminum, sulfur and phosphorus), TGA, and SEM–EDS. Herein, the determinations of inorganic elements were obtained by using an ICP-OES instrument (Model: Agilent 725 ICP-OES; Agilent Co., Santa Clara, CA, USA). The TGA instrument (Model: TGA-51; Shimadzu Co., Tokyo, Japan) was operated in the temperature range of 25 to 1000 °C at the heating rates of 5, 10, 15 and 20 °C/min. The analyses with SEM (Model: S-3000N; Hitachi Co., Tokyo, Japan) and EDS (Model: 7021-H; HORIBA Co., Osaka, Japan) were used to observe the microstructural structures and elemental compositions on the surface of the samples.

3. Results

3.1. Thermochemical Property of Rice Residues

Concerning the thermochemical property of the rice residues, they are listed in Tables 1–3, which are discussed in the following subsections.

Table 1. Proximate analysis and calorific values of rice straw (RS) and rice husk (RH).

Property	RS	RH
Proximate analysis [a,c]		
Ash (wt%)	9.48 ± 0.4	12.11 ± 0.1
Volatile matter (wt%)	74.29 ± 0.4	71.35 ± 0.8
Fixed carbon [b] (wt%)	12.07 ± 0.2	8.13 ± 0.1
Calorific value (MJ/kg) [a,c]	16.94 ± 0.21	16.05 ± 0.46

[a] Mean ± standard deviation for three determinations. [b] By difference. [c] The values were determined with a dry sample (approximately 0% water contained).

Table 2. Contents of relevant inorganic elements of rice straw (RS) and rice husk (RH).

Inorganic Element [a]	RS	RH	Method Detection Limit (ppm)
Silicon (Si)	0.265 wt%	4.987 wt%	0.70
Potassium (K)	0.486 wt%	0.582 wt%	0.90
Sodium (Na)	ND [b]	73.56 ppm	0.10
Magnesium (Mg)	425.7 ppm	287.3 ppm	0.12
Calcium (Ca)	612.9 ppm	683.9 ppm	0.40
Titanium (Ti)	ND	4.97 ppm	0.10
Iron (Fe)	ND	96.42 ppm	0.10
Aluminum (Al)	36.63 ppm	66.60 ppm	0.20
Sulfur (S)	693.1 ppm	343.9 ppm	0.20
Phosphorus (P)	687.1 ppm	289.3 ppm	0.10

[a] On a dry basis. [b] Not detectable.

Table 3. Contents and percentages of mineral oxides in rice straw (RS) and rice husk (RH).

Mineral Material [a]	RS	RH
Potassium oxide (K_2O)	0.585 wt% (35.54%) [c]	0.701 wt% (5.99%)
Silicon dioxide (SiO_2)	0.567 wt% (34.45%)	10.668 wt% (91.17%)
Sulfur trioxide (SO_3)	1731.5 ppm (10.52%)	859.1 ppm (0.73%)
Phosphorus pentoxide (P_2O_5)	1574.5 ppm (9.57%)	663.0 ppm (0.56%)
Calcium oxide (CaO)	857.6 ppm (5.21%)	956.9 ppm (0.82%)
Magnesium oxide (MgO)	706.0 ppm (4.29%)	476.5 ppm (0.41%)
Aluminum oxide (Al_2O_3)	69.2 ppm (0.42%)	125.8 ppm (0.11%)
Ferric oxide (Fe_2O_3)	ND [b] (0.00%)	137.8 ppm (0.12%)

Table 3. *Cont.*

Mineral Material [a]	RS	RH
Sodium oxide (Na$_2$O)	ND (0.00%)	99.2 ppm (0.08%)
Titanium dioxide (TiO$_2$)	ND (0.00%)	6.7 ppm (0.01%)

[a] On a dry basis. [b] Not detectable. [c] The values in parentheses denote the percentages of metal oxides in ash.

