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High-temperature dielectric properties and pyrolysis reduction characteristics of different biomass-pyrolusite mixtures in microwave field

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Abstract

Exploring the dielectric properties of mineral-biomass mixtures is fundamental to the coupled application with biomass pyrolysis and microwave technology to mineral reduction. In this work, the microwave dielectric properties of five pyrolusite-biomass mixtures were measured by resonant cavity perturbation technique and the pyrolysis reduction characteristics were systematically investigated, including poplar, pine, ageratina adenophora, rapeseed shell and walnut shell. Results indicated that the dielectric properties commonalities of five mixtures with temperature represented by increasing firstly, dropping intensely and finally rising slightly, with excellent responsiveness to microwaves; which the change trend was mainly attributed to the crystal transformation of amorphous MnO_2 and pyrolusite reduction reactions by biomass pyrolysis. Meanwhile, the heating characteristics successfully matched the dielectric properties of the mixtures, and the pyrolusite reduction process by biomass can be divided into two stages: biomass pyrolysis and pyrolusite reduction. The work highlights the universal feasibility of the novel coupled method for mineral reduction.

Keywords: biomass pyrolysis; low-grade pyrolusite; dielectric properties; heating characteristics; microwave heating

1 Introduction

Biomass is the only carbon-bearing resource which can partially replace fossil fuel, via two main processes including chemical conversion and biochemical conversion into gaseous, liquid and solid fuels and other chemical raw materials and products, involving technologies such as gasification, liquefaction, pyrolysis, solidification and direct combustion (Demirbas,

2000; Wei et al., 2017). Rapid population growth and economic development have rendered the maintained robust growth of energy demand, representing energy issues increasingly prominent. Currently, burning fossil fuel is the main way to supply energy source in national production (Abnisa and Wan Daud, 2014), although with the non-renewable characteristic, meanwhile accompanied with vast amounts of contaminants such as SO₂, CO₂ and complex nitrogen oxides, aggravating environmental pollution and violating the development concept of low-carbon economy and sustainable development (Kalogirou, 2004). Therefore, as an abundant, clean and renewable energy source, biomass resource has attracted growing attention in the field of mineral processing, organic synthesis, adsorbents and catalysts, etc., (Adsul et al., 2011; Guo et al., 2018; Kumar et al., 2018). Among utilization technologies reported for biomass, biomass pyrolysis has received growing interest in mineral processing, referring to by biomass pyrolysis to generate reductive volatiles and charcoal, followed by the pyrolysis products react with metal oxides in minerals. Luo et al. reported that direct reduction of mixed biomass-Fe₂O₃ briquettes using biomass-generated syngas instead of coke, successfully reduced iron ore to pig iron (Fe) with iron content up to 94.7% (Luo et al., 2011). Cheng et al. used cornstalk as reducing agent to efficiently reduce low-grade manganese oxide ore into manganese monoxide (MnO) at a temperature regime of 500-600 °C (Cheng et al., 2009). In comparison of traditional coal reducing agent, biomass pyrolysis reduction can effectively reduce emission of acid gas (NO_x and SO_x) and greenhouse gas (CO_x), with low content of sulfur (S) and nitrogen (N) and its carbon neutral characteristics; meanwhile, with the biomass pyrolysis temperature lower than 400 °C, hence biomass can quickly reduce minerals at lower temperatures with high efficiency, greatly decreasing energy consumption

and efficiently achieving clean production.

Manganese monoxide (MnO) as the most basic manganese oxide, has been widely reported widespread applications in chemical, battery, catalyst and magnetic materials, etc. (Sun et al., 2018; Xin et al., 2012; Zhou et al., 2016). Currently, manganese oxide ore is mainly as raw material to produce MnO by carbon reduction roasting method. However, low-grade manganese ore with the average grade being ca. 21.4 %, accounts for 93.6 % of the total reserves in China. Meanwhile, as a nonrenewable fossil fuel, coal resource will eventually be depleted; moreover, the method was plagued with high temperature, high-energy consumption, high costs and environmental restrictions (Ismail et al., 2010). Hence, it urgently demands to develop new processes for preparing MnO from low-grade pyrolusite, with environmentally benign and cost effective reducing agent and reduction technologies.

