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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

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

Table 1
Product yields of lignocellulosic biomass pyrolysis using microwave heating.

| Biomass	Experimental parameters	Yield (wt%)			Ref.
		Gas	Liquid	Solid	
Larch	Sample weight: 191 g; microwave power: 1.5 kW; reaction time: 18 min.	60.8	18.1	21.1	[19]
Pine wood sawdust	Sample weight: 15 g; microwave power: 0.3–1 kW; reaction temperature: 470 °C; reaction time: 12 min.	60.0	22.7	17.3	[20]
Pine wood sawdust	Feeding rate: 2 kg h^{-1}; reaction temperature: 500 °C; particle size: 0.5–1.0 mm.	15.0	69.9	15.2	[21]
Peanut shell	Feeding rate: 2 kg h^{-1}; reaction temperature: 500 °C; particle size: 0.5–1.0 mm.	17.1	52.4	30.5	[21]
Maize stalk	Feeding rate: 2 kg h^{-1}; reaction temperature: 500 °C; particle size: 0.5–1.0 mm.	19.0	51.3	29.8	[21]
Rice straw	Sample weight: 3–5 g; microwave power: 300 W; reaction temperature: 400 °C; reaction time: 30 min; particle size: < 0.425 mm.	49.4	22.6	28.1	[22]
Corn stover	Microwave power: 700 W; reaction temperature: 600 °C; reaction time: 13 min; particle size: 2 mm.	41.3	32.7	26.0	[23]
Corn stover	Sample weight: 100 g; microwave power: 875 W; reaction temperature: 450–550 °C; reaction time: 20 min; particle size: 6.2 mm in diameter and 10–20 mm in length.	34.4	37.0	28.6	[24]
Aspen	Sample weight: 100 g; microwave power: 875 W; reaction temperature: 450–550 °C; reaction time: 20 min; particle size: 4.8 mm in diameter and 4–8 mm in length.	38.9	35.9	25.2	[24]
Wheat straw	Sample weight: 100–150 g; microwave power: 1.2 kW (max); reaction temperature: 180 °C (max); reaction time: 10 min.	14	57	29	[25]
Wheat straw	Sample weight: 5–30 g; reaction temperature: 600 °C; reaction time: 10 min; particle size: < 0.09 mm.	~23	~31	~47	[26]
Oil palm shell	Microwave power: 450 W; reaction time: 25 min; particle size: 1–100 mm.	~19	~13	~68	[27]
Oil palm fiber	Microwave power: 450 W; reaction time: 25 min; particle size: 0.3–0.6 mm.	~12	~8	~80	[27]
Douglas fir	Sample weight: 120 g; microwave power: 700 W; reaction temperature: 400 °C; reaction time: 15 min; particle size: 7 mm in diameter and 15 mm in length.	13.1	50.2	36.7	[28]
Prairie cordgrass	Sample weight: 100 g; microwave power: 700 W; reaction temperature: 600 °C; reaction time: 13 min; particle size: < 4 mm.	46.7	24.3	29.1	[29]
Rice husk	Sample weight: 50 g; microwave power: 700 W; reaction temperature: 600 °C; reaction time: 20 min.	~35	~22	~43	[30]
Waste office paper	Sample weight: 150 g; microwave power: 1.2 kW; reaction temperature: < 200 °C; particle size: < 5 mm.	15	42	43	[31]
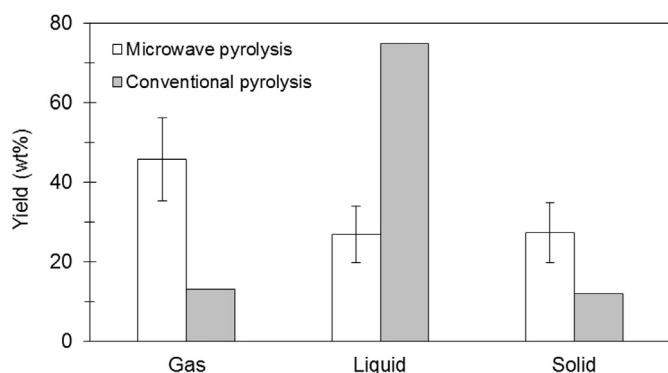
Fig. 1. Product distributions of microwave and conventional pyrolysis (data taken from Refs. [9,19,20,22–24,29,30]).

