Effects of operating conditions and pre-densification on the torrefaction products of sorghum straw

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Abstract: The effects of operating conditions and pre-densification on the torrefaction performance parameters and the properties of the torrefied sorghum straw were studied. A full-factor experiment was performed on a fixed tube furnace, in which sorghum straw powder and pellets were heated to 230℃, 260℃, 280℃ and 300℃ at 2.5℃/min, 5℃/min and 7.5℃/min, respectively. The pyrolysis characteristics of the sorghum straw torrefied under various operating conditions were complemented by thermogravimetric analysis. It was observed that the high temperature led to the high calorific value of the torrefied sorghum straw with an acceptable mass and energy yield. The sorghum straw torrefied at a temperature above 280℃ had a higher heating value (HHV) that was comparable to that of the low rank coal while maintaining its energy yield above 85%. The results suggested that temperature was an important factor determining the properties of the torrefied products, and the heating rate would affect the internal temperature of the torrefied biomass by affecting the heat transfer during the torrefaction. The energy densification index of the pellets decreased uniformly as the heating rate increased proportionally, indicating that pre-densification can be used as a potential method to solve the heat transfer delay in the fixed reactors at high heating rates, especially for high temperatures.

Keywords: torrefaction, pre-densification, pyrolysis characteristics, operating condition, sorghum straw, heat transfer

DOI: 10.25165/j.ijabe.20201304.5517

Citation: Liu X Z, Yao Z L, Cong H B, Zhao L X, Huo L L, Song J C. Effects of operating conditions and pre-densification on the torrefaction products of sorghum straw. Int J Agric & Biol Eng, 2020; 13(4): 219–225.

1 Introduction

The urgent need to reduce CO_2, NO_x and SO_x emissions promotes the development and utilization of renewable energy[1]. Wasted biomass is considered as a potential renewable energy source to replace fossil fuels for its trace amounts of sulfur, nitrogen and heavy metals and its widespread distribution[2]. Sorghum straw is one of the main sources of biomass energy because of the high drought tolerance, high energy storage and low production costs of sorghum[3]. However, the high moisture content, low energy density and low calorific value, etc. inherent properties of raw sorghum straw create challenges for transportation, storage and direct utilization efficiency[4]. Pyrolysis, heating biomass at high temperatures (~500℃) under anaerobic conditions, is a commonly used thermochemical method for biomass upgrading. The factors affecting pyrolysis have been studied in many research, temperature and biomass type are the main factors affecting the distribution of pyrolysis products[5,6]. Chlorella heated at 350℃ produced a maximum yield of bio-oil, while cottonseed yielded the maximum bio-oil yield at 550℃[7].

Torrefaction, a thermal pretreatment method performed at 200℃-300℃ under an inert atmosphere, which can convert raw biomass into materials with high energy density and low storage cost[8,9]. The destruction of the fibers in biomass during torrefaction can improve the grindability of biomass, reducing the grinding energy consumption[10,11]. The thermal decomposition of hemicellulose and cellulose and the destruction of the lignin structure in biomass during torrefaction make it easier to pyrolyze[12]. Wen et al.[13] found that hemicellulose in bamboo decreased considerably at 250℃-300℃. Since the hydroxyl and O-acetyl groups in hemicellulose are the main sources of water and acetic acid in bio-oil[14], torrefaction has often been used prior to fast pyrolysis to decrease the moisture content and acidity in bio-oil[15]. In addition to the effect of torrefaction on pyrolysis or gasification, the reaction mechanism of torrefaction[16,17] and the effect of temperature on torrefaction has also been studied in many research. Torrefaction can also be regarded as a low temperature pyrolysis of biomass, producing ‘solid fuels’ that can be used for heating and power production with satisfactory yields[18].

Besides temperature, the heating rate and particle size of biomass also affect the torrefaction performance of the biomass because of heat transfer limitations. However, the effects of

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Received date: 2019-11-09 **Accepted date:** 2020-05-16

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heating rate and pre-densification on torrefaction are rarely investigated. Although various devices have been designed to improve the heat transfer efficiency during biomass torrefaction, the relatively simple construction and behavior of the fixed reactor make it superior to other complicated reactors. This paper aims to investigate the effects of temperature, heating rate and densification on the heat transfer mechanism during torrefaction, which affects the torrefaction performance parameters and the properties of the torrefied biomass. In this work, the sorghum straw powder and the sorghum straw pellets were torrefied at different temperatures and heating rates in a fixed tube furnace. The thermal decomposition characteristics of sorghum straw torrefied under various operating conditions were complemented by thermogravimetric analysis. According to the experimental results, the effects of operating conditions and densification on torrefaction were analyzed.