3.1.1. Proximate Analysis

The proximate analysis is often used to determine the constituent classes of a fuel sample. Obviously, the volatile matter contents of rice residues (i.e., 74.29 wt% and 71.35 wt% for rice straw and rice husk, respectively, on a dry basis) were close to those of the reports [37–41], indicating a significant release of the condensable and non-condensable vapors from the lignocellulosic constituents of the biomass sample. Thus, its amount depends on the temperature to which it is heated because the biomass samples may contain appreciable amounts of volatile alkali materials with lower melting points. According to the standard reference [42], it showed that the melting points of potassium oxide (K$_2$O) and phosphorus pentoxide (P$_2$O$_5$) are 350 °C (decomposition) and 340 °C, respectively. The ash content represents the inorganic minerals left after the sample is completely burned under the controlled combustion process. It was found that the ash content of rice straw is lower than that of rice husk, thus resulting in the relatively higher contents of volatile matter and fixed carbon in the former. In this work, the ash content of rice husk (i.e., 12.11 wt%) was close to that (i.e., 14.93 wt%) reported in the previous study [43]. Concerning the slagging or fouling in the industrial boilers or gasifiers, the contents of alkali metals (e.g., potassium) in the ash may play a significant role in the energy use of rice residues, which will be further addressed in the subsequent section.

3.1.2. Calorific Value

The calorific value (also called heating value) of biomass is a measure of the energy released when it is completely combusted in an adequate oxygen atmosphere. Table 1 also lists the calorific values of rice straw and rice husk, showing 16.94 MJ/kg and 16.05 MJ/kg, respectively. It should be noted that the data in Table 1 refer to gross calorific value (also called higher heating value) because they were determined with a so-called bomb calorimeter. Compared to most crop residues and biomass fuels such as wood [1], they are relatively low because rice residues have high ash contents. On the other hand, these rice residues are mainly composed of lignocellulosic components with high oxygen content, causing lower calorific values in comparison with most fossil fuels such as coal [33,44].

3.1.3. Inductively Coupled Plasma Analysis for Inorganic Elements

In this work, the contents of inorganic elements were obtained by using inductively coupled plasma-optical emission spectrometry (ICP-OES) [35]. As listed in Table 2, the primary inorganic elements in the ash are silicon (Si), potassium (K), magnesium (Mg), calcium (Ca) and phosphorus (P). Less amounts of sodium (Na), titanium (Ti), iron (Fe) and aluminum (Al) are also present in the rice residues. Table 3 further summarizes the contents and percentages of inorganic elements as oxides in rice straw and rice husk using the data in Table 2. With regards to the compositions (as oxides) in the ash derived from the rice residues, the rice straw ash mainly contained SiO$_2$ (34.45%), K$_2$O (35.54%), SO$_3$ (10.52%) and P$_2$O$_5$ (9.57%), but the rice husk ash consisted mostly of SiO$_2$ (91.17%). In the present study, the SiO$_2$ content in the rice straw ash was significantly lower than that of the reports [37–41], indicating a high variance in the chemical characterization of the lignocellulosic biomass, even for the same crop species.

3.1.4. Elemental Analysis

In this study, the elemental contents on the surface of the rice residues were preliminarily analyzed with energy dispersive X-ray spectroscopy (EDS) while observing the

textural structure with scanning electron microscopy (SEM). The basic principle of EDS is based on the generation of X-rays from a specimen through the electron beam associated with the SEM analysis. The X-rays are generated according to the characteristic energy and wavelength of the elements present in the sample. Therefore, the observation of peaks in the spectrum can determine the elemental contents of the specimen. The dominant elements (not shown here) were carbon (C) and oxygen (O) with small amounts of silicon (Si) and potassium (K). The high oxygen and carbon contents were associated with the lignocellulosic constituents. The chemical formula of cellulose and hemicellulose can be represented by $(C_6H_{10}O_5)_n$ and $(C_5H_8O_4)_n$, respectively [1]. Therefore, the theoretical contents of carbon (C), oxygen (O) and hydrogen (H) in the lignocellulosic residues are approximately 45 wt%, 49 wt% and 6 wt%, respectively. Due to the hydrogen content not being obtained with EDS, it is better to determine the contents of organic elements using an elemental analyzer (EA). In the EA instrument, a sample with a known weight is fully combusted to decompose it into gases (i.e., H_2O, CO_2). These combustion products are separated from each other and then analyzed to quantify the elemental contents by comparison with the standards.

