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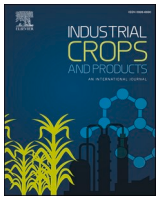

Organosolv fractionation of a lignocellulosic biomass feedstock using a pilot scale microwave-heating reactor

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ABSTRACT

Bamboo is among the short-rotation and dedicated energy crops which serve as lignocellulosic feedstock for future bio-refinery. A pilot scale microwave fractionation system (PMFS) was developed and used for the organosolv fractionation of bamboo sawdust. The key component of the system, a 1000 L microwave-heating reactor, was designed with unique features for high efficiency of microwave energy utilization and uniform temperature distribution. More than 800 kg reactant can be heated at 65% energy efficiency with temperature differences between top and bottom reactor positions of less than 4 °C. The operational parameters of the PMFS were investigated, and the fractionation products from the PMFS process were characterized and compared with those obtained from lab scale experiments. Higher lignin (93.2%) and hemicellulose (84.7%) removal rates without serious cellulose degradation (cellulose retention 89.1%) were achieved with the PMFS. Recovered lignin has relatively narrow molecular weight distributions (polydispersity index ≈ 2). The mass balance of the fractionation process showed that 81.5% utilization efficiency of the bamboo feedstock was obtained by organosolv fractionation with the PMFS. The results from this study provide insightful information for the industrial implementation of microwave-assisted thermochemical conversion of lignocellulosic biomass.

1. Introduction

Renewable and sustainable biomass feedstocks are of great interest for liquid fuel and chemical production given diminishing petroleum resources and their associated environmental issues (Ragauskas et al., 2006). Lignocellulosic biomass has received increasing attention to replace petroleum resources owing to its wide availability, bio-renewability, and low cost (Huber et al., 2006; Wang et al., 2013; Xie et al., 2016). Bamboo are commonly classified as short-rotation woody crops and is one of the most abundant biomass feedstocks in the world. In Asia, approximately 6–7 million tons of bamboo are produced annually (Zhang et al., 2018). Although the integrated utilization of bamboo may provide great potential for the production of biofuels and valuable chemicals, the inherent recalcitrance and heterogeneity of lignocellulosic biomass like this often hinders its direct conversion (Demartini et al., 2013; Schutyser et al., 2018). Pretreatments steps (e.g., chemical, physical, etc.) are usually applied to deconstruct the rigid structure of lignocellulosic feedstocks and therefore improve the efficiency of conversion processes yielding biofuels and chemicals (Hassan et al., 2018, 2019).

Among the pretreatment options is organosolv pulping, which can maximize the utilization of lignocellulosic biomass since it has the ability to efficiently fractionate biomass into crude cellulose, an aqueous hemicellulose-derived stream, and an organosolv lignin without severe modification and deterioration of these fractions (Borand and Karaosmanoğlu, 2018; Shuai and Luterbacher, 2016; Patri et al., 2019). One particular solvent, ethylene glycol (EG), is commonly used for laboratory biomass fractionations since it has relatively high polarity permitting easy penetration into the lignocellulosic matrix, and the capacity to extract and/or fragment lignin (Schuerch, 1952; Schutyser et al., 2015).

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Also, it has been demonstrated that the active terminal groups released during lignin degradation can be stabilized by EG to reduce condensation reactions (Deuss et al., 2017). Together with EG being environment-friendly solvent with a relatively low cost, the above properties make EG one of the most promising solvents that can be used for the lignocellulosic biomass fractionation processes on an industrial scale.

Microwave heating has the characteristics of being fast, volumetric and selective; it has been extensively studied for its potential in biomass thermochemical conversion processes, including hydrothermal and organosolv pretreatments (Sturm et al., 2014; Li et al., 2018). A study from Alio and co-workers (Alio et al., 2019) suggests that microwave irradiation can significantly reduce the processing time of biomass organosolv pretreatments as well as to improve the overall production efficiency compared to traditional heating methods. Furthermore, it has been reported that microwave irradiation could deconstruct the compact matrix of lignocellulosic biomass and facilitate the separation of the lignin (Mikulski et al., 2019). Even with these advantages, microwave-assisted biomass conversion processes in organic solvents (e.g., liquefaction, hydrothermal pretreatments, etc.) remain at a laboratory scale. This is mainly due to the need for a sealed reaction system to maintain the reaction temperatures which may be above the boiling point of the reaction solvent(s), and to avoid the loss of volatile products. The manufacture of a pressurized industrial-scale reactors using microwave irradiation as the heating source still faces some technical changes, owing to the requirement for the materials to make the reactor need to be microwave transparent, yet mechanically strong enough to withstand any pressure that can build during processing. Moreover, the penetration depth of the microwave energy at a frequency of 915 MHz, with most polar organic solvents, is only a few centimeters on average, limiting the scale-up of microwave-heating reactors (Zhou et al., 2017).