2 Materials and methods

2.1 Biomass characterization

The sorghum straw pellets used in the torrefaction tests were purchased from Daxing District, Beijing, China. The pellets are cylinders with a diameter of about 6 mm and a length of about 12 mm. The bulk density of the pellets is 803.1 kg/m^3. Since this study aims to investigate the effect of particle size on the heat transfer during torrefaction, the sorghum straw powder was obtained by grinding sorghum straw pellets and then passing through a 35 mesh sieve (particle size<0.5 mm). The density of the obtained sorghum straw powder is 175.6 kg/m^3.

The chemical composition of sorghum straw was measured by Van Soest method[19], which was performed twice and the average of the two measurements was taken as the result. According to the measurement results, the sorghum straw used in this study was composed of 36.2% cellulose, 22.7% hemicellulose, and 33.3% lignin. The standard deviation of each measured value is less than 0.016.

The ultimate analyses were performed using the PerkinElmer 2400CHNS/O elemental analyzer with a mass of approximately 1 mg/sample. The ultimate analyses were performed twice for each sample and the presented percentages are the average of the obtained results, and the oxygen element (O) was calculated from the difference between the elements C, H, N, S and 100%.

The moisture in the sample was measured by a drying oven, in which the uncovered glassware containing (1±0.1) g sample was heated at 105 ℃±2 ℃ for more than 180 min. The mass reduction of the sample after heating was the moisture content in the sample. The volatile content was measured using a muffle furnace, in which a porcelain crucible containing (1±0.1) g sample was heated at (900±10) ℃ for (420±5) s. The mass reduction of the sample after heating was the volatile content in the sample. The ash content was measured by the muffle furnace, in which a porcelain crucible containing (1±0.1) g sample was heated from room temperature to 250 ℃ at 5 ℃/min and maintained for 60 min, then raised to 550 ℃ at 5 ℃/min and maintained for more than 120 min. The residual mass of the sample was the ash content in the sample. The fixed carbon content was determined by subtracting the moisture, volatile matter and ash content from 100%. The proximate analyses were performed three times for each sample and the presented values are the media of the results.

The higher heating value (HHV) of the sample was measured using the TianHong ZDHW-A5 microcomputer automatic calorimeter. The measurements were performed three times for each sample and the average value was taken as the HHV of the tested sample. The lower heating value (LHV) of the sample was calculated by Equation (1)[20]:

$$\mathrm{LHV_{dry}} = \mathrm{HHV_{dry}} - 2.442\times(8.936\mathrm{H_{dry}}/100) \quad (1)$$

where, $\mathrm{H_{dry}}$ is the mass percentage of hydrogen element; LHV and HHV are given in MJ/kg. The properties of raw sorghum straw are shown in Table 1.

The thermal properties of the sample were measured using DECAGON thermal properties analyzer KD2 Pro. The presented values are the media of measurements taken at three different locations of the sample, as shown in Table 2.

The standard deviations of the three measurements of ultimate analysis, proximate analysis, calorific value and thermal properties of raw sorghum straw are no more than 0.0039, 0.0022, 0.17 and 0.015.

Table 1 Raw sorghum straw properties

Ultimate analysis /wt.%, db		Proximate analysis /wt.%, db		Calorific value /MJ·kg^{-1}, db	
C	49.36±0.50	Moisture	1.02±0.00	HHV	19.86±0.22
H	5.76±0.08	Volatile Matter	85.22±0.25	LHV	18.58±0.24
N	0.23±0.02	Fixed Carbon	12.81±0.27		
O*	44.45±0.42	Ash	0.95±0.02		

Note: db means dry basis; * means by difference.