Microwave heating (2450 MHz) as a novel green method, has attracted increasingly attention in the comprehensive utilization of manganese ore resources (Chen et al., 2016; Ye et al., 2018; Li et al., 2019a). Actually, Ye et al. investigated the contrast experiments on microwave heating and traditional heating for carbothermal reduction of manganese ore with coal as reducing agent, and reported that microwave heating offered excellent merits such as shorter reaction time, lower reduction temperature and energy consumption, higher reduction efficiency and environmentally-friendly (Ye et al., 2014). Assuredly, the unique characteristics of microwave heating are related to its special heating essence. Based on the interaction between microwave and material, microwave heating directly transfers microwave energy with a high frequency electromagnetic wave to the reactive molecules or atoms inside

the material, through dielectric loss of material converting microwave energy into heat energy and then generating a thermal effect to heat the material (Takatsu and Kurogi, 1999). The microwave-absorbing ability of materials primarily depends on the complex permittivity of materials. The complex permittivity is the basis to determine the responsiveness of a material to microwaves, which are affected by the frequency of magnetic field, temperature and chemical composition, etc., wherein temperature is particularly important. Li et al. investigated the dielectric properties of manganese ore-walnut shell mixtures with temperature at a mixing ratio of 10:1.2, and results indicated that dielectric properties of mixtures were significantly influenced by temperature (Li et al., 2019b). Therefore, to make microwave heating efficient, before performing microwave processing, it is fundamentally important to investigate the high-temperature dielectric properties of materials. Moreover, the simple temperature rising profile measured in microwave field is able to investigate the performance of the microwave heating, referring to that the microwave heating characteristics of a material correspond to its dielectric properties, further contributing to verify the rationality of the dielectric properties analysis.

Previous work focused on the respective utilization of biomass as reducing agent or microwaves as energy source for mineral reduction, while few detailed studies have reported the coupled application of biomass pyrolysis and microwave technology to mineral reduction. Moreover, recent work have verified that the merged method with biomass pyrolysis and microwave technology can be applied efficiently into pyrolusite reduction, through replacing conventional heating and traditional coal reducing agent and further achieving energy conservation and emission reduction and clean production, even explored the dielectric

properties of the mixture of low-grade pyrolusite with a single biomass at a mixing ratio of 10:1.2 (Li et al., 2019a; Li et al., 2019b), while it can't adequately represent the common dielectric properties law of biomass-manganese ore mixtures and even clarify the universal feasibility of the merged method for mineral reduction. Hence, in the present work, five typical biomass including herbaceous, shell, and woody biomass materials, were chosen to comparatively investigate the commonalities between the high-temperature dielectric properties of biomass-manganese ore mixtures, further convincingly clarify the universal feasibility of the merged method for manganese ore reduction. Meanwhile, the microwave heating characteristics of five mixtures were evaluated to supportively verify the rationality of the dielectric properties analysis. Furthermore, combined with the dielectric properties and thermochemical characteristics analysis, the reduction mechanism of the novel merged method for pyrolusite reduction was reasonably deduced. This study can provide significant reference for applications of microwave technology and biomass pyrolysis coupled to manganese ore reduction, even extending to other minerals reduction.

2 Materials and methods

2.1 Materials

Pyrolusite used as the reduced material, was received from CITIC Dameng Mining Industries Limited (Nanning City, Guangxi Province, P.R. China). The chemical compositions of pyrolusite were provided by Analysis and Testing Center of Daxin Branch of CITIC Dameng Mining Industries Limited (Chongzuo City, Guangxi Province, P.R. China), and the analytical results were as follows: T_{Mn} , 28.81%; SiO_2 , 25.83%; Fe^{3+} , 7.76%; Al_2O_3 ,

2.52%; CaO, 1.24%; MgO, 1.16%; S, 0.27%; P, 0.14%, respectively. From the analytical results, it can be summarized that the received pyrolusite was low-grade manganese ore with low manganese content ($<30\%$) and high iron content ($\text{Mn/Fe}>3$).

Five typical biomass materials in Yunnan province chosen as expected reducing agents, including poplar and pine (woody biomass), ageratina adenophora (herbaceous biomass), rapeseed shell and walnut shell (shell biomass), were acquired from Chuxiong Nutshell Processing Factory (Chuxiong City, Yunnan Province, P.R. China), with an abundant resource and wide acquisition channels at very economical prices in Yunnan Province. The ultimate and proximate analysis results of biomass materials were provided by Advanced Analysis and Measurement Center of Yunnan University, and the analytical results were detailed in Supplementary data. Wherein the ultimate analysis was performed in accordance with the elemental analysis method of coal (GB/T476-2001), the mass percent of oxygen (O) was obtained by subtraction; and the proximate analysis was referred to the recommended methods of Solid Biofuel Technical Specification of EU (CEN/TC355) and National Standard of the People's Republic of China (GB/T28731-2012). From ultimate analysis results (see Supplementary data), it was clearly observed that carbon (C), hydrogen (H) and oxygen (O) were the main elements in biomass materials, accounting for more than 95%; while from proximate analysis results (see Supplementary data), volatiles and fixed carbon accounted for a large proportion. In biomass pyrolysis products, reductive volatiles (carbon monoxide (CO) and hydrogen (H_2)) and fixed carbon (C) are the main components which have a reducing effect on pyrolusite (Zhang et al., 2013; Li et al., 2019a). Therefore, based on the analytical results, it can be speculated that the five biomass materials have good reduction effects on

low-grade pyrolusite, with a large proportion of elemental carbon (C), elemental (H), elemental oxygen (O), volatiles and fixed carbon.

