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In-depth study of rice husk torrefaction: Characterization of solid, liquid and gaseous products, oxygen migration and energy yield

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ABSTRACT

Torrefaction is a promising method for biomass upgrading, and analysis of all products is the essential way to reveal torrefaction mechanism. In this study, torrefaction of rice husk was performed at 210–300 °C. Results showed that the fuel properties of solid products were greatly enhanced upon removal of oxygen. The gaseous products were mainly CO_2 (52.9–73.8 vol%), followed by CO (26.3–39.2 vol%). The liquid product was mainly water and some tar, and the latter contained acids, furans, ketones, aldehydes, and phenols, among which the relative content of acids was the highest. Torrefaction temperature has obvious effects on the oxygen migration. Within the temperature range of 210–300 °C, 9.5–63.2% of oxygen in rice husk was migrated to the gaseous and liquid products. The H_2O was the major contributor to deoxygenation, followed by CO_2 and CO. Thus, formation of H_2O, CO_2, and CO during torrefaction is important as it achieves the purpose of intense deoxygenation.

1. Introduction

Biomass is an important renewable resource which can be converted into solid, liquid and gaseous fuels. The utilization of biomass via thermochemical conversion such as pyrolysis has made great progress (Li et al., 2017; Zhang et al., 2009). Due to the disadvantages of strong hydrophilicity, difficulty in grinding, high water and oxygen content, and low energy density for raw biomass resources, pretreatment is the first and one of the key steps in the thermochemical conversion and bioconversion of biomass (Cen et al., 2016; Chen et al., 2014c; van der Stelt et al., 2011; Zhao et al., 2017; Zhao et al., 2016). Torrefaction pretreatment (also known as torrefaction deoxygenation pretreatment) is a heat treatment process at reaction temperatures between 200 °C and 300 °C under normal pressure and isolated oxygen conditions, which has been proved to be a promising method for biomass upgrading (Bach and Skreiberg, 2016; Ciolkosz and Wallace, 2011; Sukiran et al., 2017).

In recent years, the benefits of torrefaction for solid products of biomass, such as decrease in oxygen content, increase in carbon content, easier grinding and storage, and improvement of high heating value (HHV), have been widely reported (Chen et al., 2017a; Chen et al., 2015c; Chew and Doshi, 2011; Gil et al., 2015; Phanphanich and Mani, 2011; Wannapeera and Worasuwannarak, 2015). Arias et al. found that the torrefied wood was brittle and easy to grind, and water could not be reabsorbed by the fiber structure of biomass because of the destruction of a large number of hydroxyl functional groups (Arias et al., 2008). In the case of chemical structure changes, Zheng et al. found the rank order of thermal stability of biomass major constituents during torrefaction was cellulose > lignin > hemicelluloses, resulting in severe polycondensation of hemicellulose and lignin during torrefaction (Zheng et al., 2015). The removal and conversion of oxygen is the key to biomass torrefaction. Zhang et al. found that after torrefaction at 280 °C for 10 min, the oxygen content and O/C ratio of rice husk decreased significantly from 38.59% and 0.74 to 27.68% and 0.44, respectively, while the HHV increased from 16.58 MJ/kg to 18.73 MJ/kg (Zhang et al., 2015). Chen et al. also pointed out that oxygen-containing organic groups of cotton stalk were gradually broken down and eliminated during torrefaction, which resulted in simplification of the organic groups in cotton stalk and lower oxygen content (Chen et al., 2015a). These previous studies achieved remarkable advances in understanding the torrefaction characteristics of biomass at different temperatures. However, the migration characteristics of oxygen during torrefaction process of rice husk have not been fully investigated.

Moreover, it is noteworthy that the torrefaction product of biomass contains not only solids, but also small amounts of liquid and gaseous products. In reviewing the literature, most of the studies focused on solid products, and only few researches have been carried out on liquid and gaseous products. Ren et al. studied the integrated process of microwave torrefaction and pyrolysis of corn stover, and the results