Table 2 Thermal properties of sorghum straw with different particle sizes

Thermal conductivity /W·m^{-1}·K^{-1}		Volumetric specific heat/MJ·m^{-3}·K^{-1}		Thermal diffusivity /mm^2·s^{-1}	
Powder	0.09±0.01	Powder	0.69±0.01	Powder	0.14±0.01
Pellets	0.21±0.02	Pellets	1.85±0.01	Pellets	0.10±0.02

2.2 Torrefaction experiments

The torrefaction tests were carried out in OTF-1200X-100 fixed tube furnace. Approximately 50 g sample was evenly dispersed in a quartz boat with a diameter of 80 mm and a length of 200 mm, and the quartz boat was placed in the middle of the furnace tube with a diameter of 94 mm and a length of 1000 mm. Two cylindrical carbon blocks with a diameter of 92 mm and a height of 50 mm were inserted into the two ends of the furnace tube to reduce the heat dissipation at both ends of the tube. Nitrogen was used as the inert gas, and a wet flow meter was connected between the nitrogen cylinder and the tube furnace to measure the nitrogen amount.

Before heating the sample, approximately 20 L nitrogen was introduced into the tube to drain the air in the tube. When the sample was heated, the nitrogen flow rate was reduced to 150 mL/min to reduce the heat loss caused by the nitrogen flow. The sample was first heated to 105 ℃ and held for 5 min, and then heated to a specified torrefaction temperature ($\mathrm{T_{tor}}$) at a specified heating rate and held for 10 min at the set temperature. When tube temperature dropped to 100 ℃, the quartz boat containing the torrefied sample was taken out of the tube. A full factorial experimental design was adopted to investigate the effects of temperature, heating rate and densification on torrefaction. The specified test values for temperature and heating rate are listed in Table 3.

Three torrefaction performance parameters, mass yield (M_Y), energy densification index (I_ED) and energy yield (E_Y) are defined as follows[21]:

$$M_{\mathrm{Y}}(\%,\mathrm{daf}) = \frac{m_{\mathrm{torrefied}}}{m_{\mathrm{sorghum}}}\Bigg|^{\mathrm{so}}_{\mathrm{da}} \tag{2}$$

$$I_{\mathrm{ED}}(-)\big|_{\mathrm{daf}} = \frac{\mathrm{LHV}_{\text{torrefied sorghum}}}{\mathrm{LHV}_{\mathrm{sorghum}}}\Bigg|_{\mathrm{daf}} \tag{3}$$

$$E_{\mathrm{Y}}(\%,\mathrm{daf}) = M_{\mathrm{Y}}(\%,\mathrm{daf}) * I_{\mathrm{ED}}(-)\big|_{\mathrm{daf}} \tag{4}$$

2.3 Thermogravimetric analysis (TGA)

Thermogravimetric (TG) tests were performed in a SHIMADZU simultaneous TGA/DTA analyzer model DTG-60A. The TG curves were calibrated before the TG tests according to the instrument instructions. The sample used in the TG test was approximately 7 mg, and nitrogen (99.99% purity) with a flow rate of 100 mL/min was used as the purge gas. The samples were heated from room temperature to 900℃ at 5℃/min, 10℃/min, 15℃/min and 20℃/min, respectively, and the TG curves were recorded by the analyzer software.

3 Results and discussion

3.1 Effects of operating conditions on torrefaction

Table 3 presents torrefaction performance parameters and calorific values of the torrefied sorghum straw, the standard deviations of the performance parameters and the calorific values are less than 0.098 and 1.093. The mass yield (M_Y) and energy yield (E_Y) of torrefied sorghum straw decreased as the temperature increased, which mainly results from the thermal decomposition of hemicellulose for its low degree of polymerization[22].

The main chemical properties of torrefied sorghum straw are listed in Table 4, and the standard deviations of experimental values are less than 0.037. The increased temperature led to a deepened thermal degradation of sorghum straw, which can be deduced from the following results: (a) The color of torrefied sorghum straw changed from faint yellow to brownish black or even dark with the increased temperature, as shown in Figure 1, the volatile content decreased while the ash and fixed carbon content increased as the temperature increased, especially for temperatures above 260℃. (c) The hydrogen and oxygen content of sorghum straw decreased while carbon content increased as the temperature increased. These were consistent with the results observed by Brachi et al.[23], who found that the presence of CO_2 and H_2O in the volatiles when biomass was heated from 225℃ to 300℃. The mass loss of the torrefied sorghum straw is mainly due to the decarboxylation and dehydration of hemicellulose, which releases CO_2 and H_2O that richer in oxygen and hydrogen than carbon[24]. However, the nitrogen content of the torrefied sorghum straw showed an irregular change with the increased temperature.