product than conventional pyrolysis. The average gas, liquid, and solid yields were approximately 46, 27, and 27 wt%, respectively [19,20,22–24,29,30]. Therefore, almost half of the biomass can be converted into permanent gases by using the technique of microwave pyrolysis. The product distribution of microwave pyrolysis is different from that of conventional pyrolysis. The typical gas, liquid, and solid product yields of fast pyrolysis are 10–20, 60–75, and 15–25 wt%, respectively [32]. Therefore, compared with conventional pyrolysis, microwave pyrolysis can produce more gas product and less liquid product.

3.2. Solid product

The solid products (i.e., char or biochar) of microwave pyrolysis can be different from those of conventional pyrolysis. One of the differences is surface structure. Guo and Lua reported that pores of various sizes were observed on the surface indicating to some extent the heterogeneous nature of the char produced by conventional pyrolysis, whereas many orderly pores with round shape and uniform sizes were found all over the surface of the char produced by microwave pyrolysis [33]. Miura et al. pointed out that the micropores of the char produced by conventional pyrolysis were filled with large amounts of the carbon-like adhesives, whereas those produced by microwave pyrolysis were quite clean and exhibited a more open structure as a result of the release of volatile matter [19]. In addition, Salema and Ani reported that large and deep cracks were found in the conventional pyrolysis char, whereas pores were observed in the microwave pyrolysis char without any cracks [27]. The surface area of the char produced by microwave heating was larger than that produced by conventional heating [34], and it increased with increasing reaction (microwave irradiation) time [33,34], reaction temperature [26,33], and microwave power level [22,27,33]. Taking microwave pyrolysis of oil palm stone as an example, a microwave power level of 450 W was considered as the minimum to cause any significant changes in the properties of char [33]. After microwave pyrolysis at a sufficient microwave power level and for a sufficient reaction time, the specific surface area of the char produced can be higher than 400 m^2 g^{-1} [33,34].

Microwave pyrolysis also changes the heating value of biomass. Huang et al. reported that the heating values of raw rice straw and its biochar produced at microwave power levels of 200–350 and 400–500 W were approximately 15, 19, and 17 MJ kg^{-1}, respectively [22]. The increase in heating value should be attributable to the devolatilization of hemicellulose and cellulose, whose heating values are much lower than that of lignin, the more thermo-resistant biopolymer. At relatively low microwave power levels, the thermal degradation of lignin should be insignificant. However, when the microwave power level is higher, the devolatilization of lignin would be substantial, leading to the production of char with lower heating

values. Microwave torrefaction is a technique to produce char with high heating values as its primary goal, provided that the reaction temperature is controlled at 200–300 °C [35–39]. However, the yields of gas and liquid products of microwave torrefaction are very low, and thus they could be only regarded as minor byproducts.

3.3. Liquid product

The condensable part of vapor produced from biomass pyrolysis, which is generally named as bio-oil, pyrolysis oil, or pyrolysis liquid, is usually a dark-brown organic liquid [40]. The heating value of bio-oil is approximately half that of conventional fuel oil [41]. This could be owing to the relatively high oxygen and water contents of bio-oil, and thus further upgrading and refining processes are needed to increase its heating value. As aforementioned, microwave pyrolysis of biomass can also produce bio-oils. The properties of bio-oils produced by microwave and conventional pyrolysis are listed in Table 2. It can be seen that the properties of microwave pyrolysis bio-oil were slightly different from those of conventional pyrolysis bio-oil. More specifically, microwave pyrolysis seems to show a potential for the production of bio-oils with higher carbon content and heating value and lower oxygen content [31,42–44]. Furthermore, Yu et al. reported that the properties and stability of bio-oils can be improved by blending methanol or ethanol into the bio-oils [42].

