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Thermal behavior and reaction kinetics analysis of pyrolysis and subsequent in-situ gasification of torrefied biomass pellets

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ABSTRACT

Torrefaction followed by densification improves the heating value, grindability, and logistical treatment efficiency of biomass. Study of the pyrolysis and gasification of torrefied biomass pellets has great significance for the efficient conversion and utilization of biomass. In this study, the thermal behavior and reaction kinetics of pyrolysis and following in-situ CO_2 gasification of torrefied corn stalk pellets were investigated in a macro-thermogravimetric analyzer. Torrefaction reduced the amounts of volatiles released during pyrolysis and the maximum pyrolysis rate of pellets decreased with the increase of torrefaction temperature. A three-pseudo-component model applied for the pellet pyrolysis process suggested that the contribution of hemicellulose reduced as indicated by a decrease in activation energy, while lignin contributed more to the overall kinetics with the increased torrefaction temperature. The gasification of chars after the pyrolysis of torrefied pellets based on the nucleation and growth model indicated that as the torrefaction temperature increased, the gasification reactivity decreased, as implied by the evolutions of pore structures, ash compositions and graphitized crystal structures of the pellet pyrolysis chars. The higher activation energy increased the reaction resistance during the pellet gasification process. The results showed that torrefaction and densification together influenced the reaction behavior, reactivity and overall kinetics of biomass.

1. Introduction

Biomass, as an alternative and clean energy which converts solar energy and CO_2 from atmosphere into chemical energy through photosynthesis, plays an important role in fossil fuel substitution and climate change mitigation [1,2]. Various methods, such as pyrolysis, gasification, combustion and anaerobic digestion, have been developed to transform biomass into gas, liquid or solid fuels [3]. However, the application of biomass also suffers from its high moisture content, low calorific value, hygroscopicity, and low energy and bulk densities, which lead to low logistical and conversion efficiencies [4]. Fortunately, torrefaction and densification have been proved to be promising methods to improve the properties of biomass to enhance its potential for industrial application [5].

Torrefaction pertains to a thermal pretreatment technology where raw biomass is heated at 200–300 °C with no or little oxygen for the fractional decomposition of hemicellulose and cellulose. Through torrefaction, biomass turns into a hydrophobic product with enhanced energy intensity and improved physical and chemical properties [6,7]. Densification is applied to compact biomass into a uniform form, such as pellets, briquettes and logs, to increase volume density and reduce its transportation, handling and storage costs [8]. A combination of torrefaction and densification will contribute to the improvement of the bulk and energy density, and hydrophobicity of biomass, which together benefit the energetic conversion efficiency and logistical efficiency [9,10]. The superior fuel properties of torrefied biomass pellets compared with untreated biomass required the development of the subsequent pyrolysis and gasification conversion technologies for torrefied pellets. Yang et al. [11] investigated the effect of torrefaction and densification on bio-oil product from pyrolysis of biomass, and results showed that torrefaction reduced the oxygen content in bio-oil and densification enhanced the depolymerization of cellulose and hemicellulose during pyrolysis. Sarkar et al. [12] found that gasification of torrefied and densified switchgrass resulted in the highest yield of H_2 and CO, and the highest syngas heating value. Pinto et al. [13] compared the gasification gas obtained from raw stumps with those

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obtained from densification, torrefaction and torrefaction followed by densification in a fluidized bed reactor, results showed that stumps derived from torrefaction followed by densification resulted in the best gas quality at the gasification temperature of 850 °C. Through torrefaction and densification, the chemical and physical properties of biomass changed, which dramatically affecting the resulting pyrolysis and gasification results.

Thermogravimetric (TG) analysis was recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) to be one of the most effective methods to describe the thermal conversion performance, kinetics and mechanism of biomass and coal [14]. Through TG analysis, the thermal characteristic values such as TG/DTG data, peak value, reaction period, and temperature at peak value could be obtained. In addition, the reaction kinetic parameters such as the activation energy, pre-exponential factor and the mechanism function could be identified [15,16]. The pyrolysis and gasification behavior and kinetics can be investigated in depth through TG analysis, which will benefit the design, optimization, and even scaling up of the industrial biomass conversion plant level [17]. Some studies have reported the pyrolysis and gasification kinetics of either torrefied biomass or densified biomass [18–24]. Ru et al. [18] and Wang et al. [23] employed a distributed activation energy model to explain the pyrolysis behavior of torrefied biomass and found that torrefaction improved thermal stability of biomass and changed the contributions of three pseudo-components to devolatilization. Bach et al. [19] recently declared that non-oxidative torrefaction did not influence the kinetics of the three main biomass components, but changed their contribution factors. Tapasvi et al. [24] described the pyrolysis of torrefied woody biomass by three pseudo-components model and showed that prolonged heating at 275 °C resulted in a undesirable loss of the cellulose component. Rezaei et al. [21] explained that the pellet size and volume density changed by densification influenced the devolatilization and heat diffusion process during pyrolysis or gasification. However, the studies focused on the pyrolysis/gasification performance, kinetics and mechanism of biomass pretreated by both torrefaction and densification are rather limited. Pyrolysis, a promising method that can convert biomass into valuable products including solid, liquid and gases, is the first step for gasification. Moreover, the gasification of char derived from biomass pyrolysis requires an extremely long conversion process compared with biomass pyrolysis and volatile reforming [25]. Compared with raw biomass, raw pellet or torrefied biomass, the pyrolysis of torrefied pellet might have different reaction kinetics and follow different decomposition pathways. The residual char resulting from pyrolysis of torrefied pellet might have different properties, which further influence the gasification performance. However, there is a lack of knowledge of the pyrolysis reaction kinetics of torrefied pellets and the following in-situ gasification of chars derived from pyrolysis of torrefied pellets. Moreover, the results obtained from the pyrolysis/gasification of a whole torrefied pellet are very rare despite those results being more pertinent to the pellet industrial application. The data of the pyrolysis and following in-situ gasification kinetics of torrefied pellets will guide the design, modification and optimization of thermal conversion equipment.

