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Torrefaction of Rice Husk using TG-FTIR and its Effect on the Fuel Characteristics, Carbon, and Energy Yields

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A torrefaction testing method using TG-FTIR is presented, ensuring accuracy of torrefaction temperature and time. Torrefaction experiments of rice husk were performed at different temperatures (200, 230, 260, and 290 °C) for 30 min. The effect of torrefaction on the fuel characteristics was studied. Yields of carbon and oxygen, as well as solid and energy, were also considered. TG-FTIR analysis showed that in the depolymerization stage of the torrefaction process, CO_2 characteristic peaks appeared, while those of carbonyl compounds and aromatic hydrocarbons were weaker. In the devolatilization stage, the characteristic peaks of CO_2 and H_2O were significant. Meanwhile, carbonyl compounds, aromatic hydrocarbons, and phenols were gradually produced. After that, each absorption peak gradually became weaker. After torrefaction at 290 °C, more than 76.6% of energy was retained in torrefied rice husk, while the solid yield was only 65.6%. 1.8%~52.2% of oxygen in rice husk was released in the torrefaction temperature range of 200 °C to 290 °C. Torrefaction increased the heating value, reduced the oxygen content, and improved the storability, which indicates that torrefaction is an effective way to improve the properties of rice husk.

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INTRODUCTION

Biomass is an important renewable energy and is widely used in thermo-chemical conversion for solid, liquid, and gas fuel production. However, the undesirable qualities of raw biomass, such as high moisture content, low energy density, storage difficulties, poor grinding performance, and dispersed production locations, limit its utilization (van der Stelt *et al.* 2011; Wannapeera *et al.* 2011; Bates and Ghoniem 2013; Chen *et al.* 2012a, 2014a). When biomass is heated to a temperature between 200 and 300 °C in an inert atmosphere environment, moisture and part of the light volatile matter in the biomass are released. This moderate thermal treatment, known as biomass torrefaction, has been shown to effectively improve the quality of biomass raw materials (Chen *et al.* 2011c; Chew and Doshi 2011; Ren *et al.* 2013b; Wannapeera and Worasuwannarak 2012). It can also reduce the high costs of the transport, treatment, and storage of biomass, as well as promote the further development of biomass utilization technology (Batidzirai *et al.* 2013; Svanberg *et al.* 2013). In recent years, the torrefaction of biomass has attracted wide attention.

Biomass torrefaction is a complex low-temperature pyrolysis process. Thermogravimetric analysis (TG) coupled with Fourier transform infrared spectrometry (FTIR) technology is a very useful tool for biomass pyrolysis study, because not only can it obtain mass loss characteristics with temperature but also realize the exact qualitative identification of volatile gas components in real time (Meng *et al.* 2013). Although TG has been used in many studies of biomass torrefaction, there are few reports available in the literature regarding torrefaction of rice husk using TG-FTIR.

In addition, the establishment of the torrefaction conditions in TG or TG-FTIR is very important for torrefaction study. Many previous studies have adopted a test method of temperature programming using TG; that is, biomass samples did not directly or quickly reach the required torrefaction temperature, but first experienced a temperature programming process, which usually took 10 to 30 min to reach the torrefaction temperature (Eseltine *et al.* 2013; Ren *et al.* 2013a; Rousset *et al.* 2013; Sabil *et al.* 2013). However, this testing procedure is debatable, and probably not suitable for TG-FTIR, because decomposition reactions occurred during the temperature programming period; as a consequence, the volatile matter detected by FTIR in this period were not the volatile matter released by the biomass at the torrefaction temperature. This may lead to remarkable errors in the determination of torrefaction time and torrefaction mechanism analysis.

The objectives of this study are to present a torrefaction testing method using TG-FTIR, ensuring accuracy of torrefaction temperature and torrefaction time, and to determine the effect of torrefaction on the fuel properties, solid and energy yields, as well as carbon and oxygen yields of torrefied rice husk. In this study, the torrefaction experiments were repeated many times to obtained enough sample for fuel analysis use. The fuel characteristics, such as proximate analysis, ultimate analysis, heating value, and hydrophobic properties, were studied.