The compositions of liquid products from microwave pyrolysis of biomass are complicated. Huang et al. reported that the components of liquid product produced from microwave pyrolysis of rice straw could be divided into three groups: alkanes from C12 to C32, polars including phenol and its derivatives, and polycyclic aromatic hydrocarbons (PAHs) with 2–3 rings and their derivatives, with the percentages of approximately 44, 26, and 9 area%, respectively [22]. Zhang et al. pointed out that the chemical compositions in oil fraction of liquid product produced from microwave pyrolysis of corn stover could be classified into several groups, such as aliphatic hydrocarbons, aromatic hydrocarbons, oxygen-containing aliphatic compounds, oxygen-containing aromatic compounds and others (nitrogen-containing compounds and unidentified compounds) with the relative content of oxygen-containing aliphatic compounds and oxygen-containing aromatic compounds approximately 50 and 40%, respectively [45].

3.4. Gas product

The composition of gas product from microwave pyrolysis of lignocellulosic biomass, including wheat straw [26], rice husk [30], coffee hulls [43], pine sawdust [46], and rice straw [47], is shown in Fig. 2. As can be seen, the primary components of the gas product were H_2, CH_4, CO, and CO_2, with the concentrations of approximately 32, 9, 33, and 23 vol%, respectively. The fraction of undetermined components (e.g., light hydrocarbons) would be only 3 vol% or even less. Therefore, microwave pyrolysis could be a promising technique for the production of H_2-rich fuel gas [43,47]. Fig. 2 also shows that microwave pyrolysis can produce more H_2 and CO but less CH_4 and CO_2 than conventional pyrolysis, so the gas product of microwave pyrolysis can provide more bioenergy due to its higher heating value. As the reaction temperature increased, both H_2 and CO concentrations substantially increased whereas CO_2 concentration substantially decreased. However, the change in CH_4 concentration was not obvious. The considerable variations in CO and CO_2 concentrations could be attributable to the self-gasification of char [48]:

$$C + CO_2 \leftrightarrow CO \tag{1}$$

This disproportionation equation, called the Boudouard reaction, is one of the most important reactions in biomass gasification. The relatively high amount of potassium present in the raw biomass feedstock would act as a catalyst to favor the self-gasification phenomenon [48]. The high H_2 content of gas product could be attributable to the water gas reaction:

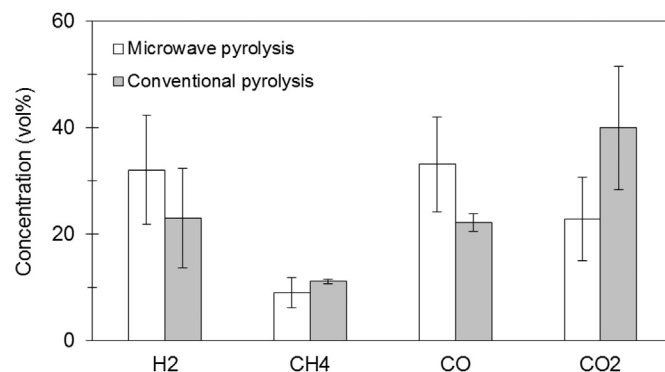$$C + H_2O \leftrightarrow CO + H_2 \tag{2}$$

Fig. 2. Compositions of gas products from microwave and conventional pyrolysis (data taken from Refs. [26,30,43,46,47]).

Table 2
Properties of bio-oils produced by microwave and conventional pyrolysis.