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showed that the liquid products of torrefaction consisted mainly of ketones/aldehydes, furan derivatives, organic acids, and phenolics (Ren et al., 2014). Han et al. performed torrefaction of *Eupatorium adenophorum* Spreng., and found that oxygen was present in the form of CO_2, CO, H_2O and oxygenated compounds in the gaseous and liquid products, and dehydration was the main pathway of torrefaction deoxygenation of biomass (Han et al., 2015). Chen et al. analyzed the solid and liquid torrefaction products of bamboo, and the results showed that the liquid product contained about 50% water as well as some organic compounds such as acids, alcohols, ketones, phenols, aldehydes, and esters (Chen et al., 2015b). Chen et al. found that the HHV of liquid products, obtained from the torrefaction of palm oil fiber pellets in inert and oxidative environments, was between 10.1 and 13.2 MJ/kg, which increased to 23.2–28.7 MJ/kg after dehydration (Chen et al., 2016). Chen et al. proposed a method of using the liquid products of cotton stalk torrefaction to wash biomass and remove the metal elements and ash (Chen et al., 2017b). These previous studies demonstrated that liquid and gaseous products play a crucial role in the torrefaction of biomass, and thus in-depth analysis of all products is the essential way to reveal the mechanism of torrefaction process. However, until now, the properties of liquid and gaseous products, as well as distribution of oxygen and energy for torrefaction of rice husk has not been reported.

In this study, the effect of torrefaction temperature on the quality of solid, liquid and gaseous products of rice husk was studied. The oxygen migration and energy distribution were also discussed, in order to provide valuable data for understanding torrefaction characteristics and further utilization of rice husk.

2. Materials and methods

2.1. Materials

Rice husk is an abundant biomass material in China. In this study, rice husk that was obtained from Jiangsu Province was used as materials for torrefaction. Prior to the experiment, rice husk were dried in an oven at 105 °C for 12 h to eliminate its water, and then ground into particles with size of 0.125–0.3 mm.

2.2. Torrefaction process

Torrefaction of rice husk was performed using a fixed bed torrefaction device. Details of the experimental set-up and experimental process can be found in the previous study (Chen et al., 2014a). Nitrogen was used as carrier gas with a flow rate of 200 mL/min during the torrefaction experiment. When the reactor was heated to the set temperature, the rice husk (10 g) was put into the reactor and torrefied at this temperature for 30 min. In this study, four torrefaction temperatures of 210 °C, 240 °C, 270 °C, and 300 °C were chosen for experiments. In order to obtain enough liquid and gaseous products for subsequent analysis and testing, the experiment was repeated more than 5 times under the same conditions.

After the experiments were accomplished, the solid products (torrefied rice husk) in the quartz reactor were cooled and collected for further analysis. The liquid products (water and tar) were mainly in the condensate tube, and the reactor and condenser were washed with acetone for fully collecting the liquid product. The yields of the solid and liquid products were calculated by the weighing method.

The gaseous products were collected from the gas collecting bag. The volume fraction of each gas in the gaseous product (equal to the molar percentage under the experimental conditions) and the carrier gas were measured by a gas chromatography analyzer. The volume of the carrier gas used in the experimental process was known. Thus the total volume of the gaseous product can be calculated. Then, the mass and yield of the gaseous products were calculated by multiplying the density of each gas.

2.3. Sample labels

In this study, the raw rice husk was denoted as RH and the torrefied rice husk was denoted as TRH-X, where X represented the torrefaction temperature. For example, TRH-270 represents the solid products of rice husk after torrefaction at 270 °C for 30 min.

The solid yield and energy yield of solid products, liquid products, and gaseous products were calculated from the below formulae:

$$Y_{\text{mass}} = M_{\text{product}}/M_{\text{feed}} \times 100\% \tag{1}$$

$$Y_{\text{energy}} = Y_{\text{mass}} \times HHV_{\text{product}}/HHV_{\text{feed}} \tag{2}$$

where, Y_{mass} and Y_{energy} represent the mass yield and energy yield, respectively; M represents the mass, and HHV denotes the high heating value. The subscripts “feed” and “product” stand for the rice husk and torrefaction products of rice husk.

2.4. Products characterization

For solid samples, the proximate analysis, ultimate analysis, and HHV were performed according to the Chinese National Standards GB/T28731-2012, using an elemental analyzer (Vario macro cube, Elementar, Germany), and using an adiabatic oxygen bomb calorimeter (XRY-1A, Changji Geological Instruments, China), respectively. The contents of hemicellulose, cellulose, and lignin of rice husk were determined according to the Chinese national standards. Holocellulose content and lignin content were determined according to GB/T 2677.10-1995 and GB/T 2677.8-1994, respectively. Cellulose content was determined by nitric acid-ethanol method, and hemicellulose content was calculated by difference (Zheng et al., 2012). For gaseous samples, the volume fraction of each gas was detected by a gas chromatograph analyzer (GC-TCD 7890, Shanghai Tianmei, China), and the HHV was calculated approximately by summing each gas concentration with its corresponding HHV.