In this study, a pilot scale microwave fractionation system (PMFS), based on a 1000 L microwave-heating reactor (MHR), was developed and configured for bamboo fractionation using EG as the reaction solvent and sulfuric acid as the catalyst. To the best of our knowledge, this is the first report of a microwave-assisted fractionation system with a pressurized microwave reactor at 1000 L volume scale. The heating efficiency of the microwave reactor and microwave reflectivity of the PMFS during fractionation process were evaluated. The fractionation products obtained from the pilot scale process were characterized and the results compared with those from lab-scale experiments. The findings from this study could provide a necessary demonstration of a pilot scale MHR, thereby facilitating the industrial implementation of microwave-assisted thermochemical treatments of lignocellulosic biomass.

2. Materials & methods

2.1. Materials

Bamboo sawdust, purchased from S. L. Wood Co., Ltd. (Huizhou, Guangdong Province, China), was screened to pass through a 40-mesh sieve and oven dried at 105 °C for 24 h before use. The chemical composition of the bamboo feedstock was determined using a modified protocol based on NREL/TP-510–42618; the results are shown in Table 1 for comparison to those reported for other feedstocks. Polyester grade EG was purchased from Deying Chemical Co., Ltd., (Jinan, Shandong province, China). Sulfuric acid (98%) was kindly provided by Leshan Sanjiang Bio-Tech Co., Ltd. (Leshan, Sichuan province, China). All other chemicals used in this study were of analytical grade, commercially available, and ready for use.

2.2. Configuration of the PMFS

The schematic diagram of the PMFS and post-separation system is shown in Fig. 1. The PMFS consists of a microwave generator, a 1000 L MHR and a post-separation system. The microwave generator was custom-made by MCVEY Microwave Technology Co., Ltd. (Kunshan, China). The maximum output power of the microwave generator is 75 kW at the operating frequency of 915 MHz. The real-time microwave output power and microwave reflection rate were obtained through a digital control panel. The post-separation system contains two plate and frame filter presses, one distillation tower, and three storage tanks (1000 L of each), each equipped with mechanical mixing system.

The MHR is the key component of the PMFS; a schematic diagram of the reactor is shown in Fig. 2. The stainless-steel MHR has a capacity of 1000 L and is designed for a maximum reaction temperature and pressure of 200 °C and 1 MPa, respectively. Currently, most pressurized microwave-heating reactors reported in literature are designed with separate reaction vessels, made from a chemically inert and microwave transparent materials such as Teflon or glass, that line the chambers of the pressure-resistant reactors (Takeda et al., 2019; Pillai et al., 2004). During the microwave heating process, the reactor itself is under atmospheric pressure while the encapsuled and sealed reaction vessel, and inner walls of the reactor, are under the pressure for reactions that have volatile solvents/products, hence creating internal pressure. One example for this type of reactor is the Microwave Extraction System made by Milestone, Italy.

Despite the prevalent application of this “double-chamber” design, the capacity of the reaction vessels is limited by the volumes of the outer reactor chambers that are commercially available. In addition, although the inside reaction vessels are made from microwave transparent materials, the reactors are not, thus some microwave energy will be lost to heating the reactor itself. With the “double-chamber” design, the microwaves generated from the outside source pass the walls of both the reaction vessel and reactor to reach inside and heat the substrates. A

Table 1
The yield and properties of crude cellulose, and values for cellulose retention, the removal of hemicellulose, and removal of lignin for the lab-scale and pilot-scale fractionation processes.

