



## A gas-pressurized torrefaction method for biomass wastes

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### ABSTRACT

Torrefaction is an efficient way for the biomass dewatering and upgrading before its thermal conversion and utilization. In this work, a gas-pressurized (GP) torrefaction method was proposed to torrefy the biomass wastes. The effect of gas pressure on biomass torrefaction was studied and the reaction mechanism was investigated in detail. The results indicated that the GP torrefied biomass had lower volatile matter content and higher carbon content than the torrefied biomass obtained by traditional method with carrier gas under atmospheric pressure (AP). The high heating values of GP torrefied rice straw and sawdust at 250 °C were as high as 17.9 MJ/Kg and 24.5 MJ/Kg, much higher than those of AP torrefied rice straw and sawdust which were 13.6 MJ/Kg and 19.2 MJ/kg, respectively. The GP torrefaction at 250 °C removed as high as 77.88% and 66.68% of oxygen in rice straw and sawdust, respectively. Furthermore, it converted part of the volatile matter into fixed carbon through promoting aromatization reactions. The GP torrefied biomasses had richer pores and higher specific surface area than the AP torrefied biomasses. This can increase the reactivity for subsequent thermal conversion of the torrefied biomass. It was also found that the gas pressure significantly promoted the thermal decomposition of the hemicellulose and cellulose. The main difference of the reaction mechanism between the GP torrefaction and AP torrefaction was the secondary reactions between the volatiles and biomass. It was because the volatiles were not removed timely during GP torrefaction. Furthermore, the pressure was essential for effectively promoting the secondary reactions.

### 1. Introduction

On account of the increase of energy demand and the requirement of alternative to fossil fuels for sustainable environment, the role of renewable energy is increasingly prominent. Biomass is an important renewable energy source and accounts for approximately 10% of global energy consumption [1], because of its rich reserves, low sulfur and nitrogen contents, “carbon neutral” and so on [2]. It is believed that thermochemical conversions, such as combustion, gasification and pyrolysis, are feasible technologies for the biomass utilization as fuel. However, these technologies are challenging due to the inferior fuel properties of biomass, such as high water and oxygen contents, low calorific value, strong hygroscopicity, etc. [3]. Therefore, one of the key challenges for biomass utilization as fuel is to develop efficient

pretreatment technology, which can make biomass compete with fossil fuels. Torrefaction is a promising pretreatment technology, which can improve the fuel properties of the biomass and therefore offers some solutions to above issues [4]. In general, the torrefaction is conducted in an inert atmosphere (such as N<sub>2</sub>) at a relatively lower temperature range, typically from 200 °C to 300 °C. By torrefaction, the moisture contained in the biomass is substantially reduced, and the components of low molecular weight organic volatile and oxygen containing functional groups are reduced. As a result, hydrophobic solids with high fixed carbon content and high calorific value are produced [5]. The torrefied biomass has the properties like coal, and can be used to replace coal to a certain extent.

There have been many studies on biomass torrefaction [4,5]. The main target of the torrefaction is to remove oxygen and hence increase

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the carbon content of the biomass effectively [6,7]. However, the oxygen content of the torrefied biomass by conventional methods is still in the range of 28–46% [8–11]. It is because that only partial of oxygen and volatile matter in the biomass are removed at so mild treatment condition. It is necessary and potential to further improve the oxygen and volatile matter removal of the biomass and improve their fuel properties, through optimizing the methods or conditions. This is one of the most attractive topics in biomass torrefaction. Chen et al concluded that low severity of torrefaction conditions were proper to produce high energy density fuels, considering the weight loss during the biomass torrefaction [12]. Response surface methodology was used for optimizing torrefaction conditions for high energy density solid biofuel from oil palm biomass and fast growing species in Malaysia. It was demonstrated that while the reaction time had less impact on the energy density of torrefied biomass, the effect of reaction temperature was considerably stronger under the torrefaction conditions used in this study [13]. The atmosphere was also studied to improve the efficiency and economic feasibility of the torrefaction technology. Tran et al studied the spruce torrefaction under the conditions relevant to oxy-fuel combustion flue gases. It was found that the energy yields were 79.17%, 84.12% and 88.32% for the torrefaction in N<sub>2</sub>, CO<sub>2</sub>, and the mixture of CO<sub>2</sub> and steam, respectively. So they mentioned that biomass torrefaction integrated with oxy-fuel combustion was possible [14]. Some researches indicated that biomass torrefaction combined with other pretreatment method can improve the upgradation efficiency. Ma et al proposed to combine the torrefaction with washing to reuse the liquid products obtained from torrefaction and pyrolysis products [15,16]. In addition, some researches have also improved the properties of torrefied biomass by introducing other conditions. Wang et al introduced the microwave irradiation to the biomass torrefaction process. They found that the calorific value increased 26% for rice husk and 57% for sugarcane residue by microwave-induced torrefaction, through further decreasing their oxygen contents [17]. Bach et al introduced hot compressed water to torrefaction, and concluded that wet torrefied woods had higher pyrolysis rate [18]. It is well known that the gaseous phase pressure can promote the chemical reaction with gas involved, such as pyrolysis, gasification of biomass and coal [19,20]. Sheng et al. concluded that an increase in the gaseous phase pressure of coal pyrolysis resulted in a growth of methane yield and a reduction of hydrogen yield [21]. The gaseous phase pressure influenced the size and the shape of biomass particles through a general increase in void proportion and decrease in cell wall thickness for biomass pyrolysis [22]. Moreover, the pressure can also facilitate the removal of extractable in biomass during the hydrothermal carbonization [18]. Melligan et al. found that the surface area of the bio-char decreased and the carbon content increased as the gaseous phase pressure increase for the biomass pyrolysis at 550 °C by a batch reactor [23]. As biomass torrefaction is actually a mild pyrolysis process. So the gaseous phase pressure may have similar effect on biomass torrefaction. But the effect of the gas pressure on the biomass torrefaction has not been studied by other researchers. So that we proposed a torrefaction under gas pressure to improve the fuel properties of torrefied biomass, which was named gas-pressurized (GP) torrefaction. In order to confirm the effect of the GP torrefaction method, the GP torrefactions of a woody and a non-woody biomass were conducted by a batch autoclave reactor. The traditional torrefactions were also conducted by a horizontal tube reactor and a thermo-gravimetric analyzer for comparison. The elemental composition, chemical structure and physicochemical properties of the torrefied biomasses were characterized and compared in detail. Furthermore, the reaction mechanism of the GP torrefaction was discussed.