The liquid product obtained from rice husk torrefaction comprised a mixture of water and tar. The water content of liquid product was determined via Karl-Fischer titration. The remaining liquid product was weighted and mixed with anhydrous magnesium sulfate to remove the water. Then, it was further treated in a vacuum rotary evaporator to remove acetone, and finally the water-free liquid product (tar) was collected. The organic components of tar were determined by gas chromatography coupled to a mass spectrometer (GC/MS 7890A/5975C, Agilent Company, USA). The ultimate analysis of tar was performed using an elemental analyzer (Vario macro cube, Elementar, Germany), and oxygen was estimated by the difference. The HHV of tar was calculated using the following empirical equation (Han et al., 2015). The symbols C, H, S, and O in Eq. (3) represent the mass fraction of carbon, hydrogen, sulfur, and oxygen in the tar, respectively. And then, the HHV of liquid product was calculated from the HHV and mass fraction of the tar.

$$HHV_{\text{tar}} = 0.352\ \text{C} + 0.944\ \text{H} + 0.105(\text{S}-\text{O}) \tag{3}$$

3. Results and discussion

3.1. Products distribution

Fig. 1 shows the product distribution of rice husk at different torrefaction temperatures. Mass balance at different temperatures was calculated to validate the reliability of experimental data. The sum yield of all products at different temperatures was less than 100% but all greater than 96.8 wt%, because of difficulties in completely collecting products and experimental errors during measurement and calculation. Generally, the mass balance at different temperatures confirmed the reliability of the experimental data.

Mass loss of rice husk during torrefaction was mainly due to the

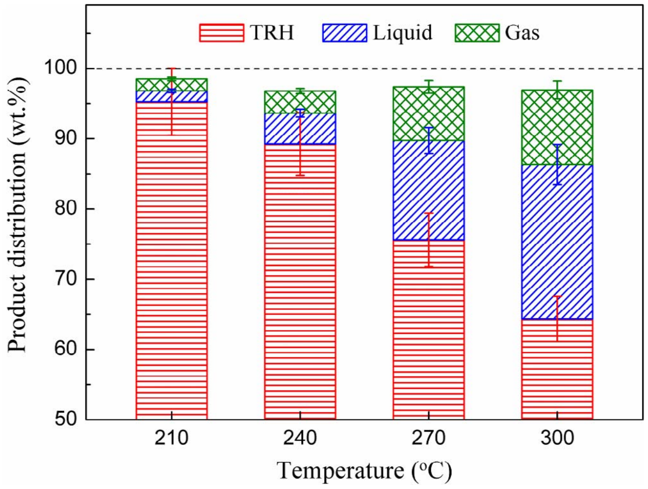

Fig. 1. Profiles of solid, liquid, and gaseous products from rice husk torrefaction at different temperatures.

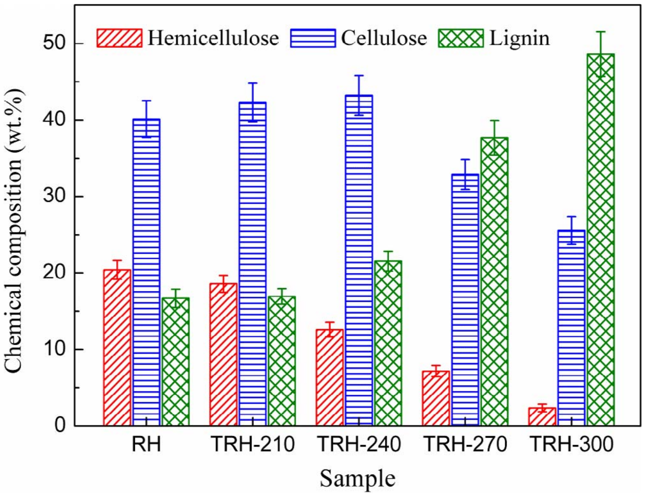

Fig. 2. Chemical composition analysis of raw and torrefied rice husk.