EXPERIMENTAL

Materials

The material used in this study was rice husk, which was selected from suburb of Hefei city. The rice husk was screened into a particle size of 40 to 60 mesh, and then dried for 6 h at 110 °C for experiments use. The contents of hemicellulose, cellulose, and lignin in rice husk were 40.1%, 20.3%, and 15.1%, respectively, as determined by the Van Soest method. In this study, RH, DRH, and TRH-X stood for the raw rice husk (moisture content 9.5% on dry basis), the dried rice husk, and the torrefied rice husk (X indicating torrefaction temperature), respectively.

TG-FTIR Analysis of Torrefaction Process

The torrefaction experiments were performed using a thermogravimetric analyzer (TGA Q5000IR, TA Instrument, USA) connected to a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Scientific, USA). Unlike some other TG-FTIRs, the TGA Q5000IR has a new infrared furnace that ensures precise temperature control capacity and can achieve a heating rate as high as 500 °C/min (Chen *et al.* 2013). The samples were rapidly heated from room-temperature to the torrefaction temperature, and then maintained for 30 min.

For each test, an accurately weighed 20 mg sample was used, and the flow rate of the carrier gas (N_2, purity > 99.99%) was maintained at 70 mL/min. The transfer line connecting the TGA and FTIR was heated at a constant temperature of 200 °C to avoid condensation of the volatile matter. FTIR online analysis of the volatiles and the IR spectra were recorded between 4000 cm^{-1} and 1000 cm^{-1}. A computer connected to the TGA and FTIR automatically recorded the experimental results for simultaneously analyzing the volatile products with corresponding TGA data. After the experiment, nitrogen was continually bowed for 30 min to remove the volatiles in FTIR.

In this study, the torrefaction temperatures were chosen as 200, 230, 260, and 290 °C, and the torrefaction time was 30 min. In order to analyze the fuel properties, carbon and energy yields of rice husk, the torrefaction experiments under the same conditions were repeated more than 15 times to obtained enough samples, as one experiment can only obtained limited samples of 10~15mg.

Analysis of Fuel Properties

Proximate analysis was performed using a thermogravimetric analyzer (TGA Q5000IR, TA Instrument, USA) according to the literature (Munir *et al.* 2009; Aqsha *et al.* 2011). In brief, the samples (10 mg) were heated at a rate of 10 °C/min from room temperature to 110 °C, and held for 10 min to dry the samples (under N_2, 100 mL/min). The samples were then heated from 110 °C at a heating rate of 20 °C/min to 900 °C (under N_2) and held for 7 min to obtain the mass loss associated with volatiles release. Then, the blowing gas was changed from N_2 to air, and then air (100 mL/min) was introduced into the furnace chamber to make the samples combustion. The mass loss associated with this is the fixed carbon. The remaining material after combustion is the ash.

Ultimate analysis was carried out using an elemental analyzer with an instrument precision of <0.5% (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference: O(%) =100% - C(%) - H(%) - N(%) - S(%) - Ash(%).

The higher heating value was computed using Eq. 1, as developed by Friedl *et al.* (2005). The letters (C, H, and N) in Eq. 1 present the percentage of carbon, hydrogen, and nitrogen as determined by ultimate analysis.

$$HHV = 1.87C^2 - 144C - 2802H + 63.8C \times H + 129N + 20147 \tag{1}$$

The equilibrium moisture content (EMC) of torrefied rice husk was measured by a constant temperature and humidity incubator with temperature precision of ≤2 °C and humidity precision of ±4% R.H. (SPX-250C, Shanghai Boxun, China). The torrefied samples (100 mg) were exposed to an environment with constant humidity and temperature (30 °C, relative humidity 50%) over a long period of time (more than 7 days). Then, 10 mg of the sample was heated using the thermogravimetric analyzer (TGA Q5000IR, TA Instrument, USA) from room temperature to 110 °C at a heating rate of 10 °C/min, and then held for 10 min to obtain the mass loss associated with moisture release. This moisture content was considered to be the EMC.

FTIR analysis of the sample was carried out using a Fourier transform infrared spectrometer (Nicolet 6700, ThermoScientific Instrument, USA) by the KBr tablet method. The wavenumber was in the range of 4000 cm^{-1} to 1000 cm^{-1}.