Table 3 Torrefaction conditions and results of sorghum straw powder

Test No.	HR / ℃ min^{-1}	T$_{tor}$ / ℃	Torrefaction performance parameters			Calorific value/MJ kg^{-1}, db	
			M_Y/%,daf	I_{ED}(-)	E_Y/%,daf	HHV	LHV
1	2.5	230	91.56±0.38	1.07±0.00	97.97±0.16	20.67±0.69	19.49±0.66
2	2.5	260	85.44±0.47	1.10±0.01	93.98±0.38	21.47±0.74	20.34±0.77
3	2.5	280	73.73±1.13	1.18±0.01	87.02±0.27	23.19±0.87	22.12±0.92
4	2.5	300	60.02±0.81	1.29±0.04	77.43±1.14	26.17±1.00	25.14±0.98
5	5	230	95.46±0.26	1.04±0.01	99.28±0.67	20.36±1.01	19.13±1.05
6	5	260	90.63±0.71	1.08±0.02	97.87±1.22	20.94±1.27	19.81±1.23
7	5	280	82.48±2.00	1.11±0.07	91.55±3.62	22.23±1.23	21.12±1.23
8	5	300	71.22±2.35	1.20±0.12	85.45±5.85	25.01±1.35	23.95±1.40
9	7.5	230	96.96±1.08	1.03±0.01	99.87±0.89	20.10±0.56	18.86±0.66
10	7.5	260	92.62±1.03	1.07±0.01	99.10±0.51	20.70±0.85	19.47±0.92
11	7.5	280	85.46±0.89	1.12±0.02	95.72±1.28	21.87±1.04	20.73±1.06
12	7.5	300	76.97±1.97	1.15±0.05	88.52±1.71	22.70±1.67	21.62±1.68

Note: daf means dry-ash-free; db means dry basis; HR means heating rate.

Table 4 Main chemical properties of torrefied sorghum straw powder

Test No.	Ultimate analysis/wt.%, db				Proximate analysis/wt.%, db		
	C	H	N	O*	Volatile	Ash	FC
1	51.86±0.58	5.41±0.12	0.43±0.03	42.07±0.45	82.73±0.98	1.09±0.02	15.17±0.96
2	54.35±0.82	5.18±0.15	0.43±0.04	39.78±0.69	79.88±0.91	1.23±0.03	17.88±0.88
3	60.01±1.09	4.92±0.23	0.43±0.02	34.30±0.81	70.84±1.12	1.70±0.10	26.44±1.02
4	63.62±5.21	4.72±0.45	0.27±0.04	31.22±4.83	60.91±1.77	1.98±0.13	36.09±1.65
5	50.74±0.78	5.60±0.37	0.36±0.04	43.21±0.56	83.90±1.82	1.10±0.09	13.99±1.80
6	53.09±0.94	5.32±0.32	0.28±0.03	41.12±1.12	81.25±1.48	1.21±0.05	16.52±1.42
7	54.80±1.24	5.09±0.23	0.23±0.03	39.68±1.18	75.03±1.25	1.46±0.10	22.49±1.17
8	60.01±1.65	4.85±0.24	0.21±0.02	34.75±1.46	65.87±3.05	1.89±0.17	31.22±2.89
9	50.49±0.97	5.65±0.44	0.25±0.02	43.42±0.45	84.01±1.36	1.13±0.02	13.85±1.36
10	51.87±0.85	5.63±0.53	0.25±0.03	42.05±0.56	82.64±1.29	1.19±0.05	15.16±1.26
11	53.23±0.85	5.22±0.21	0.22±0.03	41.12±0.97	77.55±1.46	1.35±0.06	20.09±1.41
12	55.97±2.40	4.94±0.11	0.31±0.04	38.59±2.37	73.42±3.00	1.59±0.11	23.97±2.93

Note: db, dry basis; * means by difference.

a. 30 ℃ b. 230 ℃ c. 260 ℃ d. 280 ℃ e. 300 ℃

Figure 1 Snapshots of sorghum straw powder torrefied at 2.5 ℃/min

The decrease in the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) elemental ratio of the torrefied sorghum straw resulted in an increase in higher heating value (HHV) of the torrefied sorghum straw, as shown in Table 3 and Figure 2. As the temperature increased, the composition of the torrefied sorghum straw moved from the characteristic region of biomass to that of low-rank fossil fuels such as peat and brown coal. The torrefied sorghum straw, whose energy content increased by a factor above 1.1, provided an HHV on a dry basis comparable to that of low rank coal[25]. These results are in line with the typical mass and energy yields obtained from the previous biomass torrefaction studies[26].