removal of water and volatile matter. Torrefaction temperature had a significant effect on the yield of solid product. When the torrefaction temperature was 210 °C, the mass loss of rice husk was not obvious and the solid yield was 95.3 wt%. This is because this torrefaction temperature was lower than the decomposition temperature of hemicellulose which is the most unstable component in biomass. In the lower temperature range of 210–240 °C, the solid yield decreased slowly and the final yield was above 89.3 wt%. But in the higher temperature range of 270–300 °C, the mass loss was obvious, and the final yield at 300 °C was only 64.4 wt%. This was mainly because the thermal cracking reaction intensified and more volatile products were formed at higher temperatures. In contrast, the yields of liquid and gaseous products increased gradually with torrefaction temperature.

3.2. *Solid products*

The results of proximate analysis, ultimate analysis, and HHV of rice husk before and after torrefaction are listed in Table 1. It can be seen that the volatile content of rice husk reduced from 66.1 wt% to 41.3 wt% when the torrefaction temperature increased from 210 °C to 300 °C. At higher torrefaction temperatures (270–300 °C), the volatile content decreased obviously, which indicated that higher torrefaction temperature had a more obvious effect on volatile content. The fixed carbon and ash content of rice husk gradually increased with the removal of volatile matter during torrefaction. For example, the ash content of TRH-210 was 16.2 wt%, while the ash content of TRH-300 was 23.4 wt%.

With increase in torrefaction temperature from 210 °C to 300 °C, the carbon content of rice husk gradually increased, whereas the oxygen content decreased sharply from 36.3 wt% to 21.8 wt%. Table 1 also lists the H/C and O/C atomic ratios of rice husk before and after torrefaction. The H/C and O/C atomic ratios of torrefied rice husk decreased with increasing torrefaction temperature. It implied that more oxygen and hydrogen were removed from rice husk at higher torrefaction temperatures, and carbon was enriched in the torrefied rice husk. Compared to the results of previous studies, the H/C and O/C atomic ratios of TRH-300 was similar to those of lignite and peat, indicating that the elemental distribution of torrefied rice husk was approaching to lignite coal with increasing torrefaction temperature (Loo and Koppejan, 2007; Pentananunt et al., 1990; Prins et al., 2006; Yue et al., 2017).

The removal of volatile matter in rice husk and the change of elemental content had a direct relationship with decomposition of cellulose, hemicellulose, and lignin in rice husk. The chemical compositions of rice husk before and after torrefaction are shown in Fig. 2. It can be seen that hemicellulose was the major component decomposed during torrefaction. The hemicellulose content of torrefied rice husk decreased sharply from 18.6 wt% to 2.3 wt% when the torrefaction temperature increased from 210 °C to 300 °C. Decomposition of hemicellulose generated more CO_2, CO, H_2O, and oxygen-containing organic compounds during torrefaction. These results were accordance with the literature (Chen et al., 2014b; Chen and Kuo, 2011; Lu et al., 2016; Ma et al., 2015).

A small amount of cellulose and lignin of rice husk was also decomposed during torrefaction. The cellulose content first increased and then decreased with increase in torrefaction temperature, mainly because the initial pyrolysis temperature of cellulose was approximately 280 °C (Zheng et al., 2012). Cellulose decomposition enhanced the carbonization effect of rice husk and increased the fixed carbon content of the torrefied rice husk. Lignin is the most thermally stable component in biomass, pyrolysis of which occurs in a wide temperature range (Ma et al., 2016). Due to the decomposition of hemicelluloses and cellulose, the content of lignin in torrefied rice husk increased gradually. In addition, the carbonization of hemicellulose and cellulose can also increase lignin content.

The fuel properties of torrefied rice husk were greatly enhanced upon removal of oxygen. As can be seen from Table 1, the HHV of TRH-

Table 1
Fuel properties of raw and torrefied rice husk.