Solid Yield and Energy Yield

Solid yield and energy yield are two important parameters used to evaluate the effects of biomass torrefaction. The definition of solid yield and energy yield are as follows:

$$Y_{\text{mass}} = \frac{M_{\text{product}}}{M_{\text{feed}}} \times 100\% \tag{2}$$

$$Y_{\text{energy}} = Y_{\text{mass}} \frac{HHV_{\text{product}}}{HHV_{\text{feed}}} \tag{3}$$

where Y_{mass} and Y_{energy} stand for solid yield and energy yield, respectively. The subscripts "feed" and "product" stand for the dried rice husk and torrefied rice husk, respectively.

Carbon Yield and Oxygen Yield

Elemental yield values were calculated as follows,

$$Y_{\text{carbon}} = \frac{M_{\text{carbon in product}}}{M_{\text{carbon in feed}}} \times Y_{\text{mass}} \times 100\% \tag{4}$$

$$Y_{\text{oxygen}} = \frac{M_{\text{oxygen in product}}}{M_{\text{oxygen in feed}}} \times Y_{\text{mass}} \times 100\% \tag{5}$$

where Y_{carbon} and Y_{oxygen} stand for carbon yield and oxygen yield, respectively. The terms $M_{\text{carbon in product}}$, $M_{\text{carbon in feed}}$, $M_{\text{oxygen in product}}$, and $M_{\text{oxygen in feed}}$ are the carbon mass in the torrefied rice husk, carbon mass in the dried rice husk, oxygen mass in the torrefied rice husk, and oxygen mass in the dried rice husk, respectively. These data can be obtained from ultimate analysis.

RESULTS AND DISCUSSION

Torrefaction Analysis using TG-FTIR
Evaluation of torrefaction conditions

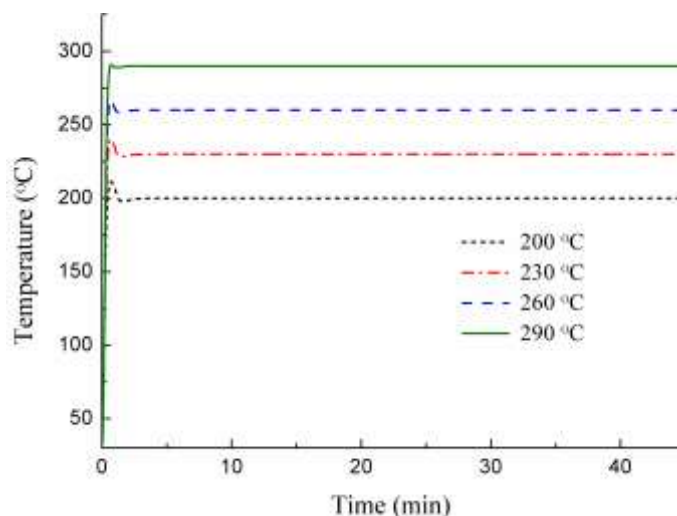The temperature profiles of rice husk in TG are illustrated in Fig. 1.

Fig. 1. Temperature profiles of sample in TGA under different torrefaction conditions

The heating rate of material was very rapid. The time needed to heat the sample to the torrefaction temperatures (200, 230, 260, and 290 °C) was less than two minutes, after which the sample's temperature did not change until the experiment end. Thus, it was clear and easy to confirm the torrefaction time, as the heating period was very short.

If the heating period of sample heated to the torrefaction temperature is as long as 10 to 30 min, it is difficult to precisely determine the torrefaction time and to perform products analysis. On the one hand, such a sample does not reach the torrefaction temperature, thus this period (about 10 to 30 min) should not be simply included in the torrefaction process. On the other hand, this period cannot be ignored because the structure of biomass has been changed and the decompose reactions have occurred. In the present study, the testing method, based on the rapid heating of TG and its precise temperature control capability, can avoid the controversy of torrefaction time and the inaccurate analysis of physical and chemical properties of biomass by FTIR.