2.2 Instrumentation

The schematic diagram of dielectric test system was illustrated in Fig. 1, wherein Fig. 1(a) presented the dielectric test device, and Fig. 1(b) demonstrated the magnified graph of cylindrical resonant cavity (TM_{0n0}) in dielectric test device, respectively. The dielectric properties of materials were determined in the cylindrical resonant cavity (TM_{0n0}) by cylindrical cavity perturbation method. As shown in Fig. 1(a), the dielectric test device was composed by a cylindrical resonant cavity (TM_{0n0}), eddy current heating system, induction heater and temperature controller, water cooling machine, air pump, computer and vector network analyzer (Agilent-N5230C). Additionally, as shown in Fig. 1(b), the cylindrical resonant cavity (TM_{0n0}) in dielectric test device mainly consisted of microwave cavity, coupling device, detector and exciter, alundum tube and sample insertion holes, groove and slit.

2.3 Procedure

Samples for dielectric test are required to be solid powder materials; hence, before dielectric test, raw bulk pyrolusite and five biomass materials were ground and screened to a particle size regime of 60-180 mesh. Referred to previous work, the optimum mixing ratio of manganese ore to biomass was 10:1.0 (Zhang et al., 2013); while the manganese ore used in the present work was low-grade pyrolusite, therefore, a $m_{\text{ore}}/m_{\text{biomass}}$ mixing ratio was chosen at 10:1.2. The specimens were prepared by mixing pyrolusite and five different biomass powders with a particle size of 140 mesh at the mixing ratio of 10:1.2 for 10 min in a

porcelain mortar. And in order to avoid the influence of moisture on the dielectric properties and thermal characteristics of materials, the specimens were dried at 105 °C for 12 h in an electric blast drying oven (DHG9079A, Shanghai YiHeng Scientific Instruments Co. Ltd).

After drying, the dried samples were introduced to the dielectric test device (Agilent-E5071C, MYWAVE) to measure the complex permittivity of mixtures from room temperature to 800 °C, with 50 °C interval as a temperature variable node, and the complex permittivity was obtained through four steps by cavity calibration, quartz empty tube calibration, charging and loading quartz tube test, and recalculation of the just measured complex permittivity. Two-frequency system of 2450 MHz and 915 MHz was attached to the dielectric device, while microwave equipment applied in laboratory are mostly equipped with a frequency of 2450 MHz, therefore, the dielectric properties of five pyrolusite-biomass mixtures were measured at 2450 MHz. In addition, 33.6 g of five pyrolusite-biomass mixtures were placed into corundum crucible and then introduced into the box-type microwave furnace (HM-X08-16, MAKEWAVE) to measure the heating characteristics in microwave field, under microwave irradiation at 2450 MHz with 1200 W from room temperature to 800 °C; wherein the mass of pyrolusite was 30.0 g and the mass of each biomass sample was 3.6 g, with the same $m_{\text{ore}}/m_{\text{biomass}}$ mixing ratio of 10:1.2. And the thermochemical characteristics of five pyrolusite-biomass mixtures were examined by the high-temperature TGA thermogravimetric analyzer (TGA/DSC 1/1600, METTLER TOLEDO, Switzerland), measured from 25 °C to 800 °C at a heating rate of 20 °C/min with Argon (Ar) flow rate of 60 mL/min as shielding gas.

2.4 Measurement principle of complex permittivity

Commonly, the dielectric properties of materials are characterized by the measurement of complex permittivity, including the dielectric constant (ϵ_r'), dielectric loss (ϵ_r'') and loss tangent ($\tan \delta$); the complex permittivity can be defined as follows (Carter, 2001):

$$\epsilon = \epsilon_r' - j\epsilon_r'' \quad (1)$$

Where ϵ is the complex permittivity of materials; ϵ_r' is the real part of the complex permittivity; ϵ_r'' is the imaginary part of the complex permittivity being. Additionally, $\tan \delta$ is being named dielectric loss tangent, expressed as (Santra and Limaye, 2005):

$$\tan \delta = \frac{\epsilon_r''}{\epsilon_r'} \quad (2)$$

Based on the above formula, ϵ_r' , ϵ_r'' and $\tan \delta$, the three values are related to each other, knowing that two of them can obtain the third value; wherein ϵ_r' and $\tan \delta$ are two basic parameters that measure the complex permittivity of a material. Typically, ϵ_r' value of materials is larger when materials with a stronger polarity; meanwhile, the material with a higher dielectric loss tangent ($\tan \delta$) renders it with a higher heating efficiency in microwave field. Therefore, referring to microwave heating essence, it could be speculated that microwave heating technology can be applied efficiently to process pyrolusite-biomass mixtures, which was attributed to that low-grade pyrolusite contained various metal compounds showing excellent microwave-absorbing ability (He et al., 2019); and biomass composed by three main components of cellulose, hemicellulose and lignin and some extracts soluble in polar or weakly polar solvents, which has certain polarity.