Fractionation Process[a]	Yield of crude cellulose (%)	Crude cellulose composition (%)			Cellulose retention (%)	Removal of hemicellulose (%)	Removal of lignin (%)
		Cellulose	Hemicellulose	Lignin			
LCF	49.2 (0.14)[b]	79.27 (1.60)	13.85 (1.45)	5.98 (0.15)	90.5	43.8	80.1
LMF	41.3 (0.69)	86.23 (0.39)	4.28 (0.42)	2.93 (0.53)	82.1	82.6	90.0
PMFS	41.5	91.47 (0.93)	3.76 (0.27)	2.03 (0.41)	89.1	84.7	93.2
Original bamboo sawdust		43.10 (1.04)	24.65 (0.30)	30.07 (0.14)	–	–	–

[a] Lab-scale fractionation processes with conventional heating (LCF) and microwave heating (LMF); PMFS = pilot scale microwave fractionation system.
[b] Standard deviations shown in parentheses.

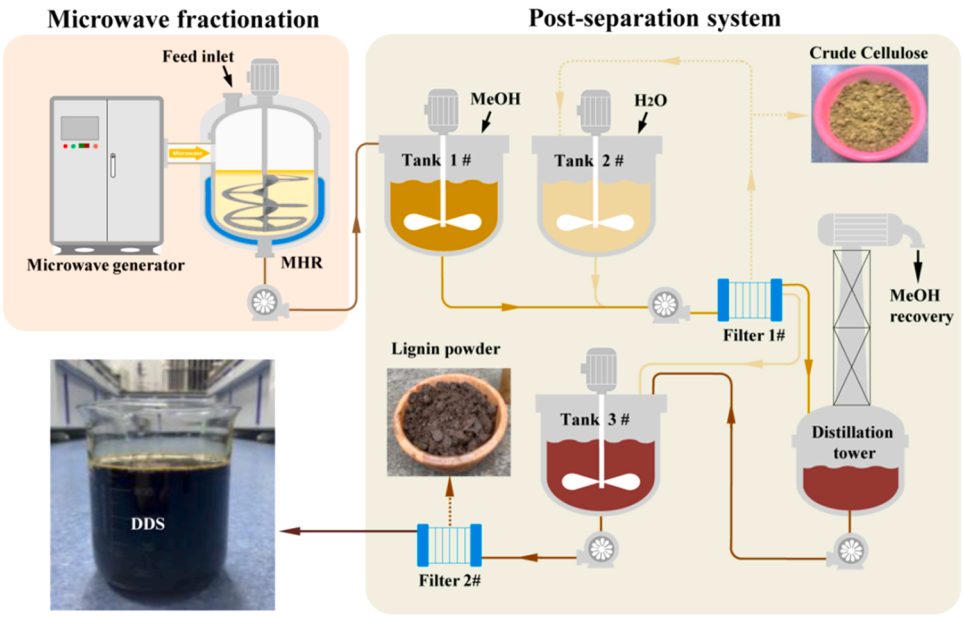

Fig. 1. Schematic diagram of pilot scale microwave fractionation system (PMFS).