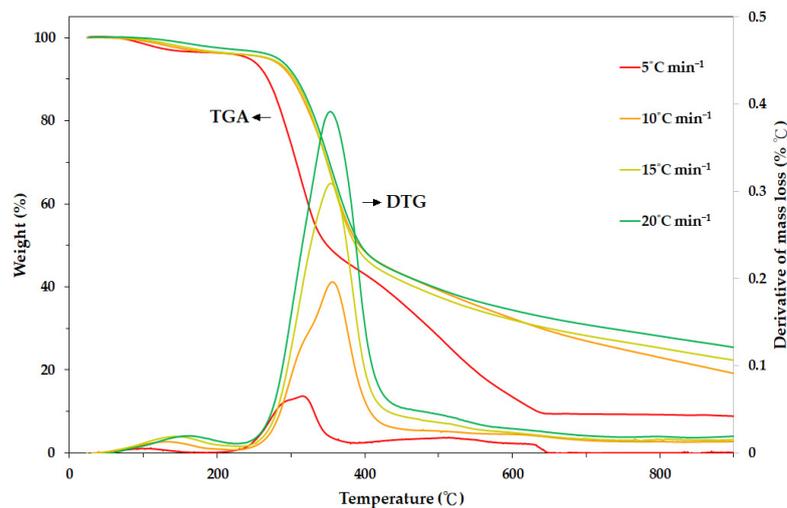### 3.2. Thermogravimetric Analysis (TGA) of Rice Residues

The TGA curves of the rice residues at four heating rates (i.e., 5, 10, 15 and 20 °C/min) up to a temperature of 900 °C under a nitrogen flow of 50 cm^3/min are depicted in Figure 2. The derivative of the resulting TGA (also abbreviated DTG) is indicative of the conversion rate, thus showing several peaks corresponding to the different thermal decomposition processes, which can be associated with the lignocellulosic constituents of the biomass. Obviously, these TGA/DTG curves for the rice straw and rice husk showed similar patterns. Below 200 °C, the initial drying and devolatilization of the biomass samples occurred. As the temperature was raised, significant weight loss was observed in the temperature range of 200–400 °C. There are two peaks, including a plateau (or shoulder) located at the lower temperature region. This region represented the thermal decomposition of hemicellulose. However, the second peak, located at the higher temperature region, often represented that of cellulose. Above approximately 400 °C, most of the devolatilization should be caused by the lignin decomposition. The order of thermal stability should be followed by hemicellulose (low), cellulose and lignin (high) [45]. On the other hand, the higher the heating rate from 5 to 20 °C/min, the more the curves were shifted to higher temperature values. This is typical behavior for effects caused by heat transfer processes. This was due to the non-conductive feature of the lignocellulosic biomass, causing the thermal degradation delay as the heating rate increased. Depending on the biomass sample and heating rate, the peaks of the rice straw (shown in Figure 2) showed major mass loss in the temperature range of 336–379 °C (approximately) as compared to those of the rice husk in the temperature range of 336–357 °C (approximately).

To specify the characteristics of the biomass sample from the TGA curve, three important temperatures can be identified from the DTG curve [46]. The ignition (onset decomposition) temperature referred to the temperature at which the sample began to be decomposed (or burnt). This temperature could be roughly determined by the intersection of the two tangents. The first tangent was parallel to the abscissae axis of the TGA curve, whereas the second tangent was determined at the point of the maximal weight loss rate. The maximum peak temperature could be identified by using a DTG curve, presenting the maximal weight loss rate of the biomass sample. The burnout temperature presented the point at which the sample weight loss had finished by defining an approximate baseline reached. Table 4 lists the data on the ignition temperature, the maximum peak temperature and the burnout temperature, showing the shift toward higher temperatures with an increasing heating rate. Similar observations have been reported in the previous works [35,36] and other studies [47,48]. This shifted feature was attributed to the non-conductive characteristics (i.e., low heat transfer coefficient) of the biomass sample, leading to the delay of thermal degradation (not enough time to heat and further decompose the sample) at the