TG-DTG analysis of torrefaction process

Figure 2 shows the TG and DTG curves of rice husk during torrefaction. Torrefaction, as a thermal treatment, contains the depolymerization, devolatilization, and carbonization stages. The rice husk was dried, and thus there was not an obvious water loss process (in TG curves) and water loss peak (in DTG curves). With increasing torrefaction temperature, the mass loss rate of rice husk increases, and the corresponding time of the maximum mass loss rate gradually delays.
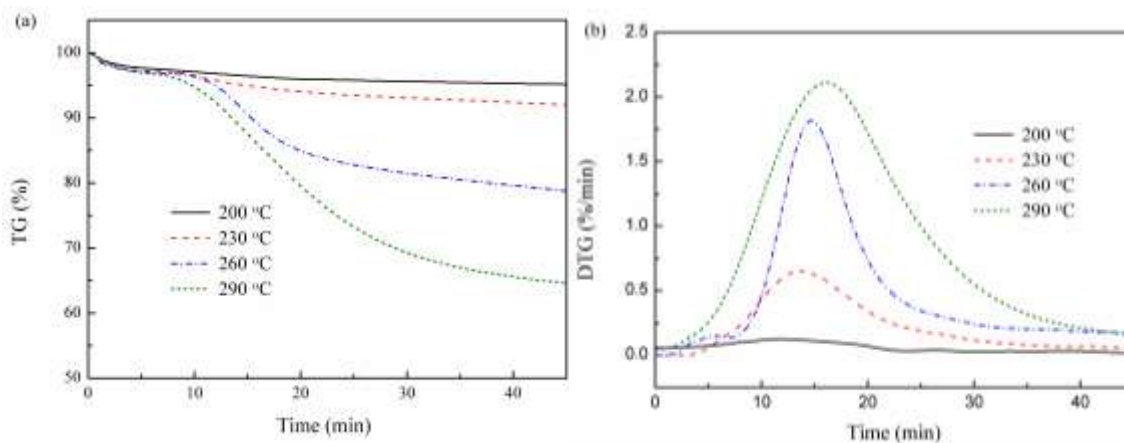

Fig. 2. TG (a) and DTG (b) curves of rice husk under different torrefaction conditions

TG-FTIR analysis of torrefaction process

Figure 3 shows the infrared spectrogram of volatile matter corresponding to the maximum mass loss rate of rice husk under different torrefaction temperatures. CO_2 and H_2O show relatively high absorption peaks in Fig. 3. A part of organic carbohydrate (C=O) was also detected. According to the literature, they could be substances such as acetic acid, ketones, furans, *etc.* (Chen *et al.* 2011a). Because of their low concentrations, CH_4 and other gases were not detected. With increasing torrefaction temperature, the absorption peaks of other substances in the volatile component such as phenols, aromatic hydrocarbon, carbonyl compound, and low hydrocarbon were gradually enhanced.

During torrefaction, the dehydration reactions substantially destroy hydroxyls and form a non-polar unsaturated structure, leading to the difficult formation of hydrogen

bonds by fiber structure and water. Moisture is difficult to absorb by torrefied rice husk, and the torrefied rice husk shows hydrophobic properties. The infrared spectrogram shows that absorption peaks corresponding to the lignin pyrolysis products appeared in succession, indicating that the tight fiber structure of rice husk was partly damaged.
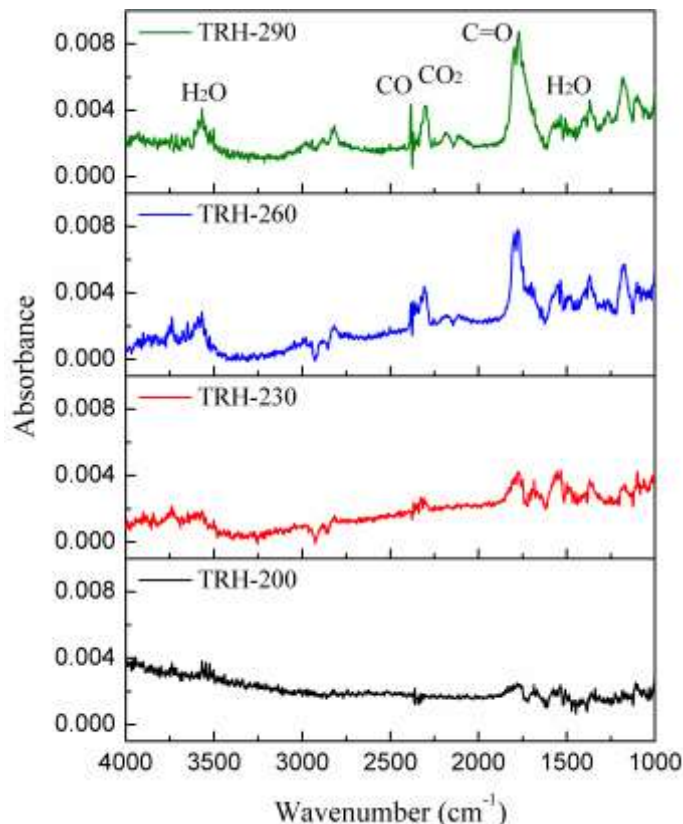