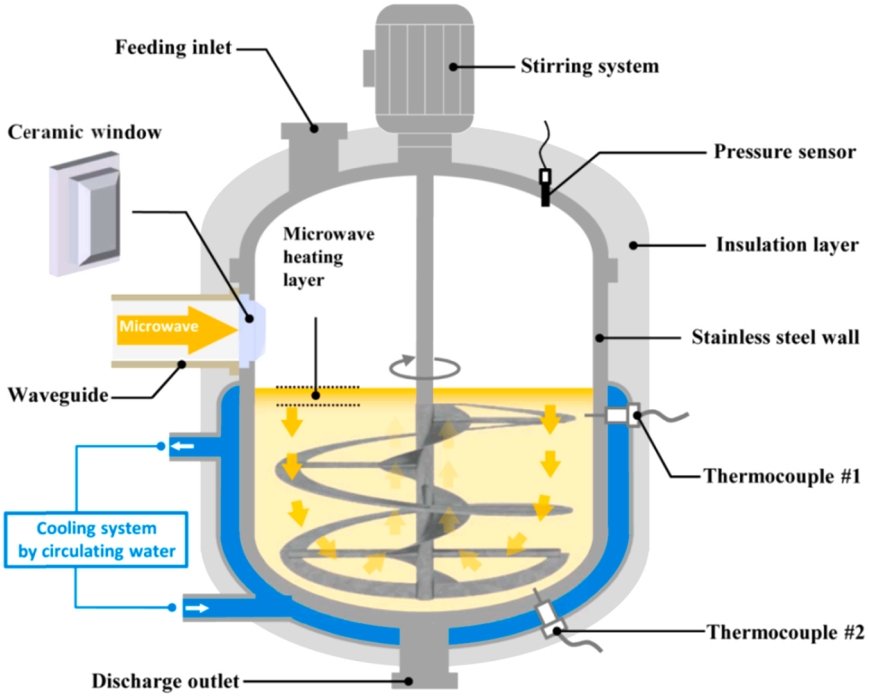

Fig. 2. Schematic diagram of the microwave-heating reactor (MHR).

window made from microwave transparent material is therefore required in the wall of a reactor made from stainless steel, a material which will reflect most of the microwave energy. Note that commonly used microwave-transparent materials used for the above-mentioned reaction vessels (e.g. Teflon) do not provide sufficient strength to withstand high pressures under high temperatures.

In this study, the pilot scale microwave reactor was designed as "single-chamber" reactor. In other words, microwave energy travels into the stainless-steel reactor through a window on the wall made of ceramic which is microwave transparent. In addition, the shape of the ceramic window was designed as a square-pyramid frustum (Fig. 2) to withstand pressures up to 1 MPa. The entire MHR was wrapped with an insulation shell to reduce heat loss and save energy. Due to the limited penetration depth of the microwave energy in reactant (The dielectric properties of the reactant and the penetration depth of microwave energy in the reactant were shown in Supplementary data), efficient mixing during the reaction is required. Therefore, the stirring system of the MHR is equipped with a double screw blade (Fig. 2). During the reaction, the inner blade moved the substrate near the center axis upward while the outer blade transports the substrate near the wall downward. Therefore, the heat exchange between the hot upper substrate and cool lower substrate is efficient, and quickly reaches a uniform temperature for the whole reaction mixture. The reactor also has a double layer along the outside of the lower half to allow the circulation of cold water to cool the

product after the reaction/extraction is complete.

2.3. Fractionation of bamboo sawdust with PMFS and benchtop equipment

For the fractionation of the bamboo feedstock with the PMFS, a mixed solvent of EG/H2O (10/1, v/v) was used as the fractionation solvent at a solvent to bamboo ratio of 7.3/1 (w/w). H2SO4 was used as the catalyst at 5.5% weight percentage of bamboo feedstock. In a typical fractionation process, a mixture of 100 kg of original bamboo sawdust (among that absolute dry portion accounts for 91 kg), 726 kg of mixed solvent and 5.5 kg of sulfuric acid (≈92%) was fed into the MHR and premixed for 10 min before turning on the microwave generator. Heating continued for about 160 min until thermocouple #2 (see Fig. 1) reached the desired temperature of 140 °C. The microwave generator was then turned off and the fractionation reaction continued for another 40 min with the MHR holding at 140 °C under continuous stirring. At the end of reaction time, the cooling system of the MHR was turned on to cool the reactant below 60 °C. The resulting reaction mixture was first pumped to tank #1 and diluted with MeOH. After 10 min of mixing, the diluted mixture was filtered by filter press #1 to separate the solid residue from the filtrate. The filtrate was then pumped to distillation tower for MeOH recovery. After distillation, concentrated liquid residue was pumped into tank #3 for temporary storage. The solid residue was transferred to tank #2 and washed with 450 kg × 2 water. With each washing cycle, the washing mixture was filtered by filter press #1 to separate the solid residue from the filtrate. The filtrate was transported to tank #3 and combined with the liquid residue from distillation. After the final washing cycle, the solid residue was collected and oven-dried at 105 °C for 24 h to obtain crude cellulose as a fibrous mass. The mixture in tank #3 was thoroughly stirred to precipitate the lignin fraction, which was collected by filtration with filter press #2 and oven dried at 40 °C for 48 h to obtain organosolv lignin as a powder. The filtrate, designated as degradation derivatives solution (DDS), was sampled, and stored at − 20 °C for analysis. The yields of crude cellulose and organosolv lignin powder were calculated as percentages, by weight, of the dry bamboo feedstock.