higher heating rate. In this regard, these key points were shifted toward higher temperature values as the heating rates increased from 5 to 20 °C/min.
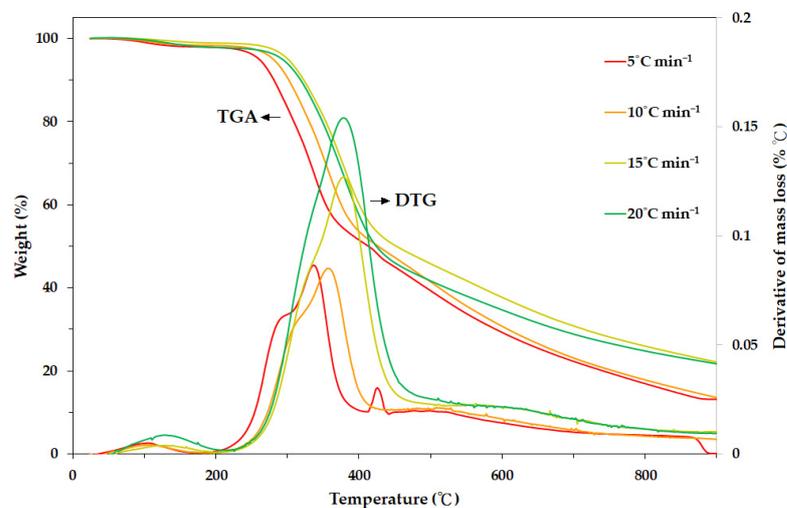
(**a**) Rice straw (RS)

(**b**) Rice husk (RH)

Figure 2. TGA/DTG curves of (**a**) rice straw (RS) and (**b**) rice husk (RH) at 5, 10, 15 and 20 °C/min.

Table 4. Thermogravimetric analysis (TGA) characterization of rice straw (RS) and rice husk (RH).

Biomass/Heating Rate (°C/min)	Ignition Temperature (°C)	Maximum Peak Temperature (°C)	Burnout Temperature (°C)
Rice straw (RS)			
5	268	336	372
10	282	358	388
15	297	377	425
20	304	379	436
Rice husk (RH)			
5	268	336	357
10	290	352	393
15	298	355	395
20	303	357	399

4. Discussion

As mentioned above, rice straw and rice husk presented a relatively good thermo-chemical characteristic, suggesting that they are suitable for energy use as biomass fuels. However, the target rice residues contained main inorganic elements (including silicon, potassium, magnesium, calcium, sulfur and phosphorus) and higher ash contents in comparison with other crop residues. These components could lead to serious slagging, fouling and corrosion in industrial utilities such as a boiler [1,49,50]. According to the classification by Vassilev et al. [38], these inorganic compositions can be classified into the following groups:

- Acidic ash elements with high melting points (e.g., Si, Al, Fe, Na, Ti).

For example, the melting points of silicon (Si) and silicon dioxide (SiO_2) are approximately 1410 °C and 1710 °C, respectively.

- Base ash elements with less volatiles at high temperature (e.g., Ca, Mg).

In the case of calcium and calcium oxide, their melting points are as high as 842 °C and 2572 °C, respectively.

- Base ash elements with more volatiles at high temperature (e.g., K, P, S).

For instance, the melting points of potassium (K) and potassium oxide (K_2O) are approximately 64 °C and 380 °C, respectively.