Fig. 3. FTIR spectra of volatile matter at the time point of maximum mass loss (11.8 min for TRH-200, 14.1 min for TRH-230, 14.9 min for TRH-260, and 15.6 min for TRH-290)
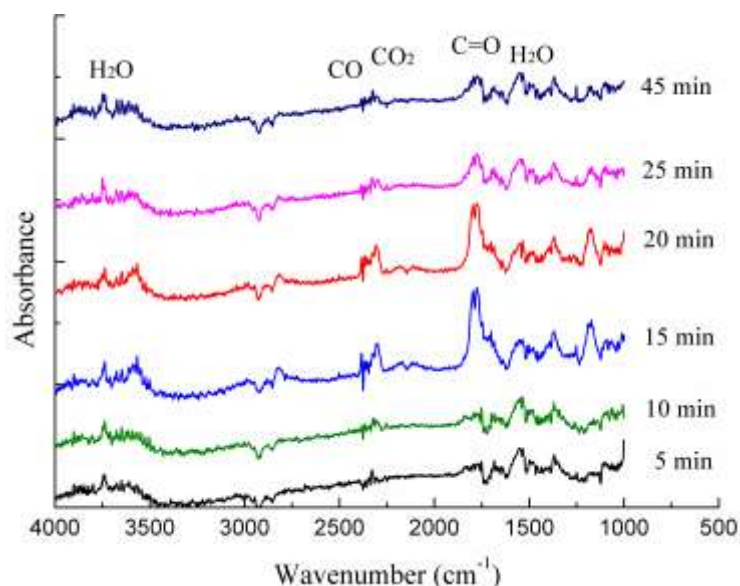

Fig. 4. FTIR spectra of volatiles at different times of TRH-260

To further analyze the generation trend of some products, torrefaction at 260 °C was selected as an example for the FTIR analysis. Figure 4 shows the infrared spectrogram corresponding to six representative time points at 260 °C torrefaction. In the depolymerisation stage (0~10mins), a CO_2 characteristic peak appeared, while the characteristic peaks of carbonyl compound and aromatic hydrocarbon were relatively weak. This indicates that rice husk had undergone depolymerization and internal restructuring, which released micromolecule compounds such as CO_2, H_2O, and CO. The pyrolysis at this moment was not obvious, similar to mass loss at this stage. However, at the devolatilization stage (10 to 25 min), the characteristic peaks of CO_2 and H_2O were obvious. In addition, in ranges of 3000 to 2650 (C-H stretching vibration), 1850 to 1600 (double-bond stretching vibration of carbonyl C=O), and 1500 to 900 cm^{-1} (C-O and C-C skeletal vibration), the absorption peaks were relatively strong, indicating that some carbonyl compounds, aromatic hydrocarbons, and phenols gradually formed and some lignin decomposition occurred. Additionally, the fiber structure of the rice husk was partly damaged. Next, in the carbonization stage (25 to 45 min), each absorption peak was gradually weakened. Overall, with the progression of torrefaction, each absorption peak first increased and then decreased.