Lab-scale fractionation processes were also conducted with both microwave and conventional heating methods. Lab-scale microwave fractionation (LMF) was performed on a Milestone Ethos Ex Microwave Extraction System (Italy) equipped with a fiber optic temperature probe. The fractionation method was described in detail in our previous work (Zhang et al., 2020), and the formula of the reaction system is the same as it in PMFS but a smaller dosage. Briefly, 3 g of oven dried bamboo sawdust, 22 g of mixed solvent, and 0.165 g of sulfuric acid (98%) were placed in a 100 ml Teflon vessel, enclosed within a matching reactor, and the unit then placed in the microwave chamber. The heating process was programmed for two stages, preheating followed by holding at set temperature as follows: the temperature increased from room temperature to 140 °C within 3 min and then maintained at 140 °C for another 40 min. During the entire heating cycle, microwave power was automatically adjusted in the range of 0 – 400 W based on continuous feedback from the fiber optic temperature probe, ensuring that the reaction temperature followed the desired profile. Upon the end of the reaction, the reaction mixture was allowed to cool and then vacuum filtered. The solid residue (crude cellulose) was washed successively with excess amount of MeOH and deionized water followed by oven drying at 105 °C to a constant weight. Dried residue was then set aside for further use. The filtrate was diluted with deionized water to precipitate the organosolv lignin which was collected by vacuum filtration and oven-dried at 40 °C for 48 h to obtain the organosolv lignin as a powder. The liquid filtrate was stored at − 20 °C for later analysis. Lab-scale conventional fractionation (LCF) was conducted with oil bath. The same reactant mixture as shown in LMF was placed in a 100 ml pressure tube that was sealed and immersed in an oil bath at 140 °C for 40 min. The post-reaction procedures were the same as for the LMF process.

2.4. Characterization of fractionation products

The chemical compositions of bamboo feedstock (see above) and crude cellulose were analyzed using a modified protocol based on NREL/TP-510–42618. Briefly, 0.3 g oven dried sample was digested using 72% H_2SO_4 at 30 °C for 1 h using a shaking water bath. The suspension was diluted to 4% H_2SO_4 solution and autoclaved at 121 °C for 1 h. After filtration, the filtration cake, acid-insoluble lignin (LIS), was washed with excessive deionized water and dried at 105 °C for 12 h. The acid hydrolysis filtrate was analyzed using an UV-2550 ultraviolet spectrometer (Shimadzu, Japan); the absorbance at 205 nm was used to estimate the content of acid-soluble lignin (LAS).

The contents of cellulose and hemicellulose in the bamboo feedstock and crude cellulose were calculated from the amounts of glucose and xylose in the acid hydrolysis filtrate as determined by high performance liquid chromatography (HPLC, Agilent 1200). A Bio-Rad Aminex HPX-87 H column and refractive index detector were used at 60 °C with 5 mM H_2SO_4 solution as the mobile phase at a flow rate of 0.6 ml min^{-1}. Before the HPLC analysis, the filtrate sample was adjusted with 12.5 M NaOH aqueous solution to a pH of around 2 and filtered with a 0.2 μm membrane filter. The morphology of the crude cellulose was analyzed by scanning electron microscopy (SEM, Quanta 200 microscope FEI, USA). The X-ray diffraction (XRD) patterns of the crude cellulose were obtained at room temperature using an Ultima IV X-ray diffractometer (Rigaku, Tokyo, Japan) with Cu Kα, at a 40 kV acceleration voltage and a 30 mA current. The samples were scanned in the range of 5–40° (2θ) at a scan rate of 5° min^{-1}. The crystallinity index (CrI) was calculated using the method in literature (Zhang et al., 2017) using the following equation:

$$\mathrm{CrI}\ (\%) = ((\boldsymbol{I}_{002} - \boldsymbol{I}_{AM})/\boldsymbol{I}_{002}) \times 100 \quad (1)$$

Where I_{002} is the intensity at 2θ at 22.5°, and I_{AM} is the intensity of the amorphous portion at 15.5°.