As shown in Table 3, it was found that the percentages of potassium (K), sulfur (S) and phosphorus (P) or their oxides were significant in rice straw ash in comparison with rice husk ash. Although the sulfur content was significantly lower than that of coal, it could result in the installation of a flue gas desulfurization (FGD) system for the removals of sulfur oxides (SOx) when reusing rice straw as a solid fuel. In addition, this biomass residue could pose high slagging and corrosion tendencies due to these elements relevant to more volatiles at high temperature. In contrast, an extremely high silica (SiO_2) content is a characteristic of rice husk ash with a lower amount of potassium oxide (K_2O), thus indicating a relatively lower slagging tendency. To further demonstrate the potential for slagging and fouling tendencies in a coal (or biomass)-fired system, several slagging and fouling indices have been developed as listed in Table 5 [31–34]. Based on the data in Table 3, Table 5 also shows the evaluation results of the slagging and fouling tendencies for rice straw and rice husk. Obviously, the latter was superior to the former based on the high silica content in the rice husk due to its high melting point and lower slagging indices ($R_{B/A}$ = 0.08 and Fu = 0.06). In this work, the rice straw contained high oxide amounts of potassium (K) and calcium (Ca) as listed in Table 3, suggesting that this biomass should pose a moderate–severe slagging tendency in the heat exchanger surfaces of boilers during combustion based on the higher slagging indices ($R_{B/A}$ = 1.29 and Fu = 0.76). Although rice straw and rice husk are high calorific biomass fuels, the former may pose a potential slagging risk in industrial boilers or biomass/coal co-firing power plants based on the results by using these slagging indices. In addition, it could result in the installation of a flue gas desulfurization (FGD) system for controlling sulfur oxides (SOx) and a high-efficiency filtration (e.g., baghouse filter or electrostatic precipitator) system for particulate removal when combusting rice straw and/or rice husk.

Table 5. Slagging tendencies of rice straw (RS) and rice husk (RH) evaluated in the present study.

Index	Expression (wt%/wt% or wt%) [a]	Slagging Degree		Slagging Tendency	
				Rice Straw	Rice Husk
Base/acid ratio ($R_{B/A}$)	(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)/ (SiO_2 + Al_2O_3 + TiO_2)	<0.206 0.206–0.40 >0.40	Slight Moderate Severe	1.29 (Severe)	0.08 (Slight)

Table 5. *Cont.*

Index	Expression (wt%/wt% or wt%) [a]	Slagging Degree		Slagging Tendency	
				Rice Straw	Rice Husk
Fouling index (Fu)	$R_{B/A} \times (K_2O + Na_2O)$	<0.6 0.6–40 >40	Slight Moderate Severe	0.76 (Moderate)	0.06 (Slight)
Slagging index (R_S)	$R_{B/A} \times S$ [b]	<0.6 0.6–2.0 2.0–2.6 >2.6	Slight Moderate Severe Highly severe	0.09 (Slight)	0.003 (Slight)
Slag viscosity index (G)	$SiO_2/(SiO_2 + Fe_2O_3 + CaO + MgO) \times 100$	72–80 65–72 50–65	Slight Moderate Severe	78 (Slight)	99 (Slight)

[a] Sources [31–34]. [b] Percentage of sulfur in dry biomass fuel.

5. Conclusions

Rice residues (i.e., rice straw and rice husk) may be the most important crop residues in many Asian countries. Therefore, there is increased interest in reusing them as biomass-derived fuels for direct energy use due to their carbon-neutral feature. In this work, it was found that the contents of volatile matter in the rice residues varied within a narrow range of 70 to 75 wt% (dry basis) based on the results of proximate analysis and thermogravimetric analysis (TGA). Though they had high ash contents ranging from 9.5 wt% to 12.1 wt%, they are suitable for energy use as biomass fuels based on the other thermochemical characteristics of rice straw and rice husk, including higher calorific values (over 16 MJ/kg) and lower inorganic element contents determined with inductively coupled plasma (ICP) and dispersive X-ray spectroscopy (EDS). As compared to the significant contents of potassium (K), sulfur (S) and phosphorus (P) in the rice straw, rice husk was superior to rice straw because of the high silica (SiO_2) or silicon (Si) content in the rice husk due to its high melting point and lower slagging indices (base/acid ratio = 0.08 and fouling index = 0.06). In this regard, it could result in the installation of a flue gas desulfurization (FGD) system for controlling sulfur oxides (SO_x) and a high-efficiency filtration (e.g., baghouse filter or electrostatic precipitator) system for particulate removal when combusting rice straw and/or rice husk. On the other hand, the evaluation results by using several slagging and fouling indices were also consistent with their contents of inorganic elements or their oxides in the rice straw ash and rice husk ash.

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