Property	Microwave pyrolysis bio-oil					Conventional pyrolysis bio-oil [44]
	Pine wood sawdust [21]	Wheat straw [25]	Waste office paper[a] [31]	Corn stover [42]	Coffee hulls [43]	
Elemental composition (wt%, dehydrated basis)						
C	48.8	58.9	49.9	60.7	74.8	54–58
H	6.8	6.9	5.8	7.7	8.3	5.5–7.0
O	43.5	33.2	44.2	–	8.5	35–40
N	0.9	1.2	ND[b]	2.0	7.8	0–0.2
S	0	0.02	0.04	0.15	0.6	–
Ash (wt%)	–	–	1.2	0.04	–	0–0.2
Water (wt%)	26.2	< 1[c]	2.6	15.2	–	15–30
pH	2.5	1.4[c]	–	2.9	–	2.5
Density (g mL^{-1})	1.15	1.2	–	1.25	–	1.2
HHV[d] (MJ kg^{-1})	15.0[e]	16–22[e]	21.8	17.5	34.4	16–19

[a] Organic phase bio-oil.
[b] ND: Not detected.
[c] Acid number.
[d] HHV: Higher heating value.
[e] Lower heating value.

The H_2 formation may also be attributable to the cracking and reforming reactions of hydrocarbons [49].

Huang et al. reported four empirical equations presenting the relationships between gas yields and lignocellulosic contents [50]:

$$H_2 \text{ yield} \left(\text{mg g}^{-1}\right) = 0.1331 \cdot H + 0.0486 \cdot C + 0.0647 \cdot L \quad (3)$$

$$CH_4 \text{ yield} \left(\text{mg g}^{-1}\right) = 0.1965 \cdot H + 0.2937 \cdot C + 0.0854 \cdot L \quad (4)$$

$$CO \text{ yield} \left(\text{mg g}^{-1}\right) = 2.3494 \cdot H + 3.3577 \cdot C + 2.0532 \cdot L \quad (5)$$

$$CO_2 \text{ yield} \left(\text{mg g}^{-1}\right) = 1.4510 \cdot H + 0.8023 \cdot C + 0.6097 \cdot L \quad (6)$$

where H, C, and L are hemicellulose, cellulose, and lignin contents in weight percent (wt%), respectively. It can be seen that lignin would play an important role for the production of the gases except CH_4, and its effect on H_2 production would be stronger than that of cellulose [50]. Huang et al. also claimed that most of the relative errors between calculated and measured gas yields can be less than 10% [50].

4. Catalytic microwave pyrolysis

In general, the addition of proper catalysts can have great effect on the product selectivity of microwave pyrolysis. In most cases, the heating performance and gas/liquid yield of microwave pyrolysis can be promoted by adding catalysts. However, it is not yet clear that these changes are owing to catalytic effect or microwave absorption.

In recent years, microwave pyrolysis along with the addition of catalysts has attracted considerable interest. Chen et al. reported that the addition of NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, and $Fe_2(SO_4)_3$ all increased the solid yield of microwave pyrolysis of pine wood sawdust, decreased gas yield more or less, and had no substantial effect on liquid yield [20]. Also all the eight additives decreased both CH_4 and CO_2 yields, whereas all of them except NaCl, TiO_2, and $Fe_2(SO_4)_3$ increased H_2 yield and all of them except Na_2SiO_3 and HZSM-5 decreased CO yield [20]. Wan et al. reported that the addition of KAc, Al_2O_3, $MgCl_2$, H_3BO_3, and Na_2HPO_4, which may function as microwave absorbents to speed up heating or participate in the "in situ upgrading" of pyrolytic vapors during the microwave pyrolysis of corn stover or aspen wood, increased bio-oil yield by either suppressing charcoal yield or gas yield or both [24]. Zhang et al. reported that the heating rate, final temperature, and gas yield of microwave pyrolysis of rice husk all increased with the addition of rice husk char and rice husk char-supported metallic (Ni, Fe, and Cu) catalysts [30]. Huang et al. reported that, during the microwave pyrolysis of corn stover, the addition of catalysts (NiO, CuO, CaO, and MgO) decreased the formation of PAHs and therefore made liquid products less toxic [51]. Kuan et al. pointed out that adding either CaO or MgO increased the gas yield of microwave pyrolysis of sugarcane bagasse, whereas adding either NiO or CuO increased the liquid yield [52]. The work of Zhang et al. shows that adding HZSM-5 aluminosilicate zeolite to the microwave pyrolysis of corn stover increases the production of aliphatic and aromatic hydrocarbons but decreases the production of oxygen-containing aliphatic and aromatic hydrocarbons [45].