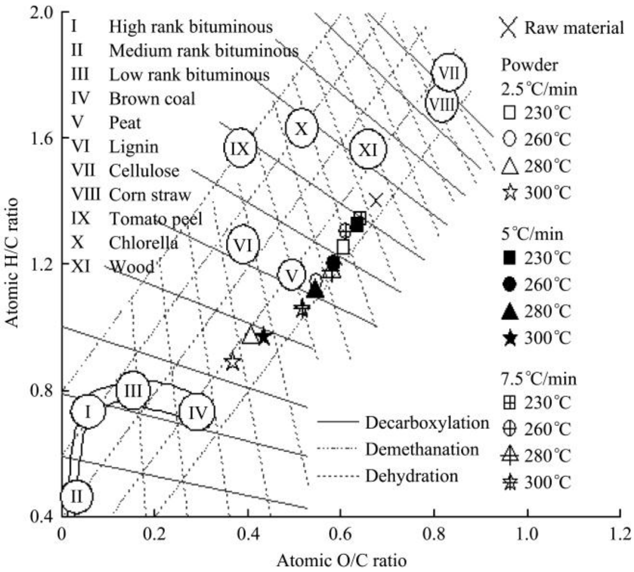

Figure 2 Van Krevelen diagram for torrefied sorghum straw powder

Affected by heat transfer limitations, the mass loss of torrefied sorghum straw decreased with the increased heating rate at the same temperature. The changes in the content of carbon, hydrogen and oxygen decreased as the heating rate increased, indicating that the thermal degradation degree of sorghum straw decreased as the heating rate increased. In detail, the yields and properties of the sorghum straw torrefied at 260 ℃ and 2.5 ℃/min are comparable to those torrefied at 280 ℃ and 7.5 ℃/min. The calorific values of the sorghum straw treated at 300 ℃ and 7.5 ℃/min were lower than those of the sorghum straw treated at 280 ℃ and 2.5 ℃/min. The higher the temperature was, the greater the effect of heating rate on torrefaction. This is because the high heating rate increases the thermal resistance inside the sorghum straw, which delays the heat transferred from the heat wall to the inside of the sorghum straw and lowers the temperature of the sorghum straw torrefied in the quartz boat. The high heating rate causes thermal heterogeneity of sorghum straw heated in the quartz boat. In addition, the consolidation of the sorghum straw powder torrefied in the fixed tube furnace also results in uneven temperature distribution.

3.2 Effects of pre-densification on torrefaction

Tables 5 and 6 list the main results of the sorghum straw pellets torrefaction tests, the standard deviations of the torrefaction performance parameters, main chemical properties and calorific values are less than 0.043, 0.015 and 1.108. The mass yield (M_Y) of the sorghum straw pellets torrefied at a temperature above 230 ℃ was lower than that of the sorghum straw powder torrefied under the same operating conditions, and the energy densification index (I_{ED}) of the torrefied sorghum straw pellets was higher than that of the torrefied sorghum straw powder. Compared with the torrefied sorghum straw powder, under the same operating conditions, the sorghum straw pellets torrefied at temperatures above 230 ℃ have higher carbon content and lower oxygen content, which indicates that the sorghum straw pellets yielded a higher thermal degradation degree when the temperature was above 230 ℃.

