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Mini review

A review on microwave pyrolysis of lignocellulosic biomass

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ABSTRACT

This article briefly reviews the technique of lignocellulosic biomass pyrolysis by using microwave heating. Lignocellulosic biomass, such as crops, wood, agricultural and forestry residues, is a major biomass resource and has been recognized as a sustainable feedstock for the production of bioenergy and green materials. Microwave heating can be better than conventional heating because of various advantages. Hot spots, which form under microwave irradiation, would have significant influence on the yield and characteristics of microwave processing products. The solid products of microwave pyrolysis at proper microwave power levels can have high heating values and specific surface areas with higher gas and solid yields but lower liquid yield than conventional pyrolysis. By using microwave pyrolysis, almost half of lignocellulosic biomass can be converted into gas product, which is mainly composed of H_2, CH_4, CO, and CO_2, with more bioenergy because of its high H_2 and CO yields. The addition of proper catalysts provides substantial influence on the product selectivity of microwave pyrolysis. The gas and liquid yields as well as the heating performance of microwave pyrolysis can be dramatically promoted by adding catalysts. The activation energy and pre-exponential factor of microwave pyrolysis are much lower than those of conventional pyrolysis, revealing that the reaction kinetics for the two methods could be different. According to various advantages, microwave pyrolysis of lignocellulosic biomass can be a promising bioenergy technique.

1. Introduction

Renewable energy has attracted increasing interest because of the concerns about the high demand on fossil fuels and the global climate change. One of the renewable energy sources is biomass. Biomass represents an abundant carbon-neutral resource for the production of bioenergy and biomaterials, and its enhanced use would address several societal issues [1]. Bioenergy and biofuels derived from biomass feedstocks exhibit lower life-cycle greenhouse-gas emissions than fossil fuels and with little or no competition with food production. The satisfactory feedstocks include agricultural residues, sustainably harvested wood, and municipal and industrial wastes [2]. Bioenergy industry will grow in the next few decades to address societal demands to reduce net carbon emissions, and it will require major changes in supply chain infrastructure [3]. Lignocellulosic biomass, a major biomass resource, has been recognized as a potentially sustainable feedstock for the production of biofuels and other biomaterials [4]. However, because of the nature of biomass recalcitrance which means the complex structural and chemical mechanisms of plant biomass for resisting assault on its structural sugars from the microbial and animal kingdoms, it would be difficult to convert lignocellulosic biomass by biological processes and the cost could be high [4]. In this case, thermochemical processes could be a better choice to convert lignocellulosic feedstocks more quickly with lesser cost.

Thermochemical conversion processes include combustion, gasification, liquefaction, and pyrolysis [5,6]. Combustion is the burning of biomass in air to convert the chemical energy stored in biomass into heat, mechanical power, or electricity [6]. Gasification is the conversion of biomass to a fuel gas by heating in a medium such as air, oxygen, or steam [7]. Liquefaction is generally carried out at relatively low temperatures to produce liquid products [8]. Pyrolysis is a thermal decomposition process occurring in the absence of oxygen, and it is always also the first step to produce primary products in combustion and gasification processes where it is followed by total or partial oxidation of the intermediate products [9]. The products of biomass pyrolysis include solid (char), liquid (bio-oil), and gaseous fuel [10]. The yields of the three-phase

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products would vary with changing operational parameters. Lower process temperature and longer vapor residence time favor the production of char, higher processing temperature and longer vapor residence time increase the biomass conversion to gas, and moderate temperature and shorter vapor residence time are optimum for liquids production [9]. Pyrolysis consists of a complicated set of reactions involving the formation of radicals [11]. Most of the research on pyrolysis processes has been conducted by using conventional heating sources such as electric and gas heater [12]. However, biomass pyrolysis heated by microwave irradiation could be a more promising technique because of a number of advantages over conventional pyrolysis.

This review focuses on microwave heating mechanism, microwave pyrolysis of lignocellulosic biomass, characterization and applicability assessment of products, reaction kinetics, and the comparison between microwave and conventional pyrolysis methods. The aim of this review is to help to understand the principle, product distribution, reaction kinetics, and challenges of state-of-the-art microwave pyrolysis technique.

2. Microwave heating mechanism

2.1. Microwaves

In the electromagnetic spectrum, microwaves lie between infrared and radio frequencies. The wavelengths of microwaves are between 1 mm and 1 m with corresponding frequencies between 300 GHz and 300 MHz, respectively [13–15]. The two most commonly used microwave frequencies are 915 MHz and 2.45 GHz [14]. Microwave energy is derived from electrical energy with a conversion efficiency of approximately 85% for 915 MHz and 50% for 2.45 GHz [13]. Most of the domestic microwave ovens use the frequency of 2.45 GHz. Compared with 2.45 GHz, the use of 915 MHz can provide substantially larger penetration depth which is an important parameter in the design of microwave cavity size, process scale up, and investigation of microwave absorption capacity of materials [16].