Sample	Proximate analysis (wt.%, db)			Ultimate analysis (wt.%, db)					HHV (MJ/kg)
	Volatile	Fixed Carbon	Ash	[C]	[H]	[O]	[N]	[S]	
RH	68.7 ± 0.9	16.3 ± 0.4	15.0 ± 0.4	40.8 ± 0.4	5.3 ± 0.1	38.2 ± 0.8	0.6 ± 0.03	0.1 ± 0.01	15.3 ± 0.6
TRH-210	66.1 ± 0.8	17.7 ± 0.5	16.2 ± 0.3	41.6 ± 0.5	5.3 ± 0.1	36.3 ± 0.9	0.5 ± 0.03	0.1 ± 0.01	16.0 ± 0.5
TRH-240	64.1 ± 0.9	19.0 ± 0.6	16.9 ± 0.5	43.1 ± 0.6	5.1 ± 0.1	34.3 ± 0.6	0.5 ± 0.03	0.1 ± 0.01	16.7 ± 0.5
TRH-270	54.6 ± 0.7	25.2 ± 0.6	20.2 ± 0.5	46.6 ± 0.5	5.1 ± 0.1	27.5 ± 0.7	0.5 ± 0.02	0.1 ± 0.01	17.9 ± 0.5
TRH-300	41.3 ± 0.7	35.3 ± 0.6	23.4 ± 0.4	49.6 ± 0.5	4.6 ± 0.1	21.8 ± 0.6	0.5 ± 0.02	0.1 ± 0.01	19.0 ± 0.6

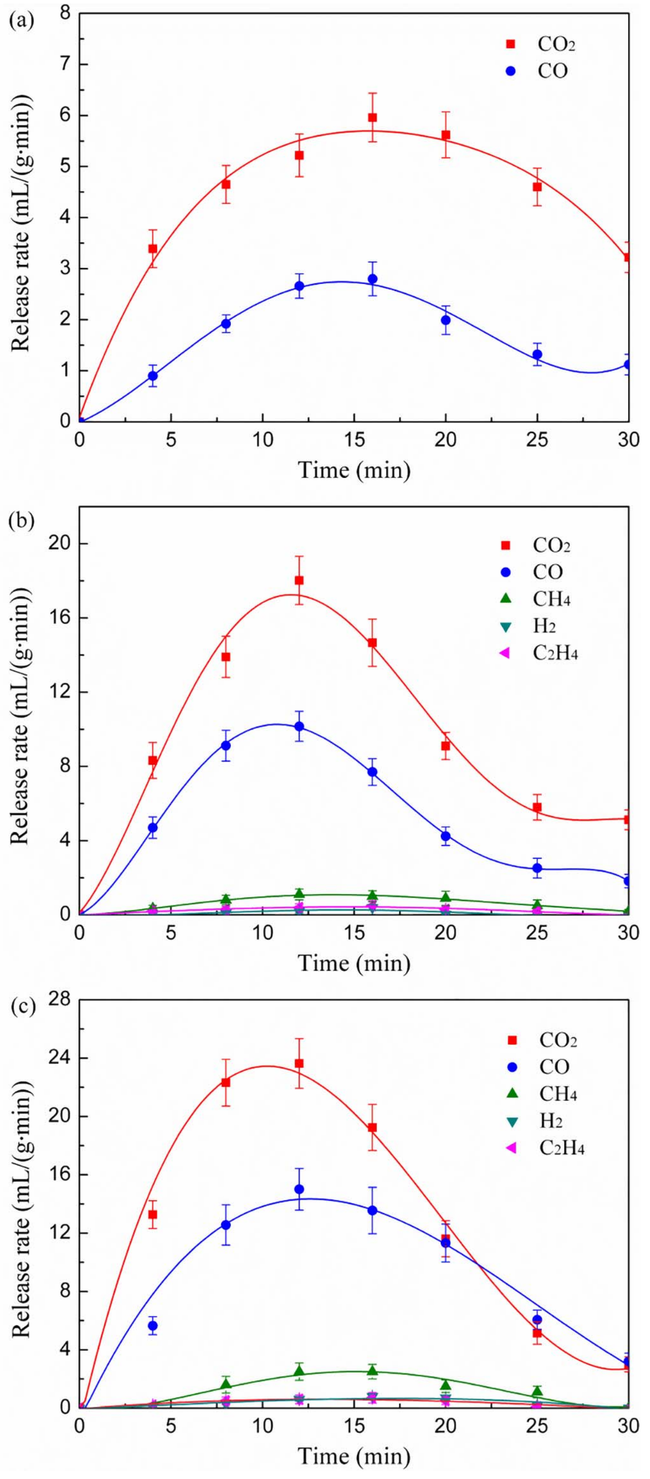

Fig. 3. Evolution pattern of gases during torrefaction process at different temperatures: (a) 240 °C, (b) 270 °C, and (c) 300 °C.

