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Characteristics of biomass fast pyrolysis in a wire-mesh reactor

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HIGHLIGHTS

- Biomass pyrolysis yield and activation energy are higher in WMR than in TGA.
- Biomass pyrolysis becomes diffusion controlled at 500 °C from kinetic control.
- Heating rate exhibits an opposite effect on the yields of tar and gas.
- Heating rate shows opposite effects on the pyrolysis products of herb biomass and woody biomass.
- High H/C and O/C and low H/O means low amounts of tar and total volatile and high gas yield.

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ABSTRACT

In contrast with thermogravimetric analyzer (TGA), where the samples stacked in the crucible inhibit the release of primary pyrolysis products that subsequently undergo secondary pyrolysis, and fluidized beds which fail to provide precise data on the yields of pyrolysis products without secondary reactions, the wire-mesh reactor (WMR) effectively avoids secondary pyrolysis and provides more accurate pyrolysis data because of the discrete and loose single-layer posput of sample particles. Meanwhile, TGA testing is far from standard practice because of its limited heating rate. Thus, the pyrolysis characteristics of four biomasses are comparatively studied in TGA with heating rates of 5, 10, 20, and 40 °C·min^{-1} and a home-made WMR with heating rates of 5, 40, 250, and 1000 °C·s^{-1}. Both TGA and WMR experiments demonstrate that increasing the heating rate shifts the main pyrolysis curve to higher temperatures due to the thermal hysteresis effect; however, the biomass pyrolysis yield is higher in WMR than in TGA. On average, the activation energies from WMR were higher than from TGA (approximately 14 and 6 kJ·mol^{-1} for herb biomasses and woody biomasses, respectively). WMR experiments indicate that it becomes diffusion controlled at 500 °C though biomass pyrolysis essentially complete at 500 °C; therefore, a further increase in pyrolysis temperature does not exhibit an increase in the product yield. The heating rate exhibits an opposite effect on the yields of tar and gas; meanwhile, both herb biomass and woody biomass show reversed results. The biomass with high H/C and O/C, as well as low H/O molar ratios, yields relatively low amounts of tar and total volatile, as well as high gas, and vice versa.

1. Introduction

Due to the worsening energy crisis and environmental issues, as well as being a sufficiently "green" renewable and CO_2-neutral energy source, biomass is getting increasing attention around the world. As one promising thermochemical conversion technology and an integral part of combustion [1], gasification [2], and IGCC [3], although pyrolysis remains an extremely complex process and influenced by many factors, such as pyrolysis temperature and heating rate [4,5], fuel properties [6,7], fuel size[4,8], ash components[9,10], and external components [11], biomass pyrolysis has received increasing attention in recent years.

Results published by Yang et al. [7] showed that the content of hemicelluloses, cellulose and lignin in biomass has a significant effect on product yields. Enriched hemicelluloses result in high CO_2 yields, high cellulose results in high CO yields, and high lignin means high H_2 and CH_4 yields. Meanwhile, as main compositions

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in biomass, lignin presented the highest activation energy followed by cellulose, and hemicelluloses showed the lowest value [12]. Those findings well explain the products difference during pyrolysis of various biomasses. Additionally, as reported by Haykiri-Acma et al. [5] that the maximum rate of mass loss, conversion rate, final pyrolysis temperature, and activation energy are affected by the heating rate; a high heating rate shows an obvious thermal lag effect that has been generally accepted. In addition, the catalytic role of ash components during pyrolysis, especially the alkali metals, has been realized [9,10]. In our earlier research using capsicum straw with different sizes in a thermogravimetric analyzer (TGA) using heating rates of 10, 20, and 30 °C·min^{-1}, we observed that the content of hemicelluloses, cellulose, and lignin, as well as ash in biomass demonstrate a significant effect on pyrolysis. However, the pyrolysis reaction rate constant is the highest at a heating rate of 20 °C·min^{-1} followed by 30 °C·min^{-1}, and 10 °C·min^{-1} was the lowest [4]. Therefore, a high heating rate does not necessarily correlate with a high reaction rate; there exists a complex competition between thermal hysteresis effects and the driving force originating from different heating rates. When the heating rate is too high, the thermal hysteresis effect may be much stronger, resulting in a decreased rate constant [4]. Otherwise, some co-pyrolysis [6,13,14] and kinetic studies [4,12,15,16] were performed.

Compared to conventional TGA pyrolysis testing with slow heating rate and long residence time, moderate temperature about 500 °C, high heating rates of 1000 °C·s^{-1} or up to a claimed 10,000 °C·s^{-1}, and very short residence time less than 2 s are the perfect reaction conditions in industry practice; thus, together with entrained flow reactor, vacuum furnace reactor, spouted beds reactor, etc., fluidized bed reactor is widely designed to get these strict conditions [14,17,18]. Also, the temperature, heating rates, and residence time have important effect on the pyrolysis products yields [17]. The higher temperature and longer residence time contribute to the secondary reactions, and the lower heating rate favors the carbonization [17]. However, similar as in TGA, it is difficult for precise products analysis because of the secondary reactions of produced vapors and tar that failed to be separated from the char immediately [18].