Table 5 Torrefaction conditions and results of sorghum straw pellets

Test No.	HR / ℃ min^{-1}	T_{tor} / ℃	Torrefaction performance parameters			Calorific value/MJ·kg^{-1}, db	
			M_Y/%,daf	I_{ED}(-)	E_Y/%,daf	HHV	LHV
13	2.5	230	92.02±0.63	1.07±0.02	98.32±2.80	20.91±0.68	19.76±0.70
14	2.5	260	84.68±0.48	1.12±0.04	94.83±3.03	21.66±0.59	20.52±0.59
15	2.5	280	70.25±0.84	1.20±0.04	84.31±2.61	23.26±0.80	22.13±0.82
16	2.5	300	53.12±0.98	1.38±0.05	73.31±4.15	26.31±0.87	25.27±0.85
17	5	230	95.86±0.68	1.04±0.01	99.69±0.39	20.05±0.53	18.82±0.56
18	5	260	88.35±0.69	1.09±0.02	96.30±0.77	20.86±1.18	19.68±1.26
19	5	280	76.15±1.07	1.14±0.04	86.81±1.93	22.57±1.52	21.43±1.44
20	5	300	62.42±0.85	1.28±0.06	79.93±2.70	24.87±1.52	23.77±1.51
21	7.5	230	96.91±0.48	1.03±0.02	99.82±1.02	19.99±0.65	18.75±0.73
22	7.5	260	93.38±0.41	1.06±0.03	98.98±1.62	20.53±0.99	19.31±0.93
23	7.5	280	85.08±0.62	1.12±0.02	95.29±2.16	21.97±1.64	20.75±1.68
24	7.5	300	73.68±0.71	1.18±0.05	86.86±3.11	23.46±1.14	22.40±1.21

Note: daf means dry-ash-free; db means dry basis; HR means heating rate.

Table 6 Main chemical properties of torrefied sorghum straw pellets

Test No.	Ultimate analysis/wt.%, db				Proximate analysis/wt.%, db		
	C	H	N	O*	Volatile	Ash	FC
13	51.40±0.41	5.28±0.14	0.31±0.02	42.85±0.27	82.61±0.66	1.09±0.02	15.29±0.64
14	54.76±0.43	5.24±0.11	0.23±0.04	39.48±0.36	79.78±0.80	1.22±0.03	17.99±0.77
15	60.85±0.95	5.16±0.13	0.31±0.02	33.48±0.88	70.37±1.23	1.71±0.09	26.90±1.13
16	66.02±1.01	4.77±0.20	0.30±0.03	28.72±0.85	62.38±1.95	1.92±0.09	34.68±1.86
17	50.51±0.54	5.64±0.31	0.23±0.01	43.42±0.38	84.52±0.70	1.13±0.07	13.34±0.66
18	53.25±0.78	5.40±0.40	0.32±0.04	40.72±0.35	81.27±0.56	1.22±0.05	16.50±0.52
19	56.81±1.20	5.21±0.34	0.32±0.04	37.41±0.85	75.68±1.03	1.42±0.05	21.88±1.00
20	61.65±1.68	5.04±0.42	0.42±0.03	32.64±1.26	65.16±1.86	1.82±0.10	32.00±1.76
21	49.07±0.45	5.67±0.39	0.36±0.05	44.62±0.12	85.74±0.91	1.08±0.11	12.17±0.81
22	51.23±0.82	5.61±0.48	0.28±0.03	42.58±0.37	84.39±0.66	1.10±0.18	13.50±0.56
23	54.09±0.96	5.58±0.52	0.33±0.04	39.71±0.51	79.66±1.32	1.18±0.16	18.15±1.21
24	56.43±1.46	4.85±0.30	0.36±0.04	38.06±1.19	73.91±1.48	1.42±0.13	23.66±1.35

Note: db means dry basis; * means by difference.

a. 30 ℃ b. 230 ℃ c. 260 ℃ d. 280 ℃ e. 300 ℃

Figure 3 Snapshots of sorghum straw pellets torrefied at 7.5 ℃/min

Since the torrefaction is thermally driven, heat transfer is the first step and controlled the thermal degradation degree of the sorghum straw torrefaction. As shown in Figure 4, the sorghum straw torrefied in the fixed tube furnace can be divided into a boundary region (0.25-0.30 diameter of pellet) adjacent to the wall, in which the heat mainly transferred by conduction through wall-particle contacts and gases around the particles, and a bulk region far from the wall, in which the heat mainly transferred by conduction through particle-particle contacts (areas or points) and radiation through particle-particle and particle void to particle void[27].