300 increased by about 24% compared to that of RH. In general, torrefied rice husk has low oxygen content, high HHV, and good performance of grinding and hydrophobicity. Thus it can be used as a clean fuel.

3.3. Gaseous products

A small amount of non-condensable gases (CO_2, CO, CH_4, H_2, and C_2H_4) was formed during torrefaction of rice husk. Fig. 3 shows the evolution pattern of the main gases with time during torrefaction process when torrefied at 240, 270 and 300 °C. The amount of gaseous products was very small when torrefied at 210 °C. Thus it was not shown in Fig. 3.

When the torrefaction temperature was 240 °C, CO_2 was the main gaseous product of rice husk torrefaction, and its release rate reached a maximum after 15 min of torrefaction, followed by a gradual decrease. Small amount of CO was also formed, but its release rate was very low compared to that of CO_2. H_2 and CH_4 were rarely detected. When the torrefaction temperature was 270 °C, CO_2 was also the main gaseous product, followed by CO. Their release rates reached a maximum after 12 min of torrefaction, followed by a gradual decrease. A small amount of H_2, CH_4 and C_2H_4 were also formed, but H_2 could not be detected when the torrefaction time exceeded 20 min. When the torrefaction temperature was 300 °C, CO_2 was also the main gaseous product, followed by CO. Their release rates reached a maximum after torrefaction for 8–12 min, and then decreased gradually. The release rates of CO and CO_2 were similar after 20 min of torrefaction. Small amounts of C_2H_4, H_2, and CH_4 were also formed, but the release rates were low.

All the gases produced from rice husk torrefaction within 30 min were collected and analyzed. The yields of gaseous products at different torrefaction temperatures are shown in Fig. 4. It can be seen that torrefaction temperature had a significant effect on the gaseous products. When the temperature was 210–240 °C, the yield of gaseous products was low. However, when the temperature increased above 270 °C, the yield of CO_2 and CO obviously increased as the elevated temperatures favored the decomposition of hemicellulose and cellulose. The yield of CO_2 was the highest, followed by that of CO. Their volume fractions were 52.9–73.8 vol% and 26.3–39.2 vol%, respectively. This indicated that large amounts of oxygen in rice husk were removed in the form of CO_2 and CO during torrefaction.

3.4. Liquid products

The liquid products contained large amounts of water. The water content was 85.9 wt%, 76.3 wt%, 70.9 wt%, and 63.4 wt% for the liquid products obtained from rice husk torrefaction at 210 °C, 240 °C, 270 °C, and 300 °C, respectively. A part of the water came from the rice husk itself, and the other part originated from thermal decomposition of the organic components especially hemicellulose. With increase in torrefaction temperature, the water content in the liquid product gradually decreased, which was due to more tar produced.

During torrefaction, hemicellulose underwent decarboxylation, glycosidic bond cleavage, inner ring C-O group fragmentation, and C-C

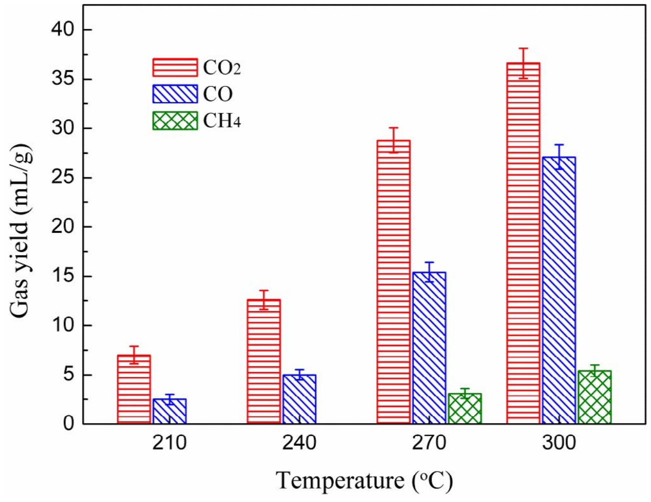

Fig. 4. Effect of torrefaction temperature on the yield and composition of gaseous products.