2.2. Microwave heating

Microwaves cause molecular motion by migration of ionic species or rotation of dipolar species or both [13] to generate heat because of the friction among molecules. Materials that can absorb microwaves are called absorbers or dielectrics, so microwave heating is also referred to as dielectric heating [15]. The extent of microwave heating a material can be determined by a term called loss tangent which is the ratio of dielectric loss factor to dielectric constant of the material [13]. In general, materials can be divided into three types according to their loss tangents: high (> 0.5), medium (0.1–0.5), and low (< 0.1) microwave absorbing materials [17]. The loss tangents of carbon materials such as charcoal, carbon black, and activated carbon, ranging from 0.1 to 0.8, are either comparable to or higher than the loss tangent of distilled water (0.118 at 2.45 GHz and 298 K), so carbon materials are good microwave absorbers that show high capacity to absorb and convert microwave energy into heat [12,18]. Materials can be classified into three categories according to their interactions with microwaves: conductors, insulators, and absorbers. Microwaves are reflected from the surface and thus do not heat metals, which generally have high conductivity and are classified as conductors [13]. Materials (e.g., glass and ceramics) transparent to microwaves are classified as insulators.

Microwave heating offers a number of advantages over conventional heating such as: (1) non-contact heating; (2) energy transfer rather than heat transfer; (3) higher heating rate; (4) material selective heating; (5) volumetric heating; (6) quick start-up and stopping; (7) heating from interior of the material body; (8) higher level of safety and automation [13]. Microwave energy is efficient in the selective heating of materials as no energy is wasted in the bulk heating of feedstocks, which is a clear advantage over conventional methods (bulk heating in furnaces) [15]. Therefore, microwave heating has been widely used in various scientific researches and industrial applications, such as food processing, sterilization and pasteurization, different drying processes, rubber vulcanization, and polymerization or curing of resins and polymers [18]. An important characteristic of microwave heating is the phenomenon of hot spot formation, which arises from the inhomogeneity of microwave field (the formation of standing waves) or dielectric property within a feedstock (a blend or a mixture) so that a local temperature inside the feedstock is much higher than the temperature measured in the bulk [15,17]. Hot spots would have significant influence on the yield and characteristics of microwave processing products. To control or utilize the hot spot phenomenon, cavity design is an important factor [15]. The effects of hot spots can be reduced by several techniques, such as increasing the size of the cavity, operating at a higher frequency, equipping a turntable, installing a mode stirrer, and hybrid heating that combines microwave heating with conventional heat transfer through radiation, convection, or conduction [14].

3. Microwave pyrolysis

Lignocellulosic biomass, such as crops, wood, agricultural and forestry residues, is mainly composed of cellulose, hemicellulose, and lignin. In general, the cellulose, hemicellulose, and lignin contents of plant biomass are approximately 35–50, 25–30, and 15–30 wt%, respectively [1]. Microwave pyrolysis has been applied to various lignocellulosic feedstocks, such as larch [19], pine wood sawdust [20,21], peanut shell [21], maize stalk [21], rice straw [22], corn stover [23,24], aspen [24], wheat straw [25,26], oil palm biomass [27], Douglas fir [28], prairie cordgrass [29], rice husk [30], and waste office paper [31].

3.1. Product yield

The gas, liquid, and solid yields of microwave pyrolysis of these biomass feedstocks are listed in Table 1. The gas product of microwave pyrolysis is primarily composed of permanent gases (i.e., H_2, CH_4, CO, CO_2, etc.) which are incondensable at room temperature, condensable hydrocarbons in the product vapor, and the solid residues left.

As can be seen, the product yields of these researches are quite different. This could be attributable to the difference in sample weight, biomass characteristics, particle size, microwave power level, reaction temperature, reaction time, product vapor residence time, reactor design, and microwave heating manner. Among these factors, the effect of reaction temperature is the most critical. When the reaction temperature was only 180–200 °C, the gas, liquid, and solid yields were approximately 15, 50, 36 wt%, respectively [25,31]. However, at the reaction temperature of 600 °C, the gas, liquid, and solid yields were approximately 41, 26, 33 wt%, respectively [23,29,30]. Therefore, the gas yield substantially increased but the liquid yield substantially decreased with increasing reaction temperature, whereas the reduction in the solid yield was not so obvious. This may imply that, when product vapors are released by the devolatilization of biomass pyrolysis, more hydrocarbons in the vapors can be converted into permanent gases at higher reaction temperature. The product distributions of microwave and conventional pyrolysis are shown in Fig. 1. As can be seen, microwave pyrolysis can produce more solid and gas products but less liquid