3 Results and discussion

3.1 Dielectric properties analysis

The dielectric properties (including dielectric constants (ϵ_r'), dielectric loss factors (ϵ_r'') and loss tangent coefficients ($\tan \delta$)) of five pyrolusite-biomass mixtures were measured to investigate some commonalities between five biomass-pyrolusite mixtures, and the results were plotted in Fig. 2.

3.1.1 Dielectric constants analysis

Fig. 2(a) demonstrated the dielectric constants. The dielectric constant (ϵ_r') reveals the ability of a material to absorb microwaves and store electromagnetic waves. It was observed from Fig. 2(a) that the ϵ_r' curves of five pyrolusite-biomass mixtures showed the same trend with temperature, with a general trend of rising first, then dropping intensely and finally rising slightly. At room temperature, the ϵ_r' of pyrolusite-biomass mixtures was at high levels with 7.631 (F/M), 8.309 (F/M), 8.607 (F/M), 9.116 (F/M) and 9.111 (F/M) for poplar, pine, rapeseed shell, ageratina adenophora and walnut shell, respectively, exhibiting strong microwave response capability, which was attributed to that low-grade pyrolusite contained various metal compounds showing excellent microwave-absorbing ability (He et al., 2019) and biomass has certain polarity. With temperatures increasing, the ϵ_r' of pyrolusite-poplar mixture increased to the maximum value with 7.980 (F/M) at 200 °C; the same maximum ϵ_r' value of other four pyrolusite-biomass mixtures appeared at 250 °C, 400 °C, 200 °C and 200 °C, with 10.546 (F/M), 10.248 (F/M), 10.146 (F/M) and 9.158 (F/M), respectively, corresponding to the mixtures with pine, rapeseed shell, ageratina adenophora and walnut shell, respectively. The ϵ_r' with higher levels at early stage was ascribed to the superimposing

results of the two phenomena on each other, wherein the dehydration stage of surface water and combined water in mixtures caused the decrease of ϵ_r' value, meanwhile the crystal transformation of amorphous MnO_2 into $\gamma\text{-MnO}_2$ resulted an increase of ϵ_r' value. The $\gamma\text{-MnO}_2$ has much higher dielectric properties than amorphous MnO_2 (Su et al., 2015), and the increment value by the crystal transformation of amorphous MnO_2 was higher than the decrement value by the removal of surface water and combined water; therefore, the superimposed ϵ_r' value represented an increase trend with temperature. Temperature continuously increasing, it was found from Fig. 2(a) that the ϵ_r' curves of five pyrolusite-biomass mixtures suddenly dropped to low levels, and the minimum values were appeared at 450 °C, 550 °C, 550 °C, 600 °C and 500 °C, with 6.746 (F/M), 7.335 (F/M), 7.411 (F/M), 7.931 (F/M) and 7.501 (F/M), respectively. The intense decrease of ϵ_r' curves was attributed to the reduction reactions of pyrolusite by biomass pyrolysis, causing that strong microwave-absorbing compositions such as MnO_2 and Fe_2O_3 in pyrolusite were gradually reduced to weak microwave-absorbing phases such as Mn_2O_3 , Mn_3O_4 , MnO , Fe_3O_4 and FeO (Su et al., 2015), further rendering the decrease of the dielectric properties of the mixtures; meanwhile, the gas generated by biomass pyrolysis caused the volume of the sample in the quartz tube to expand, causing a decrease in density and also rendering the decrease of dielectric properties. Moreover, with temperature increasing, it was observed from Fig. 2(a) that the ϵ_r' values had a slightly rise, which was mainly attributed to the conversion of MnO to Mn , wherein the microwave absorption characteristics of metal Mn were much better than metal oxide MnO (Su et al., 2015), therefore, representing an increase of ϵ_r' values of pyrolusite-biomass mixtures.

3.1.2 Dielectric loss factors analysis

Fig. 2(b) presented the dielectric loss factors (ϵ_r''). The dielectric loss factor (ϵ_r'') signifies the ability of substance converting microwave energy into heat energy. It can be observed from Fig. 2(b) that the ϵ_r'' curves of five pyrolusite-biomass mixtures presented the same trend with temperature, wherein the previous period was gently maintained at a high level with the maximum value appeared, the medium period sharply declined and the latter rose sharply. For pyrolusite-poplar mixture, the maximum ϵ_r'' value appeared at 200 °C with 0.3617 (F/M); higher than 200 °C, it was observed to suddenly drop to the minimum value at 450 °C with 0.1600 (F/M); temperature exceeding 450 °C, it increased to 0.3160 (F/M) at 750 °C. For pyrolusite-pine mixture, the maximum and minimum of ϵ_r'' value appeared at 100 °C with 0.5141 (F/M) and at 550 °C with 0.1669(F/M), respectively, and followed by a high level appeared at 700 °C with 0.3537 (F/M). For other three pyrolusite-biomass mixtures with rapeseed shell, ageratina adenophora and walnut shell, the maximum of ϵ_r'' values appeared at 200 °C with 0.4722 (F/M), at 250 °C with 0.6742 (F/M) and at 200 °C with 0.5401 (F/M), respectively; the minimum values appeared at 750 °C with 0.2206 (F/M), at 700 °C with 0.2444 (F/M) and at 500 °C with 0.1905 (F/M), respectively; additionally, the high level at the latter appeared at 700 °C with 0.3829 (F/M), at 750 °C with 0.4506 (F/M) and at 700 °C with 0.3537 (F/M), respectively.