The rates of cellulose retention, delignification and hemicellulose removal were calculated with Eqs. (2), (3) and (4) as follows:

$$\text{Cellulose retention rate}\ (\%) = (m_C/M_C) \times 100 \quad (2)$$

$$\text{Delignification rate}\ (\%) = (1 - r_L/R_L) \times 100 \quad (3)$$

$$\text{Hemicellulose removal rate}\ (\%) = (1 - r_H/R_H) \times 100 \quad (4)$$

Where M_C and m_C are the mass of cellulose in the bamboo feedstock and crude cellulose, respectively; r_L and R_L are the percentages of any residual lignin in the crude cellulose and bamboo feedstock, respectively; r_H and R_H are the percentages of hemicellulose in crude cellulose and bamboo feedstock, respectively.

The yields of sugars and their derivatives including formic acid (FA), acetic acid (AA), levulinic acid (LA), 5-hydroxymethylfurfural (HMF), and furfural in the DDS fraction were determined by HPLC using the same conditions as that for the composition of crude cellulose.

The number-average molecular weight (M_n) and weight-average (M_w) molecular weight of the organosolv lignin were determined through gel permeation chromatography (GPC) analysis using an Agilent GPC/HPLC 1200 system equipped with two Jordi Gel DVB Mixed Bed HPLC columns (250 mm × 10 mm) connected in series and maintained at a constant temperature of 30 °C. Tetrahydrofuran (THF) was used as the mobile phase at a flow rate of 1.0 ml min^{-1}. Lignin samples were dissolved in THF and filtered through a 0.22 μm membrane filter before injection, and a 10 μL sample was automatically injected. The ultimate analysis of the organosolv lignin was conducted using a EuRo Vector EA-3000 elemental analyzer (Milan, Italy). Thermal gravimetric analysis (TGA) of the organosolv lignin was performed on Shimadzu TA-60 H (Japan) under air atmosphere to determine its ash content. The analysis was carried at a temperature range from 30° to 800°C at

5 °C min^{-1} heating rate. The inter-unit lignin linkages and the aromatic and aliphatic chemical moieties of the organosolv lignin samples were analyzed using two-dimensional ^{13}C–^{1}H heteronuclear single quantum correlation (2D HSQC NMR) equipped with a Brucker Avance-400 NMR spectrometer at 20 °C. For the NMR analysis, 30 mg of lignin sample was dissolved in 0.6 ml of d_6-DMSO. The standard Bruker pulse sequence hsqcetgpsisp2.2 was used with a pulse width of 11.27 ppm, an acquisition time of 106.8 ms and a relaxation delay time of 2 s

3. Results & discussion

3.1. Heating efficiency of MHR

To evaluate the heating efficiency of the system, ethylene glycol, the primary reaction solvent used for the bamboo fractionation in this study, was chosen to be heated with the MHR to simplify the process. The loading volume was 800 L and the microwave output power was 40 kW. Unlike conventional heating, using microwaves involves dielectric heating, with the heating rate being directly related to the dielectric properties of the substrates being heated. Since temperature increases can be nonlinear as a function of heating time, some microwave heating systems may not be suitable when very steady temperature increases are required of the process. The temperatures of thermocouple #1 and thermocouple #2 were recorded at 5 min intervals along the entire heating cycle. As show in Fig. 3, the temperature ramping curves of both thermocouples are almost linear, indicating a stable heating process with the MHR. Despite the relatively large volume (1000 L) of the MHR, the maximum difference in temperatures of thermocouples #1 and #2 (ΔT_{max}) was less than 4 °C during the whole heating process, indicating a uniform temperature distribution within the MHR.

The variation of heating rate was further investigated since it was not exactly linear in the above experiment. To simplify the calculation, the entire heating cycle was divided into 30-minute intervals and the specific heat of each interval determined with the temperature at thermocouple #2 divided by 30 min. As shown in Fig. 3, the heating rate of EG increased from 0.76·K min^{-1} to 0.77·K min^{-1} in the first 30 min, and then gradually decreased to 0.66 K·min^{-1} as the temperature of the system increased. This trend is exactly in agreement with the nonlinear dielectric property of EG (Fig. S2) which showed higher microwave absorbing ability at lower temperature and weaker microwave absorbing ability at higher temperature. Nevertheless, the maximum variation in heating rate along the 150 mins heating process of the MHR was only around 0.1 K·min^{-1}, suggesting a very steady heating process of this system. In addition, the microwave reflectivity of the MHR was less than 5% during the process of heating EG (Fig. S3). The energy efficiency of the MHR using EG as the model substrate was calculated as the ratio of the increase internal energy of the substrate over the total input of microwave energy during the whole heating process as shown in equation 7 as follows:

$$R_E = \frac{cM\Delta T}{Pt} \times 100\% \quad (5)$$

Where R_E is the energy efficiency in heating EG in the MHR; c and M are the specific heat capacity and mass of substrate (ethylene glycol), respectively; ΔT is the increase in substrate temperature; t is the heating time; P is the output power of microwave generator. The result shows that the energy efficiency of the MHR in heating EG is about 65%.

3.2. Fractionation of bamboo in EG/H_2O with PMFS

Key parameters of the bamboo feedstock fractionation process using EG/H_2O (11/1, w/w) as the reaction medium with the PMFS are shown in Fig. 4. Detailed description of the process is provided in the experimental section. Similar to that of heating pure EG, the temperatures obtained from thermocouple #1 and #2 were very close, which confirms the uniform temperature distribution in the MHR; however, the heating rate displayed more obvious fluctuations than the process of heating pure EG, especially at the initial heating stage. Specifically, the heating rate increased rapidly from 0.62 K·min^{-1} to 0.74 K·min^{-1} in first 60 min and then gradually decreased to 0.65 K·min^{-1}. This fluctuation may be resulted from the heterogeneous reaction system having solids (bamboo particles) and liquids (reaction solvents). Compared with the polar solvent mixture (EG and water), bamboo particles in themselves are less efficient microwave absorbers and the heterogeneous reaction mixture would be heated less effectively under microwave irradiation (Zhou et al., 2017; Sait and Salema, 2015). In addition, the incorporation of solid biomass particles inevitably affected the flow and heat transfer process of solvent, together contributing to less efficient heating.

With the progress of the reaction, bamboo particles gradually degraded, and the reaction system became more homogenous and less viscous, therefore the heating rate became more stable as that observed with the heating pure EG. It is worth noting that after the microwave generator was turned off, both a slightly rise in the temperature (about 4 °C) and a small drop in pressure (decreased by 0.05 MPa within 3 min) were detected. The thermal inertia giving this rise in temperature is inconsistent with the immediacy of microwave heating described in the literature (Yin, 2012). This may be attributed to limits to the uniformity of large-scale microwave heating. In other words, the heating effect in

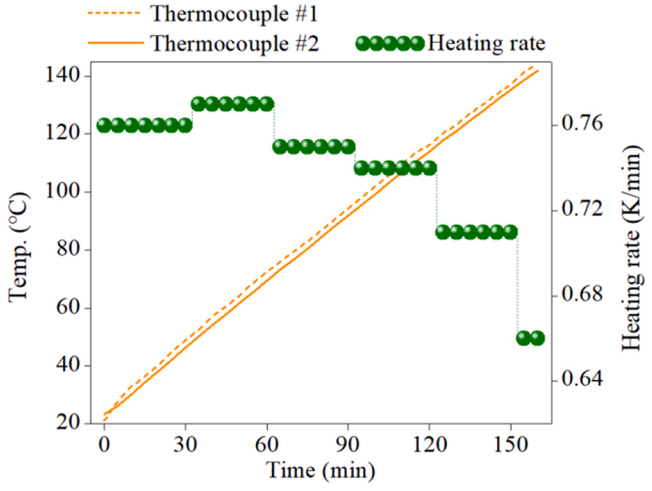

Fig. 3. The real-time temperature ramping curves and heating rate of EG in MHR.

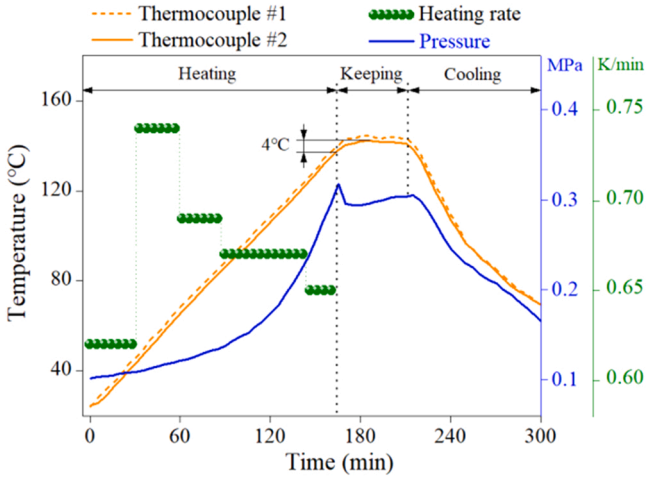

Fig. 4. The real-time temperature, pressure and heating rate of the bamboo fractionation process in MHR.