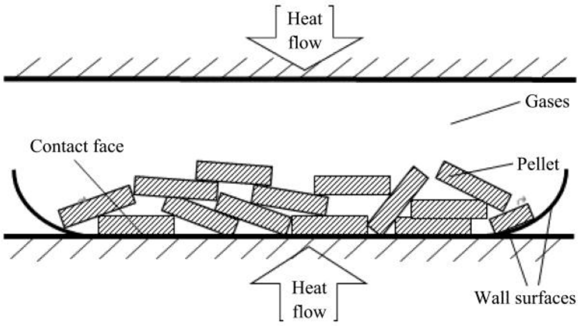

Figure 4 Schematic diagram of heat transfer during torrefaction

Due to the small particle size (less than 0.5 mm), the sorghum straw powder can be regarded as uniform and isotropic from a macroscopic point. But for the pellets, the increased particle size increases voids between the pellets, making its overall structure similar to porous media. The increase in the void fraction of the pellets in the boundary region increases the heat transfer resistance and decreases the thermal conductivity, thereby lowers the heat transfer efficiency in the boundary layer. Hence, the yields and properties of the sorghum straw pellets were lower than those of the sorghum straw powder when the temperature was lower than 260 ℃.

Compared with sorghum straw powder, the sorghum straw pellets in the bulk region have lower thermal diffusivity but higher thermal conductivity and volumetric specific heat, as listed in Table 2. Moreover, thermal decomposition will affect the heat transfer mechanism. Before thermal decomposition, the particle voids are mainly filled with nitrogen (N_2), which has a low conductivity, and neither emits nor absorbs radiation at low to moderate temperatures. Once decomposition begins, the gases in voids change from nitrogen to a mixture of CO_2 and CO, etc., which enhances the radiation from particle void to particle void. But the convection caused by the gases volatilized from the pellets delay the conductive wave into the pellets[28]. Thus, as the volatiles flow outwards, the effects of heat convection and radiation in heat transfer become more significant. In addition, the shrinkage of the pellets and the increase in the roughness of the pellet surface during torrefaction enhance the heat transfer efficiency outside the pellets.

The energy densification index of the sorghum straw pellets torrefied in the fixed bed was higher than that of the sorghum straw powder under the same operating conditions when the temperature was more than 260 ℃, especially for the heating rate that more than 2.5 ℃/min. Moreover, the energy densification index of the sorghum straw pellets torrefaction decreased proportionally with the linearly increased heating rate, indicating that densification is an effective method to improve the thermal homogeneity of the fixed reactor for high heating rates and high temperatures.

3.3 TG analysis

The conversion degree α of the sample is calculated from the TG data by Equation (5):

$$\alpha=\frac{m_0-m_{\mathrm{T}}}{m_0-m_{\mathrm{f}}} \tag{5}$$

where, α is the conversion degree; m_0 is the initial mass of the sample; m_{T} is the mass at temperature T, and m_{f} is the final mass of the sample.

The DTG curves of raw sorghum straw under different heating rates are compared in Figure 5. The main peak (350℃-400℃) and the shoulder peak (300℃-340℃) in the DTG curves correspond to the thermal decomposition of cellulose and hemicellulose, respectively[22]. About half of the sample mass loss occurred in a narrow temperature range (200℃-375℃). The increase in heating rate resulted in a higher decomposition temperature, but the DTG profiles were similar.

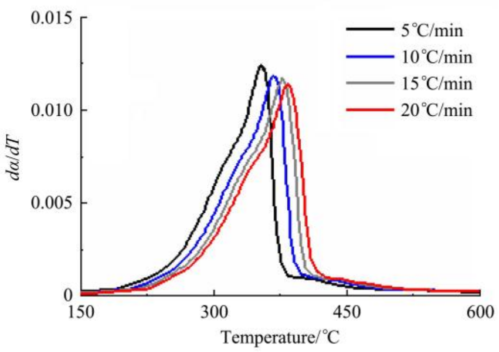

Figure 5 Comparison of DTG curves of raw sorghum straw under different heating rates

Figure 6 shows DTG curves of the solid products torrefied at different temperatures. The gradually disappeared shoulder peak in the DTG curves of the torrefied sorghum straw with the increased torrefaction temperature indicates the thermal decomposition of hemicellulose during the sorghum straw torrefaction[25]. The sharp peak in the DTG curve of the sorghum straw torrefied at 300℃ suggests that the considerable decomposition of hemicellulose and cellulose, resulting in the lower element ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C), as shown in Figure 2. The above results were consistent with the study by Cao et al.[29]