3.1.3 Loss tangent coefficients analysis

Fig. 2(c) illustrated the loss tangent coefficients ($\tan \delta$). The loss tangent coefficient ($\tan \delta$) denotes the efficiency of the material to convert the absorbed microwave energy into heat energy. It can be observed from Fig. 2(c) that the $\tan \delta$ curve of each pyrolusite-biomass

mixture sample had the same trend with the ε_r'' curves shown in Fig. 2(b). In detail, the high levels were gently maintained at the previous period, with the maximum value appeared at 200 °C with 4.53×10^{-2} for poplar, at 100 °C with 5.55×10^{-2} for pine, at 100 °C with 5.04×10^{-2} for rapeseed shell, at 250 °C with 6.99×10^{-2} for ageratina adenophora and at 200 °C with 5.90×10^{-2} for walnut shell, respectively; followed by the medium period sharply dropped, with the minimum value appeared at 450 °C with 2.37×10^{-2} , at 550 °C with 2.27×10^{-2} , at 550 °C with 3.09×10^{-2} , at 550 °C with 3.08×10^{-2} and at 500 °C with 2.54×10^{-2} , respectively; and then the latter increased sharply with temperature.

In summary, based on the analysis for Fig. 2, it can be concluded that the high-temperature dielectric properties of pyrolusite-biomass mixtures were generally at high levels, indicating the biomass-pyrolusite mixture material has good responsive to microwaves, further rendering it with a higher heating efficiency in microwave field.

3.2 Microwave heating characteristics analysis

Microwave heating characteristics of materials can verify the correctness of measured dielectric properties of materials. Therefore, five pyrolusite-biomass mixtures were introduced into the box-type microwave furnace to measure the heating characteristics, and the results were exhibited in Fig. 3.

Fig. 3(a) displayed the temperature rise curve of pyrolusite-poplar mixture. It can be concluded from Fig. 3(a) that it took 23.0 min for pyrolusite-poplar mixture to be heated from room temperature to 800 °C with microwave power at 1200 W, and the heating characteristics of pyrolusite-poplar mixture can be divided into seven stages identified by different heating rates, with 29.71 °C/min, 74.40 °C/min, 20.20 °C/min, 41.42 °C/min, 18.02 °C/min,

40.82 °C/min and 25.71 °C/min with heating time prolonging. The change trend of heating rates corresponded with the change trend of dielectric properties (Fig. 2). The heating rate at stage II with 74.40 °C/min was obviously higher than that of another six stages, with 29.71 °C/min, 20.20 °C/min, 41.42 °C/min, 18.02 °C/min, 40.82 °C/min and 25.71 °C/min, respectively, which was attributed to the crystal transformation of amorphous MnO₂ into γ -MnO₂, rendering a great increase of dielectric constant (ϵ_r') and further resulting in the highest heating rate at stage II ; moreover, the heating rate at stage VI with 40.82 °C/min was higher than that of the adjacent front and back stages with 18.02 °C/min and 25.71 °C/min, complying with the high level of ϵ_r'' and $\tan \delta$ values of pyrolusite-biomass mixtures appeared at the latter, as shown in (Fig. 2).

The temperature rise curves of other four pyrolusite-biomass mixtures with pine, rapeseed shell, ageratina adenophora and walnut shell were illustrated in Fig. 3(b), (c), (d) and (e), respectively. With the same heated mass of 33.6 g for pyrolusite-biomass mixture and the same microwave power at 1200 W, it took 21.0 min, 13.5 min, 13.0 min and 11.0 min for different pyrolusite-biomass mixtures to be heated from room temperature to closely 800 °C, with pine, rapeseed shell, ageratina adenophora and walnut shell, respectively. In addition, the same change trend of the heating rates for the four pyrolusite-biomass mixtures also appeared the same change trend as pyrolusite-poplar mixture, with the performance of low heating rates in the head and tail and high heating rates in the middle of temperature rising curves. Wherein the heating characteristics of pyrolusite-pine mixture was divided into four stages by different heating rates, with 53.77 °C/min, 98.80 °C/min, 38.20 °C/min and 25.85 °C/min; for pyrolusite-rape seed shell mixture, it was divided into four stages with 60.20 °C/min,

103.00 °C/min, 66.45 °C/min and 38.10 °C/min; for pyrolusite-ageratina adenophora mixture, it was divided into two stages with 39.76 °C/min and 110.61 °C/min; for pyrolusite-walnut shell mixture, it was divided into four stages with 54.62 °C/min, 112.00 °C/min, 83.83 °C/min and 56.79 °C/min.