5. Reaction kinetics

The reaction kinetics for microwave pyrolysis of lignocellulosic biomass has been evaluated. In general, the thermal decomposition of solid biomass at a constant heating rate can be expressed as follows by applying the Arrhenius equation:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \quad (7)$$

where α is the conversion fraction of biomass sample, T is the temperature, β is the heating rate, A is the pre-exponential or frequency factor, E is the activation energy, and R is the universal gas constant. By using the Coats–Redfern method [53], Eq. (7) can be integrated to:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{(for } n=1) \quad (8)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad \text{(for } n\neq1) \quad (9)$$

Assuming $2RT/E << 1$, Eqs. (8) and (9) can be simplified to:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad \text{(for } n=1) \quad (10)$$

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad \text{(for } n\neq1) \quad (11)$$

A plot of $\ln[-\ln(1-\alpha)/T^2]$ versus $1/T$ for $n=1$ or $\ln[(1-(1-\alpha)1-n)/(T2(1-n))]$ versus $1/T$ for $n \neq 1$ could result in a straight line with a slop of $-E/R$ and an intercept of $\ln(AR/\beta E)$, and thus E and A can be determined.

The kinetic parameters for microwave pyrolysis of lignocellulosic biomass reported in the literature [29,52,54–56] are listed in Table 3. As can be seen, all the results had high coefficients of determination (R^2). However, the activation energy and pre-exponential factor of microwave pyrolysis were much lower than those of conventional pyrolysis, revealing the difference in kinetic processes for both heating methods [56]. Besides, due to the low activation energy values, the assumption of $2RT/E << 1$ as aforementioned may be inappropriate.

6. Challenges

Although microwave pyrolysis can provide various advantages over conventional pyrolysis as aforementioned, it still faces several challenges. The bio-oil yield (up to approximately 40 wt%) of microwave pyrolysis is much lower than that from fluidized bed pyrolysis, which indicates that the high bio-oil yield production remains a large challenge for microwave pyrolysis [54]. Besides, the electromagnetic field in microwave ovens is not uniform and could lead to non-homogenous heating, and the characteristic changes in

Table 3
Kinetic parameters for microwave pyrolysis of lignocellulosic biomass.

Biomass	n	E (kJ mol^{-1})	A (1/s)	R^2	Ref.
Prairie cordgrass	1	3.1	2.26	0.42	[29]
	2	13.3	1.82	0.91	
	3	12.1	1.53	0.89	
Sugarcane bagasse	1	18.9	0.18	0.99	[52]
Douglas fir	1	16.5	15.3	0.81	[54]
	2	21	1.42	0.79	
	3	33.5	3.03	0.85	
Rice straw	1	27.1	1.06	0.97	[55]
Bamboo	1.5	24.5	198	0.97	[56]

materials during microwave heating may affect their dielectric properties and consequently cause difficulties in process controlling and modeling [57]. Moreover, the crude bio-oil produced by microwave pyrolysis needs to be further upgraded to promote its industrial favorability [58]. The other challenges include the high energy usage and products utilization of microwave pyrolysis. Therefore, microwave pyrolysis still needs to be further researched and developed to improve its production performance and product value.

7. Conclusions

Microwave heating offers a number of advantages over conventional heating. The hot spot phenomenon of microwave heating would have significant influence on the yield and characteristics of microwave processing products. Microwave pyrolysis is different from conventional pyrolysis. Microwave pyrolysis has higher gas and solid yields but lower liquid yield than conventional pyrolysis. The solid product of microwave pyrolysis can have high heating value and specific surface area, depending on the magnitude of input microwave power level. 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. Due to high H_2 and CO yields, the gas product of microwave pyrolysis has higher heating value than that of conventional pyrolysis. The addition of proper catalysts can provide 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 are different. According to the aforementioned literature results, microwave pyrolysis should have a high potential for the production bioenergy and green materials from lignocellulosic biomass.

Acknowledgement

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