This study aims to investigate the conversion behaviors, reaction kinetics of the pyrolysis and in-situ CO_2 gasification of torrefied pellets through TG analysis. Corn stalk was first torrefied at different temperatures and then formed into different torrefied pellets. Pyrolysis of torrefied pellets and CO_2 gasification of pellet pyrolysis chars were then carried out in a macro-thermogravimetric analyzer (MTGA), and compared with the raw pellet in this study. Reaction kinetics was evaluated based on the three-pseudocomponent pyrolysis model for pyrolysis and the nucleation and growth gasification model for gasification. Special attention was paid to the reaction mechanism of pyrolysis and in-situ gasification processes.

Table 1
Properties of raw corn stalk and biomass torrefied at different temperatures.

	Raw	200 °C	250 °C	300 °C
Mass yield (%)	100	86.81	76.98	45.87
Energy yield[a] (%)	100	95.97	89.47	69.08
Mass energy density[a]	1	1.10	1.16	1.51
True density (kg/m^3)	1.653	1.688	1.710	1.754
Mean particle size (mm)	0.196	0.193	0.182	0.166
LHV (MJ/kg)	15.28	16.89	17.76	23.01
Saturated moisture uptake (wt.%)	5.49	4.67	2.87	1.89
Proximate analysis, dry, wt.%				
Ash	8.69	9.47	9.55	11.29
Volatile	73.88	71.53	64.10	46.18
Fixed carbon	17.44	19.00	26.36	42.53
Elemental analysis, dry, wt.%				
C	43.25	48.18	55.03	61.70
H	5.57	5.46	4.97	4.19
N	0.60	0.69	0.82	0.94
S	0.14	0.09	0.07	0.05
O (by difference)	41.75	36.11	29.56	21.83

[a] Calculated by the reference of [18].

2. Experimental

2.1. Materials

Corn stalk, obtained from E'zhou, Hubei province, was cut, sheared, crushed, followed by drying in an oven at 105 °C for 24 h. Torrefaction of the corn stalk was then carried out in a fixed-bed tube furnace at temperatures of 200, 250 and 300 °C, respectively, for 30 min. The detailed torrefaction process was explained in previous reports [6,26]. The collected solid residuals after furnace cooled down were used as torrefied samples in this study.

The properties of raw corn stalk and torrefied samples at different temperatures were summarized in Table 1. Firstly, as the torrefaction temperature increased, mass yield, energy yield, mean particle size, moisture uptake, volatile, oxygen content and hydrogen content all decreased, but calorific value, true density, mass energy density, ash, fixed carbon and carbon contents all increased. The removal of water and oxygen-containing volatiles along with the increase of carbon content during torrefaction resulted in the increase of the heating values of torrefied samples. With the increase of torrefaction temperature, the gradual devolatilization of biomass led to the increase of weight loss with more shrinkage in particle size, while the true particle density increased due to the removal of light fractions from biomass particles. It should be notice that most of the mass loss, devolatilization, energy yield decrease, LHV increase occurred during torrefaction at temperatures above 250 °C. 250 °C was suggested to be a turning point, beyond which the effect of torrefaction was more significant than before this temperature [18]. This nonlinear effect of torrefaction on biomass may lead to a nonlinear effect for the following pyrolysis/gasification conversion. Secondly, the variation of LHV and the H/C and O/C mole ratios showed the change of elemental composition and heating value of corn stalk during torrefaction (Fig. S1). It clearly showed that oxygen and hydrogen were selectively removed by torrefaction. The linear regression relationship between H/C and O/C with $\Delta_{O/C}/\Delta_{H/C} = 0.616$ and R^2 (coefficient of determination) = 0.981 indicated that the impact of torrefaction on deoxygenation was lower than on dehydrogenation. Dehydration and deacetylation were the main reactions occurring during torrefaction to produce H_2O and acetic acid, respectively [18,27]. Finally, it was found that the mass yield reduced significantly to 45.87% when the torrefaction temperature increased to 300 °C. However, the energy yield loss was milder accordingly (i.e. ~30.92%), which means that the mass energy yield (energy per unit mass) was enhanced through torrefaction. Therefore, torrefaction is a promising technology to upgrade biomass by enhancing the energy density and reducing moisture uptake from the atmosphere.