From the above analysis, the temperature rise curves of five pyrolusite-biomass mixtures appeared the same trend, with low heating rates in the head and tail part and high heating rates in the middle part. Moreover, combined with Fig. 2 and Fig. 3, the heating characteristics with temperature in microwave field successfully matched the dielectric properties curves change, verifying the correctness of the measured dielectric properties of five pyrolusite-biomass mixtures.

3.3 Thermochemical characteristics analysis

Thermochemical characteristics of a material is related to its thermal behavior, and the change of dielectric properties is also attributed to the thermal behavior, therefore thermogravimetric measurement was introduced to investigate the thermochemical characteristics of five pyrolusite-biomass mixtures, further contributing to verify the rationality of the dielectric properties analysis, and the TG-DTG-DSC curves were illustrated in Fig. 4.

Fig. 4(a) illustrated the TG curves. It was obviously observed from Fig. 4(a) that the same trend of weight loss of four pyrolusite-biomass mixtures appeared, except from ageratina adenophora-pyrolusite mixture. And the node temperatures of ageratina adenophora-pyrolusite mixture were much lower than that of other four pyrolusite-biomass mixtures, especially representing that the second and third node temperature at 249 °C and

289 °C, respectively, while the second and third node temperature of other pyrolusite-biomass mixtures appeared near at 330 °C and 420 °C, respectively; which was attributed to the different composition proportion of cellulose, hemicellulose and lignin for five biomass materials, corresponding with the ultimate and proximate analysis results (Table 1) . The total proportion of elemental carbon (C) and oxygen (O) in ageratina adenophora was higher than that of other biomass materials; carbon monoxide (CO) was the main gas generated by biomass pyrolysis, which has a reducing effect for pyrolusite; therefore, the higher composition proportion of elemental carbon (C) and oxygen (O) can accelerate the gas-solid reduction reactions of pyrolusite-biomass mixtures. According to the node temperature, the weight loss of pyrolusite-biomass mixtures can be generally divided into four stages identified by temperatures: (1) the first stage (25 °C~150 °C), was the dehydration stage of pyrolusite-biomass mixtures. At the temperature regime, surface water and adsorbed water escaped from the material, corresponding to form a small endothermic peak in the DTG curves (Fig. 4(b)). (2) The second stage (150 °C~330 °C), was pre-pyrolysis stage, mainly occurred the removal of bound water, some depolymerization reactions and a slow glass transition phenomenon of biomass; meanwhile, crystal water and volatiles in pyrolusite were also removed, and it was observed from Fig. 4(b) that the thermal effect of mixtures was obvious in this temperature regime. Based on the thermodynamics analysis (see Supplementary data), the reduction process of MnO_2 to Mn_2O_3 , Mn_2O_3 to Mn_3O_4 , Mn_3O_4 to MnO and Fe_2O_3 to Fe_3O_4 occurred at this temperature range, hence pyrolusite was partially reduced by gas-solid reduction reactions with a small amount of reducing gas (CO , H_2). Wherein hydrogen (H_2) was produced by the glass transition of biomass; carbon monoxide

(CO) was generated by the gradual cleavage of glycoside bonds, C-O bonds and the C-C bonds in the lignin structure of biomass; and a smaller amount of the primary coke was gradually formed by free radical reaction and rearrangement reaction. It was noted from Fig. 4(b) that both the first stage and the second stage were endothermic. (3) The third stage (330 °C~420 °C), was the main reaction stage of pyrolusite-biomass mixtures, mainly the pyrolysis process of hemicellulose, cellulose and some lignin in biomass, and the reduction process of MnO_2 and Fe_2O_3 in low-grade pyrolusite. The biochar (C) and reductive volatiles contained CO, CO_2 , H_2 , CH_4 , etc., were generated by biomass pyrolysis, wherein the biochar and reductive volatiles contributed to the solid-solid and gas-solid reduction reaction of pyrolusite-biomass mixtures, respectively. It can be obviously seen from Fig. 4(b) that the thermal effect at the third stage was much larger than that of the second stage. (4) The fourth stage (>420 °C), is the slow reduction stage of pyrolusite-biomass mixtures. At this temperature range, the second pyrolysis of cellulose and lignin in the residue occurred, and porous cokes with stable graphite structure and small-molecule gas were formed by the cleavage of C-C bonds and C-H bonds (Lapuerta et al., 2004), corresponding to the gentle thermal effect at this stage (Fig. 4(b)). According to the thermodynamics analysis (see Supplementary data), the conversion process of Mn_3O_4 to MnO , Fe_3O_4 to FeO and FeO to Fe mainly occurred, and part of the unreduced Mn_2O_3 was continuously reduced to Mn_3O_4 .