FTIR analysis of torrefied rice husk

To further analyze the effects of torrefaction on functional groups of rice husk, FTIR analysis of dried and torrefied rice husk was conducted, and the results are shown in Fig. 5. As can be seen from the figure, there were several kinds of functional groups containing oxygen according to the rice husk infrared spectrogram, which presents an obvious C=O absorption peak. The high level of oxygen content in rice husk was a key reason for its low heat value. The effects of torrefaction temperature on types of organic functional groups and absorption peak intensity were significant. Compared with dried rice husk, the absorption peak of TRH-200 increased, which can be attributed to the enhancement of organic functional groups by the evaporation of moisture. Meanwhile, the release of volatile matter was limited, so that the absorption peaks of TRH-200 and DRH were very similar.
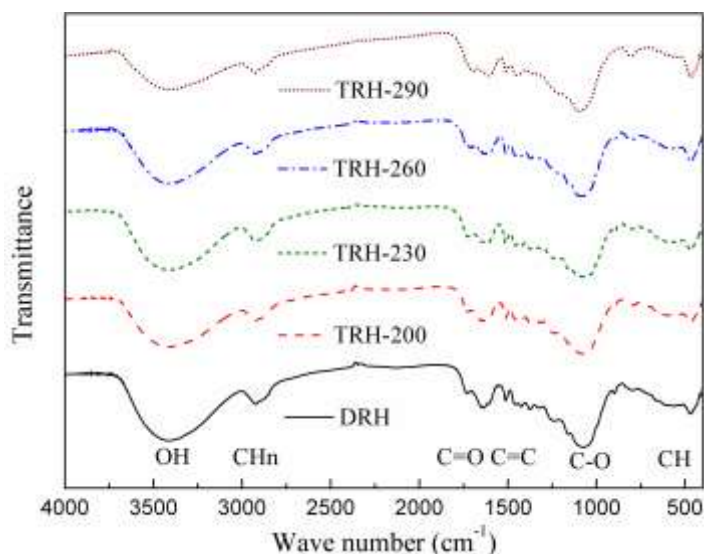

Fig. 5. FTIR spectra of dried and torrefied rice husk

For TRH-230, TRH-260, and TRH-290, the absorption peaks in some functional groups containing oxygen were reduced, which is highly correlated with hemicellulose decomposition. With increasing torrefaction temperature, the dehydroxylation reactions in the hemicellulose, cellulose, and lignin contents of rice husk gradually increased, and most of the rice husk's moisture content was removed, leading to weakened OH peak values. Meanwhile, reactions such as decarboxylation, glycosidic bond breakage, and C=O group decomposition occurred in the hemicellulose, resulting in weakened C=O in carboxyl functional groups. Obviously, with the breaking and removal of some functional groups containing oxygen, the organic functional groups of torrefied rice husk were gradually simplified, leading to a decline of oxygen content in torrefied rice husk and an increase in heat value. These results are consistent with the results in Table 1.

Effect of Torrefaction on the Fuel Properties

Proximate analysis

The results of proximate analysis, ultimate analysis, and higher heating value (HHV) of dried and torrefied rice husk are listed in Table 1. Comparing with volatiles content in DRH, small deceases were found in TRH-200 and TRH-230, while noticeable reductions were observed in TRH-260 and TRH-290. This is because high torrefaction temperature had a greater influence on the decompose of rice husk. Similar results were reported for torrefied pine chips (Phanphanich and Mani 2011) and beechwood chips (Ohliger *et al.* 2013). The fixed carbon content and ash content increased with increasing torrefaction temperature.

Table 1. Proximate Analysis, Ultimate Analysis, and Higher Heating Value of Dried and Torrefied Rice Husk

Sample	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)					HHV (MJ/kg)
	Volatiles	Fixed carbon	Ash	[C]	[H]	[O]	[N]	[S]	
DRH	64.64	19.06	16.30	42.09	5.92	35.03	0.49	0.16	16.66
TRH-200	64.80	19.08	16.11	42.34	5.85	35.01	0.52	0.17	16.77
TRH-230	60.47	22.34	17.20	44.07	5.94	31.98	0.65	0.16	17.46
TRH-260	54.42	27.05	18.53	45.91	5.38	29.33	0.66	0.18	18.14
TRH-290	39.41	37.40	23.19	49.86	4.85	21.26	0.67	0.17	19.45

Ultimate analysis

It can be seen from Table 1 that rice husk had low nitrogen and sulfur, while high carbon and oxygen contents. The nitrogen content of torrefied rice husk slightly increased with increasing torrefaction temperature. On the other hand, the sulfur content of torrefied rice husk showed no clear trend in changes. The hydrogen content exhibited a slight reduction at higher torrefaction temperatures (260 to 290 °C). With increasing torrefaction temperature, the carbon content gradually increased, while the oxygen content considerably decreased. For instance, the oxygen content of TRH-290 was 13.77% less than that of the dried rice husk. Park *et al.* (2013) suggest that the formation and release of CO_2 and CO during the torrefaction process result in the changes in carbon and oxygen contents.