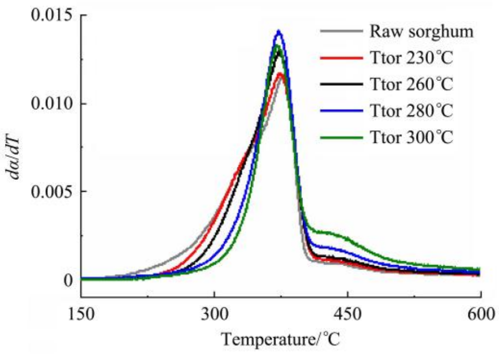

Figure 6 DTG curves of raw and torrefied sorghum straws at 15℃/min

The thermal decomposition rate of the biomass under nonisothermal conditions can be described by the Arrhenius equation:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{6}$$

where, T is the absolute temperature; β is the heating rate; A is the pre-exponential factor; E is the activation energy; R is the ideal gas constant and $f(\alpha)$ is the differential conversion function that depends on the reaction mechanism.

According to the iso-conversional method, the activation energy E is considered as a function of conversion degree α. The conversion degree α is assumed to be a function of time t and temperature T, then the integral conversion function $G(\alpha)$ is:

$$G(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}(T-T_0)\exp\left(-\frac{E}{RT}\right) \tag{7}$$

where, T_0 is the initial temperature corresponding to α=0.

For a given conversion degree, Equation (8) can be obtained from a series of nonisothermal curves, i=1, 2, ⋯; n.

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}-T_{\alpha,i_0}}\right)=\ln\left(\frac{A_\alpha}{G(\alpha)}\right)-\frac{E_\alpha}{RT_{\alpha,i}} \tag{8}$$

The plot $\ln(\beta_i/(T_{\alpha,i}-T_{\alpha,i0}))$ versus $(T_{\alpha,i})^{-1}$ should be a straight line, activation energy E_α can be estimated from the slope of the straight line. The activation energy E_α of the raw sorghum straw and torrefied products with different temperatures are shown in Figure 7. The decomposition of the hemicellulose in the sorghum straw during torrefaction resulted in a decrease in the activation energy of the solid products. The higher the torrefaction temperature was, the lower the activation energy of the torrefied product was. The activation energy of the sorghum straw torrefied at 230℃ changes little compared with the raw sorghum straw, which was mainly resulted from the moisture evaporation. The decreased activation energy of the sorghum straw treated at 260℃ and 280℃ mainly resulted from the decomposition of hemicellulose. The activation energy of the sorghum straw treated at 300℃ decreased sharply indicates the decomposition of the cellulose.

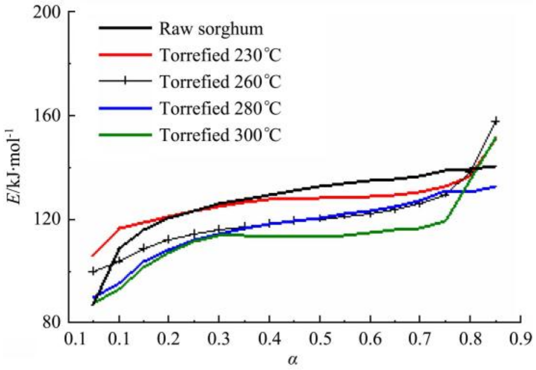

Figure 7 Comparison of the activation energy of raw and torrefied sorghum straw with different temperatures

4 Conclusions

The effects of operating conditions and pre-densification on the torrefaction of sorghum straw were investigated with a series of laboratory scale experiments based on a fixed tube furnace. The pyrolysis characteristics of the sorghum straw torrefied under various operating conditions were complemented by TGA tests. The higher heating value of the sorghum straw torrefied at a temperature above 280℃ can be comparable to that of the low rank coal while maintains satisfactory mass and energy yields.

The high heating rate results in thermal heterogeneity throughout the sorghum straw torrefied in the fixed tube furnace. A low heating rate (<5℃/min) can promote heat transfer in the fixed tube during torrefaction. Densification has the potential to solve the heat transfer delaying and the material consolidation of the fixed tube, which can achieve uniform temperature distribution in the fixed tube furnace. However, the real-time effects of operating conditions and pre-densification on the internal temperature and pressure of the fixed tube furnace require further investigation. In addition, the effect of pre-densification on torrefaction in the rotary reactor needs further study.

Acknowledgements

This work was carried out in the Chinese Academy of Agricultural Engineering under the guidance of Dr. Zonglu Yao. The first authors thank the Chinese Academy of Agricultural Sciences and the Chinese Academy of Agricultural Engineering for their financial support.

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