## 2. Materials and methods

### 2.1. Materials

A typical non-woody biomass (Rice straw, abbreviated as RS) and a

**Table 1**  
Properties of raw and torrefied RS and SD.

Samples	Proximate analysis [wt%, d.b.]			Ultimate analysis [wt%, d.b.]				HHV [MJ/kg, d.b.]
	VM	FC	Ash	C	H	N	O[diff.]	
Raw RS	75.2	15.2	9.6	44.2	4.70	0.81	50.3	12.7
200-AP-RS	74.3	15.5	10.2	42.7	5.39	0.81	51.1	13.0
200-GP-RS	49.8	33.8	16.4	51.0	4.68	1.09	43.2	16.2
250-AP-RS	68.8	19.9	11.3	45.1	4.97	0.89	49.1	13.6
250-GP-RS	40.8	40.5	18.7	55.6	4.23	1.22	38.9	17.9
300-AP-RS	43.0	35.5	21.5	51.3	3.93	1.02	43.8	15.1
300-GP-RS	30.6	47.5	21.9	57.2	3.98	1.25	37.6	18.3
Raw SD	85.5	14.1	0.4	50.1	5.88	0.04	44.0	17.5
200-AP-SD	85.2	14.4	0.4	50.4	6.08	0.02	43.5	18.0
200-GP-SD	68.4	30.8	0.7	60.1	5.86	0.08	34.0	22.6
250-AP-SD	82.5	17.0	0.5	53.0	5.97	0.03	41.0	19.2
250-GP-SD	62.1	37.1	0.8	64.9	5.46	0.09	29.6	24.5
300-AP-SD	67.2	32.0	0.8	62.2	5.46	0.06	32.3	23.1
300-GP-SD	53.8	45.2	1.0	68.5	5.25	0.12	26.1	26.0

typical woody biomass (pine sawdust, abbreviated as SD), collected from Hubei Province of China, were used as the raw materials. The two biomasses were crushed and screened to 90–212 μm and dried in a vacuum oven at 105 °C for 5 h. The proximate and ultimate analysis results of the two biomasses were shown in Table 1.

### 2.2. Torrefaction

The traditional torrefactions under atmospheric pressure (abbreviated as AP) were carried out in a horizontal quartz tube reactor as shown in Fig. 1. In each run, about 2.0 g dried biomass was placed in the middle of the reactor, which was then heated to torrefaction temperature (200 °C, 250 °C, 300 °C) by 10 °C/min, following keeping the torrefaction temperature for 15 min. 0.2 L/min of high-purity nitrogen was introduced to the reactor continuously during the torrefaction. The torrefied biomass was weighted after cooling to room temperature at the water-cooling zone of the reactor. The cooling time for the temperature decreased from the reaction temperature to 200 °C was about 5 min. It is believed that the chemical reaction cannot occur at the temperature lower than 200 °C. The non-condensable gas was collected in gas bag. The volume of gaseous products was determined by the accumulative flow meter. The weights of gaseous product were calculated in terms of their concentrations and compositions. The weight of liquid products, which included condensable organics and H<sub>2</sub>O, was calculated by difference. The AP torrefaction was also carried out by a thermo-gravimetric analyzer at same temperature to confirm the largest mass loss at each temperature point.

The gas-pressurized torrefactions (abbreviated as GP) were conducted in a batch autoclave reactor (500 mL), as shown in Fig. 1. About 15 g raw biomass was placed in the autoclave, which was then charged to 2.5 MPa by high-purity nitrogen, after purged by nitrogen to remove air adequately. The reactor was heated to torrefaction temperature (200 °C, 250 °C, 300 °C) by 10 °C/min, following keeping the torrefaction temperature for 15 min. The final pressure of the reactor was about 5 MPa. After torrefaction, the reactor was moved out immediately from the furnace and cooled down by an electric fan. The cooling time for the temperature decreased from the reaction temperature to 200 °C was about 10 min.

Some typical experiments have been repeated more than three times such as the AP and GP torrefactions at 250 °C for both rice straw and sawdust, and the deviation error was less than 5% for each run. To simplify the description, the “temperature - torrefaction method - sample” was used to represent each run. For example, “250-GP-RS” represents the gas-pressurized torrefaction (GP) of rice straw (RS) at 250 °C hereafter.

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