Fuel characteristics of O/C ratio

With increasing torrefaction temperature, the O/C ratio decayed from 1~1.10 to 0.30~0.35. In lignocellulose, the basic structure of lignin could be represented by

$[C_9H_{10}O_3(OCH_3)_{0.9-1.7}]_n$, indicating that the O/C ratio was low, in a range of 0.43 to 0.52 (Chen *et al.* 2011b). Cellulose is a polymer with a basic structure of $(C_6H_{10}O_5)_n$, where n is the degree of polymerization (n > 1000 in cellulose); whereas hemicellulose can be denoted by $(C_5H_8O_4)_n$, and the degree of polymerization is about 150 to 200 (Balat *et al.* 2008). Thus, the O/C ratios of cellulose and hemicellulose are 0.83 and 0.8, respectively. During the torrefaction of rice husk, the decomposition of hemicellulose is highest, followed by cellulose, then lignin. Different decomposition levels of biomass components result in the change of the O/C ratio in rice husk. The decrease of O/C ratio could be regarded as an good signal for the fuel characteristics improving of rice husk.

Heating value

Comparing with DRH, the increase in the HHV of torrefied rice husk due to torrefaction was within the range 0.07% to 16.75%. Similar observations were found in the study of agricultural residues (wheat straw and cotton gin waste) (Sadaka and Negi 2009) and wood chips (Meng *et al.* 2012). Torrefaction reduces the oxygen content but increases the carbon content of rice husk, thus increasing the heating value of rice husk with increasing temperature. The increase in heating value contributes to rice husk utilization.

Hydrophobicity analysis

Equilibrium moisture content (EMC) is an indicator of the hydrophobicity of a solid (Yan *et al.* 2009). The results of EMC were 9.5%, 7.8%, 6.3%, 5.6%, and 2.5% for DRH, TRH-200, TRH-230, TRH-260, and TRH-290, respectively. These values show that EMC of torrefied rice husk decreased with increasing torrefaction temperature. It can be stated that torrefied rice husk is, at least partly, hydrophobic and consequently cannot reabsorb moisture to the same extent as untreated rice husk.

Biomass often has a certain amount of moisture. The moisture content of a fuel has a direct impact on its heating value, market price, as well as thermochemical utilization. Thus, drying pretreatment is essential before biomass pyrolysis (Chen *et al.* 2012b). However, the low moisture content of torrefied rice husk is a major claim made of torrefaction (Agar and Wihersaari 2012). Torrefied rice husk potentially can be kept in heaps outdoors much like fossil coal without the need for costly dedicated storage infrastructure.

Effect of hemicellulose decomposition

The decomposition of biomass components directly lead to the property changes in the torrefied rice husk. As an amorphous polymer, hemicellulose has a high capacity for absorbing moisture from the air. With increasing torrefaction temperature, the degree of hemicellulose degradation becomes more extensive, and more and more hydroxyl groups in the hemicellulose are damaged. As a consequence, the water in the rice husk is eliminated and cannot be reabsorbed (Yan *et al.* 2009). This explains the hydrophobicity of the solid product after torrefaction. On the other hand, hemicellulose plays a fundamental role in linking the fibers of cellulose to each other (Ratte *et al.* 2011). Its devolatilization and depolymerisation can weaken and even break the whole parietal organized architectural structure. Therefore, the torrefied rice husk becomes highly friable and easy to grind.

Effect of Torrefaction on the Solid, Energy, Carbon and Oxygen Yield

The effect of torrefaction temperature on the solid yield and energy yield of torrefied rice husk is shown in Fig. 6. At low torrefaction temperature of 200 to 230 °C, the mass loss was not remarkable and the solid yield was more than 91.2% of TRH-230. The mass loss was attributable to the evaporation of moisture content and a slight decomposition of the sample. By contrast, at high torrefaction temperatures in the range 260 to 290 °C, more volatile matter was released, and thus the solid yield deceased obviously. The solid yield of TRH-290 was only 65.6%. Compared with solid yield, the energy yield decreased less with increasing torrefaction temperature. There was 76.6% of energy retained in TRH-290.