Fig. 4(b) displayed the DTG curves, indicating that pyrolusite reduction by biomass pyrolysis had different thermal effects at different reaction stages. The thermochemical process of pyrolusite-biomass mixture was mainly represented by the endothermic and exothermic process of biomass pyrolysis, and the exothermic process of pyrolusite (mainly

MnO₂) being reduced by biomass volatile into Mn₃O₄ and the exothermic process of Mn₃O₄ being continuously reduced to MnO. The first endothermic peak of five pyrolusite-biomass mixtures appeared near at 50 °C, which was ascribed to that the evaporation endotherm of surface water and adsorbed water. While the temperatures of the second endothermic peak varied with different biomass materials, corresponding to ageratina adenophora, rapeseed shell, poplar, pine and walnut shell at 226.5 °C, 299.7 °C, 375.1 °C, 379.9 °C and 382.3 °C, respectively. The appearance of the second endothermic peak was attributed to that the conversion of MnO₂ to Mn₂O₃, Mn₂O₃ to Mn₃O₄ and Fe₂O₃ to Fe₃O₄, which the three reduction reactions are endothermic reactions; moreover, the appearance of the shoulder peak was ascribed to that the weight of hemicellulose pyrolysis was decreased, reflecting in a decrease of the weight of MnO₂ reduced to Mn₃O₄ by biomass volatiles. Especially, it can be observed from the DTG curve of pyrolusite-walnut shell mixture that there was an exothermic peak at 324.6 °C, which was caused by the reaction of $\text{Mn}_3\text{O}_4 + \text{C} = 3\text{MnO} + \text{CO}$, which is an exothermic reaction. And from the DTG curve of pyrolusite-ageratina adenophora mixture, another endothermic peak was appeared at 597.6 °C, which was caused by the reaction of Fe₃O₄ to FeO. Surely, the two special peaks were supposed to appear in other DTG curves as well. While the proportion of the three main components in each biomass is different, rendering the different yield of biomass pyrolysis products, naturally resulting in various effects on the reduction behavior of pyrolusite; and various reduction reactions in pyrolusite-biomass mixtures occurred simultaneously, resulting to the occurrence of heat diffusion delay and weight delay, which were caused by the exothermic and endothermic reactions of manganese ore by biomass volatiles.

Fig. 4(c) presented the DSC curves. It was observed in Fig. 4(c) that those DSC curves presented the same trend with two epitaxial termination temperature peaks, referring to the intersection of the tangent of the DSC curve and the maximum weight loss line, where the maximum weight loss of pyrolusite-biomass mixtures occurred. For poplar, pine, ageratina adenophora, rapeseed shell and walnut shell, the first epitaxial termination temperature peak was appeared at 43.9 °C, 40.4 °C, 56.1 °C, 59.0 °C and 39.0 °C, respectively, which the peak was attributed to the removal of surface water of mixtures; the second epitaxial termination temperature peak was appeared at 371.6 °C, 383.8 °C, 394.9 °C, 306.7 °C and 351.5 °C, respectively, corresponding to the main reduction stage of pyrolusite-biomass mixtures in TG curves and the largest weight loss peak in DTG curves, which was caused by the process overlap including the small weight loss caused by continued reduction of Mn_3O_4 to MnO by biomass volatiles and the formation of volatiles by cellulose pyrolysis (Zhang et al., 2013), wherein the reaction of Mn_3O_4 to MnO is exothermic.

From the above analysis, combined with Fig. 2 and Fig. 4, the thermochemical characteristics of five biomass-pyrolusite mixtures were consistent with the dielectric properties change (Fig. 4), verifying the correctness of the measured dielectric properties.

3.4 Discussion on the reduction mechanism of pyrolusite by biomass pyrolysis

Based on the above dielectric properties and thermochemical characteristics analysis, and combined with the thermodynamic analysis (see Supplementary data), the reduction mechanism of pyrolusite by biomass pyrolysis was analytically deduced, as illustrated in Fig. 5. Biomass is mainly composed by the three components, including cellulose, hemicellulose and lignin (Skreiberg et al., 2011); therefore, the whole pyrolysis process of biomass can be

regarded as a linear superposition of the pyrolysis process of cellulose, hemicellulose and lignin; wherein the pyrolysis products of cellulose and hemicellulose are mainly volatile substances, and the lignin is mainly decomposed into charcoal (Muller-Hagedorn et al., 2003). As shown in Fig. 5, the reduction mechanism of pyrolusite by biomass pyrolysis can be regarded as two composed parts: biomass pyrolysis and pyrolusite reduction, referring to that the reducing ingredients were firstly produced by biomass pyrolysis, followed by the metal oxides in pyrolusite reacted with the reducing ingredients, which mainly included fixed carbon (C), hydrogen (H_2) and carbon monoxide (CO).