Although the characteristics of biomass pyrolysis have been investigated extensively, most research is conducted in TGA with lower heating rates and stacked samples, which is far from standard practice. Stacking in the crucible inhibits the release of primary pyrolysis products (especially tar), which subsequently undergo secondary pyrolysis. Even with a certain amount of research conducted in fluidized beds or other reactors, they failed to provide precise data on the yields of pyrolysis products without secondary reactions. Happily, the wire-mesh reactor (WMR) can effectively avoid secondary pyrolysis of tar and provides more accurate pyrolysis data because of discrete and loose single-layer posput of biomass particles that improves the rapid removal of primary products from the high-temperature heating zone [19,20].

Thus, in order to expose new information that is close to practice, the pyrolysis characteristics of two herb biomasses (rice husk and straw) and two woody biomasses (pine and pine nut shell) are studied at various pyrolysis temperatures (250–700 °C) and heating rates (5 and 1000 °C·s^{-1}) in a WMR. Meanwhile, TGA testing at heating rates of 5, 10, 20, and 40 °C·min^{-1} and kinetic analyses were conducted for comparison.

2. Experimental

2.1. Experimental apparatus

The experiments were conducted in a commercial TGA (STA409PC, NETZSCH, Germany) and a homemade WMR. In the TGA tests, biomass samples with a mass of approximately 10 mg were filled into the alumina crucible and heated to 800 °C from ambient temperature at heating rates of 5, 10, 20, 40 °C·min^{-1}. Once the target temperature was reached, the devolatilized samples were cooled at a constant rate of 40 °C·min^{-1}. Nitrogen with a flow rate of 100 ml·min^{-1} was used as the carrier gas during the entire pyrolysis process. In the WMR experiments, to avoid additional effects on heat and mass transfers and ensure efficient collection of the pyrolysis products, biomass samples with a mass of 1–2 mg were posput discretely and loose single-layer on the wire mesh; and then, the biomass samples were heated to desired temperature by controlling heating time with heating rates of 300 °C·min^{-1} (5 °C·s^{-1}) and 60,000 °C·min^{-1} (1000 °C·s^{-1}), respectively. Once reach to the desired temperature, heating was stopped and the devolatilized samples were cooled with a maximum cooling rate of 250 °C·s^{-1} (when heating rate was 5 °C·s^{-1}) and 350 °C·s^{-1} (when heating rate was 1000 °C·s^{-1}) at the initial stage.

As compared to TGA and fluidized bed reactors, the WMR effectively avoids secondary pyrolysis of tar and provides more accurate pyrolysis data. Fig. 1 shows the configuration schematic diagrams and images of the WMR and the testing system. Before pyrolysis, i.e., after the biomass samples are placed in the wire-mesh, the WMR is flushed three to four times with high purity He (99.999%) in order to empty air from the reactor. As shown in Fig. 1a, alternating the on/off positions of the ball valves 3 and 4 in the bypass (dash line) allows air to be flushed from the apparatus. First, open valve 3 and close valves 1, 2, and 4 such that high purity He passes through a CO_2/H_2O filter and flows into the WMR under a controlled flow rate (Type-YQJ-1 flowmeter, Shanghai Regulator Factory Co., Ltd, China) and total pressure (Type-3501 pressure, Rosemount, USA). Next, close valve 3 and open valve 4 (valves 1 and 2 remain closed until the end); added He is removed by the vacuum pump. Repeat this process three to four times to ensure an air-free pyrolysis atmosphere. After removing air, close valves 3 and 4, and open valves 1 and 2 in turn. As reported in a previous paper [19,20], in order to effectively remove the pyrolysis products and maintain a proper internal reaction pressure, the He flow rate was set for 0.225 m·s^{-1} for heating rates of 5 °C·s^{-1} but was elevated to 0.45 m·s^{-1} for heating rates of 1000 °C·s^{-1}.

In WMR, wire-mesh not only supports the sample but also is the heating elements that heat the biomass particles to desired pyrolysis temperature at specified heating rate. The pyrolysis products can be carried away by free convection or a specified steering flow. After pyrolysis, solid residues stay in the wire-mesh, tar vapor and condesed tar vapor, as well as noncondensable gases, flow out of the reactor along with steering flow.

In the WMR shown in Fig. 1b, a top and bottom flange (1 and 13) and an organic glass sleeve (2) which are connected by groove and silica gel ring seal compose a hermetically sealed reaction chamber. A fixed electrode (3) and a mobile electrode (10) controlled by a spring (11) are installed at the bottom flange (13). In case the pre-arranged uniformly distributed biomass particles in the wire-mesh (4) become displaced, certain pretension force from the spring (11) is transmitted to the wire-mesh. Each electrode is powered by a CONAX sealed current connector (EG-187-A-CU-N). Based on pre-experiments, a 304 stainless steel wire-mesh (70 mm width and 70 mm length) with a pore diameter of 40 μm is used as the sample supporter, and the samples are clamped in the fold wire-mesh. The wire-mesh construction not only generates the proper resistance value (0.2 Ω at ambient), which is essential for heating generation and temperature control but also maintains a small temperature gradient along both the length and width of the wire-mesh. The fold wire-mesh is directly connected to the two electrodes. Meanwhile, to retain the smoothless of the wire-mesh, a supporting quartz plate and a compacting