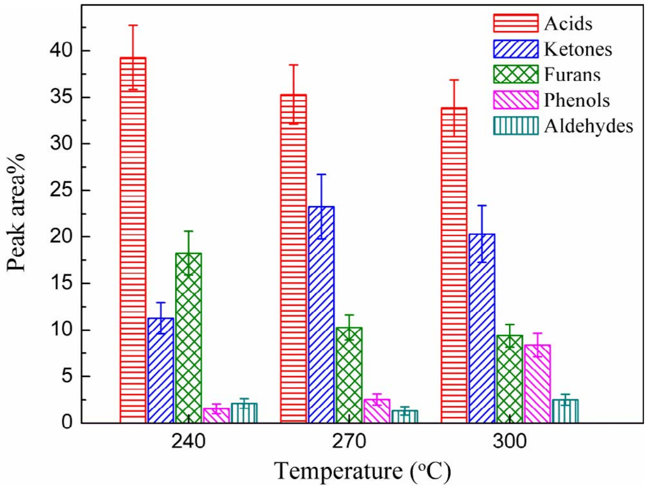

Fig. 5. Major chemical species in tar obtained from rice husk torrefaction at different temperatures.

bond breakage, and formed a series of acids, alcohols, aldehydes, and other organic compounds. Fig. 5 shows the relative contents of the organic components of tar, including acids, furans, ketones, aldehydes, and phenols, among which the relative content of acids (mainly acetic acid) was the highest. The complexity of liquid product composition increased with increase in torrefaction temperature.

Table 2 shows the elemental analysis of tar. Tar mainly contained elements of carbon, hydrogen, oxygen and nitrogen, among which the content of carbon was the highest, followed by oxygen. Some phenols and aromatic compounds were formed due to the decomposition of lignin with increase in torrefaction temperature, leading to increasing in carbon content of tar. The oxygen content of tar was above 32.6 wt%, mainly in the form of oxygen-containing organic compounds. Based on the results of element contents, the HHV of tar is calculated and shown in Table 2. The HHV of tar was 21.1–23.9 MJ/kg, indicating that it could potentially be used as fuel.

The HHV of the liquid products was low because of high water content. For example, the HHV of the liquid product obtained from torrefaction at 300 °C was only 8.7 MJ/kg. Thus the liquid products were not a good fuel used in boiler or engine. In our previous study, the liquid products obtained from torrefaction of cotton stalk were used to wash raw cotton stalk, and results showed that the metallic species in cotton stalk were obviously reduced and the quality of cotton stalk and its pyrolysis products were improved (Chen et al., 2017b).

3.5. Oxygen migration and energy distribution

Fig. 6(a) shows the oxygen distribution in torrefied rice husk, water, tar, and gaseous products. The torrefaction temperature had a remarkable effect on the distribution of oxygen. The oxygen content of rice husk reduced significantly when torrefaction temperature increased. For example, 90.5% of oxygen was retained in rice husk when torrefied at 210 °C, whereas only 36.8% of the oxygen remained in rice husk when torrefied at 300 °C. The oxygen removed from rice husk