During biomass pyrolysis stage, with microwave heating continually processing, surface water and combined water were removed from biomass, followed by different liquid products were generated by the depolymerization and ring opening reaction of cellulose and hemicellulose monomer. Wherein levoglucosan (LG) and furan (F) were produced by the depolymerization reaction of cellulose monomer (Fabbri et al., 2007); and glycolaldehyde (HAA) and hydroxyacetone (HA) were generated by the ring opening reaction of cellulose monomer; meanwhile, other alcohols, esters, dehydrated monosaccharides, etc. will also be produced. Similarly, for hemicellulose, with temperature increasing, after the removal of surface water and combined water, the depolymerization and ring opening reactions of hemicellulose monomer occurred. The great difference between cellulose and hemicellulose was the representative liquid products, which was attributed to the attached different structures and stability differences of biomass materials, mainly representing by 1, 4-dehydrated- α -D-xylopyranose (ADX) and furfural (FF) produced by the depolymerization reaction of hemicellulose monomer (Antal et al., 1991; Pouwels et al., 1987;

Shen et al., 2010). The structural formula of lignin without being determined, therefore the main pyrolysis liquid products corresponding to lignin were not illustrated in Fig. 6.

Furthermore, tar, gas and char with different states were generated by the complex cleavage of bonds and other rearrangement reactions, including C-C bond, C-O bond and C-H bond, etc. The reducing ingredients contained fixed carbon (C), hydrogen (H_2), carbon monoxide (CO) and other reducing gas, wherein hydrogen (H_2) was mainly produced by the glass transition of biomass; carbon monoxide (CO) was mainly generated by the gradual cleavage of glycoside bonds, C-O bonds and C-C bonds in the lignin structure of biomass; and fixed carbon (C) was mainly formed by the cleavage of C-C bonds and C-H bonds, free radical reactions and rearrangement reactions (Lapuerta et al., 2004).

After the reducing ingredients generated by biomass pyrolysis, the metal oxides in pyrolusite immediately reacted with the reducing ingredients, followed by the step-by-step reduction process: $MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ and $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO$ (Li et al., 2019a; Zhang et al., 2013), including the main reduction reactions of MnO_2 and the secondary reduction reactions of Fe_2O_3 . Based on the thermodynamic analysis (see Supplementary data), the step-by-step reduction process of MnO_2 to Mn_2O_3 and Mn_2O_3 to Mn_3O_4 occurred at room temperature; at temperatures higher than 288.9 °C, the conversion of Mn_3O_4 to MnO happened; temperature increased to 295.9 °C, the conversion of Fe_2O_3 to Fe_3O_4 could be achieved; with temperature increasing, the conversion of Fe_3O_4 to FeO occurred at temperatures higher than 685.8 °C. Additionally, gas generated by gasification and decarbonization reactions of carbon (C), including CO, H_2 and CO_2 , offered some contribution to accelerate the reaction rate and ensure the completion reduction of low-grade

pyrolusite.

4 Conclusions

In the present work, the high-temperature dielectric properties and pyrolysis reduction characteristics of five biomass-pyrolusite mixtures in microwave field were comprehensively investigated. Results indicated the thermal behavior of mixtures caused the dielectric properties change, with the same trend appeared: rose first, then decreased intensely and finally increased slightly. Moreover, the change trend of microwave heating characteristics with temperature was synchronized with the dielectric properties, meanwhile the thermochemical characteristics were consistent with the dielectric properties, both verifying the correctness of the measured dielectric properties. Additionally, the reduction process of pyrolusite by biomass pyrolysis contained two stages: biomass pyrolysis and pyrolusite reduction.

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Appendix A. Supplementary data

E-supplementary data for this work can be found in e-version of this paper online.

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Figure captions

Fig.1. Schematic diagram of dielectric test system, (a) dielectric test device; (b) cylindrical resonant cavity in dielectric device

Fig.2. Dielectric properties of five pyrolusite-biomass mixtures under microwave irradiation at 2450 MHz, (a) dielectric constants (ϵ_r'); (b) dielectric loss factors (ϵ_r''); (c) loss tangent coefficients ($\tan \delta$)

Fig.3. Heating characteristics of five pyrolusite-biomass mixtures under microwave irradiation at 2450 MHz with 1200 W, (a) poplar; (b) pine; (c) rapeseed shell; (d) ageratina adenophora; (e) walnut shell

Fig.4. TG-DTG-DSC curves of five pyrolusite-biomass mixtures, (a) TG curves; (b) DTG curves; (c) DSC curves

Fig.5. Reduction mechanism diagram of pyrolusite by biomass pyrolysis

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The main highlights of this work are as follows,

- Dielectric properties of pyrolusite-biomass mixtures were measured.
- Microwave heating characteristics of pyrolusite-biomass mixtures were investigated.
- Reduction mechanism of pyrolusite by biomass pyrolysis was analytically deduced.
- Exploration of biomass pyrolysis and microwave heating merged to minerals reduction.