In addition, rice husk has high ash content. The inorganic elements in ash include potassium, calcium, sodium, magnesium, silicon, phosphorus, and chlorine, *etc.* (Chen *et al.* 2014b). Although the torrefaction temperatures in the present study (200 to 290 °C) are lower than the common fast pyrolysis temperatures (400 to 600 °C), the ash may accelerate the generation of biochar, and the alkali metals (potassium and sodium) and alkaline-earth metals (calcium and magnesium) may also catalyze the secondary reactions in rich husk torrefaction, resulting in an increase of the solid yield.
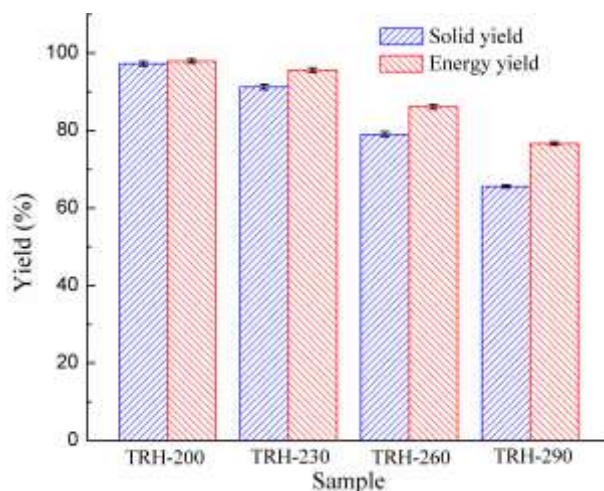

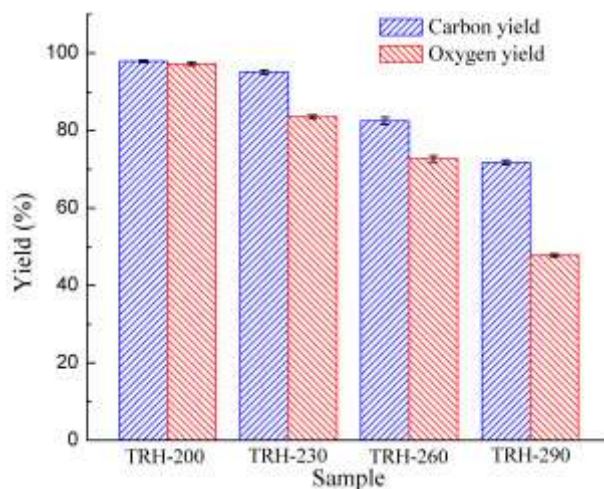**Fig. 6.** Effect of torrefaction temperature on the solid yield and energy yield of torrefied rice husk

Fig. 7. Effect of torrefaction temperature on the carbon yield and oxygen yield of torrefied rice husk

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Figure 7 shows the carbon yield and oxygen yield of torrefied rice husk. It can be seen that 2.1% to 28.2% of carbon was released in the torrefaction temperature range of 200 °C to 290 °C. This release of carbon was not much, because there was more than 71.8% of carbon retained in the TRH-290. However, the release of oxygen was remarkable. At the torrefaction temperature of 230 °C, 16.5% of oxygen was released, while as much as about 52.2% was released at 290 °C. This is very useful for rice husk utilization, as a large proportion of oxygen is released during the course of torrefaction.

CONCLUSIONS

1. By use of the procedures described in this work, the time needed to heat the sample to the torrefaction temperatures was less than two minutes. The testing method using TG-FTIR avoids certain difficulties in interpretation related to torrefaction time and the inaccurate analysis of physical and chemical properties of rice husk.

2. With the breakage and removal of some functional groups containing oxygen at higher torrefaction temperatures, the organic functional groups of the torrefied rice husk were gradually simplified, leading to a decline in the oxygen content of torrefied rice husk and an increase in heat value.

3. A CO_2 characteristic peak appeared in the depolymerization stage of the torrefaction process, and some carbonyl compounds, aromatic hydrocarbons, and phenols were gradually produced in the devolatilization stage. Finally, each absorption peak gradually became weaker during the carbonization stage.

4. Torrefaction had an important effect on the fuel characteristics. The decomposition of hemicellulose was the direct reason for changes in fuel properties such as hydrophobicity, grinding performance, and the O/C ratio of torrefied rice husk.

5. Compared with solid yield, energy yield decreased less with increasing torrefaction temperature. More than 76.6% of the energy was retained in TRH-290, while the solid yield of TRH-290 was only 65.6%. 1.8% to 52.2% of oxygen in rice husk was released in the torrefaction temperature range of 200 °C to 290 °C. Torrefaction effectively improves the energy content per unit mass of rice husk, as a large proportion of oxygen is released.

ACKNOWLEDGEMENTS

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