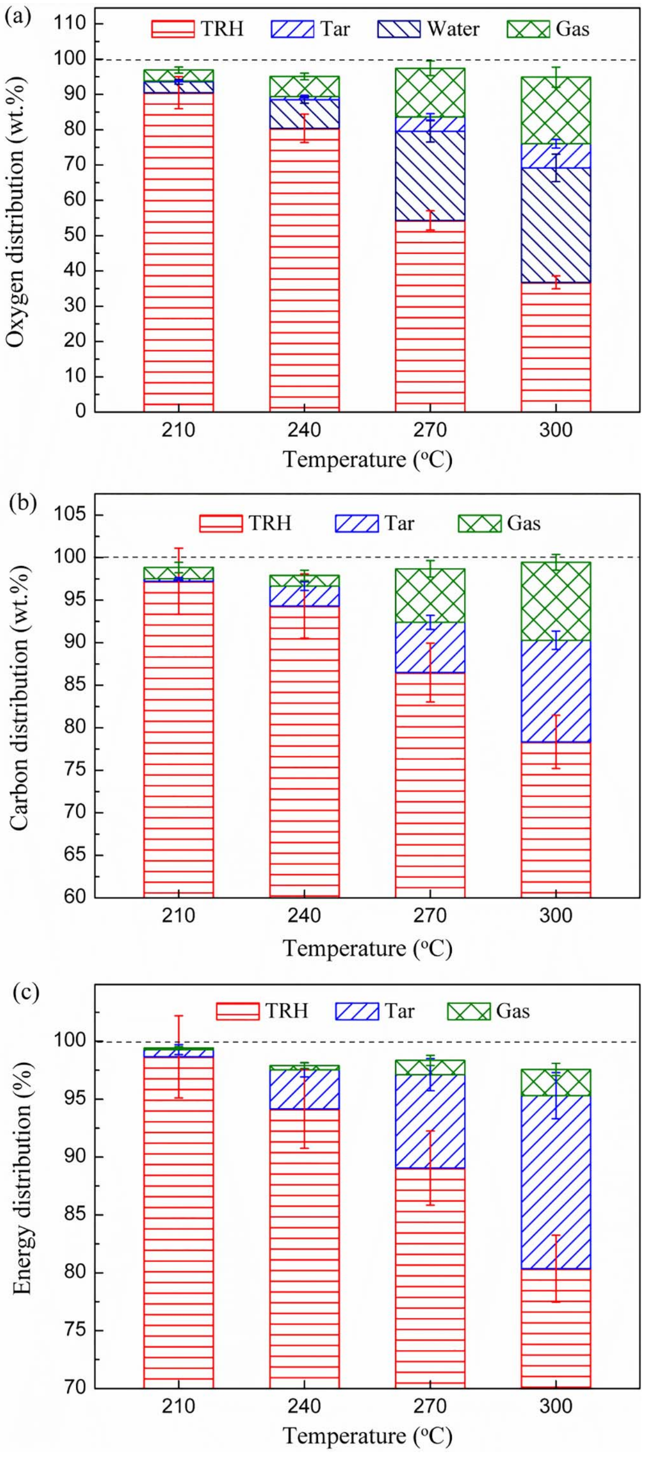

Fig. 6. Distributions of (a) oxygen, (b) carbon, and (c) energy in torrefaction products.

Table 2
Ultimate analysis and HHV of tar obtained from rice husk torrefaction at different temperatures.

Temperature (°C)	Ultimate analysis (wt.%) of tar				HHV (MJ/kg) of tar
	[C]	[H]	[O]	[N]	
210	55.3 ± 1.4	6.0 ± 0.4	38.2 ± 1.8	0.6 ± 0.04	21.1 ± 0.9
240	55.9 ± 1.0	6.2 ± 0.3	37.4 ± 1.6	0.5 ± 0.03	21.6 ± 1.0
270	58.4 ± 1.7	5.9 ± 0.4	35.1 ± 1.4	0.6 ± 0.03	22.4 ± 0.7
300	60.5 ± 1.6	6.3 ± 0.3	32.6 ± 1.4	0.6 ± 0.05	23.9 ± 1.1

during torrefaction was migrated to the gaseous and liquid products in the form of CO_2, CO, H_2O, and oxygen-containing organic compounds. Among them, H_2O were the main contributors of oxygen transfer, followed by gaseous products and tar. Thus, formation of H_2O, CO_2, and CO from rice husk during torrefaction is important as it achieves the purpose of strengthened deoxygenation.

There is a distinct difference between the oxygen migration and carbon migration. As can be seen from Fig. 6(b), most of the carbon in rice husk remained in torrefied rice husk, followed by tar and gaseous products. Carbon is the most abundant combustible element, while oxygen is the most abundant incombustible element in rice husk. Therefore, the oxygen migration and carbon migration has a significant effect on the energy distribution of torrefaction products.

The energy distribution of torrefaction products is shown in Fig. 6(c). It can be observed that the energy yields of gaseous and liquid products increased gradually as the torrefaction temperature increased. Although the energy yield of torrefied rice husk decreased, it still retained most of the energy of the raw rice husk. At medium torrefaction temperatures (about 270 °C), rice husk obtained well heating value and good deoxygenation effect as well as relatively high energy yield, whereas the yield of solid product was not too low. Therefore, medium range temperatures may be better for torrefaction.

4. Conclusions

Torrefaction pretreatment has obvious effects on the products of rice husk. The fuel properties of torrefied rice husk were enhanced upon removal of oxygen. The oxygen in rice husk was migrated to the gaseous and liquid products in the form of H_2O, CO_2, CO, and oxygen-containing organic compounds. Among them, H_2O contributed mainly to oxygen removal, followed by CO_2 and CO. With oxygen migration and carbon migration, the mass and energy yields of gaseous and liquid products increased gradually as the torrefaction temperature increased, but the torrefied rice husk still retained most of the energy of rice husk.

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