the MHR on the heating layer may not be uniform, and it may not be able to capture representative temperature readings by the thermocouple. After the microwave generator was turned off, the heat of the overheated substrate in heating layer continues to spread outward under the action of the stirring system, resulting in an increase of the readings of the temperature acquisition system.

3.3. Characterization of fractionation products

3.3.1. Crude cellulose

As shown in Table 1, the yield of crude cellulose from the LCF process (conventional heating) was 49.2%, which is higher than those from the PMFS (41.5%) and LMF (41.3%) processes (microwave heating); however, it contains higher amounts of lignin (5.98%) and hemicellulose (13.85%) as well. By comparison, the lignin and hemicellulose contents of crude cellulose obtained under microwave heating conditions, PMFS and LMF, are less than 3% and 5%, respectively. This result confirms the advantages of microwave heating over conventional heating for the biomass fractionation, especially in the removal of hemicellulose as reported in the literature (Shi et al., 2011). We attribute the slightly lower cellulose retention with LMF (82.1%), compared to PMFS (89.1%) to the PMFS's microwave heating through only a small fraction of reactant in the microwave field, thereby providing a much milder reaction condition. It's worth noting, the highest removal rate of lignin (93.2%) and hemicellulose (84.7%) were obtained with the PMFS. We attribute that to the longer effective fractionation time in the PMFS fractionation process. Our previous research shows that lignin can be separated above 100 °C with this solvent system as the reaction medium (Zhang et al., 2020). During the fractionation process with the PMFS, in addition to the 40 min of fractionation time, there is also a heating time of more than 60 min at a reaction temperature beyond 100 °C.

The SEM and XRD characterization of crude cellulose obtained from the PMFS further verified that lignin and hemicellulose were removed during fractionation using the PMFS. The SEM images clearly display a decrease in fiber diameter from the bamboo feedstock to the PMFS crude cellulose samples (Fig. S4). Large fiber bundles with average diameters around 100 μm were observed in SEM image of bamboo feedstock. After the fractionation process the fiber bundles were smaller, with a diameter of around 20 μm. The XRD patterns and the crystallinity index (CrI) results of PMFS crude cellulose and bamboo feedstock were shown in Fig. S5. Compared to the bamboo feedstock, the crystallinity index of PMFS crude cellulose samples significantly increased from 57% to 71%, which should be mainly due to the removal of hemicellulose and lignin (Ouyang et al., 2018). It is expected that nearly 100% sugar conversion can be obtained by enzymatic hydrolysis of the crude cellulose with such low lignin content (Patri et al., 2019).

3.3.2. Recovered lignin

The yields of lignin powder are shown in Table 2. The lignin yield obtained with the LMF (19.2%) was slightly lower than that for the PMFS (20.5%); note that the removal of lignin value for the LMF (90.0%) was also slightly lower than that for the PMFS (93.2%). In addition to less lignin being removed by the LMF, the fractionation conditions of the LMF process may have led to greater degradation of the isolated lignin fragments into smaller molecules which may be more difficult to recover by precipitation over water. Indeed, the molecular weight data substantiate the latter explanation with slightly lower values for the LMF lignin compared to the PMFS lignin. In comparison, the LCF system had the highest yield (21.1%) but the lowest removal of lignin value (80.1%). Since the molecular weight values are even lower than those obtained by microwave heating (LMF, PMFS), it appears that the higher lignin yield for the LCF is not a result of greater molecular size, but different chemical functionalities (e.g. lower polarity) that could facilitate precipitation.

Focusing in greater detail on the M_n and M_w distributions of the lignin powders (Table 2), all three of them show a narrow molecular weight distributions (polydispersity index (PDI) $\approx$ 2), which means that these lignin samples were composed of fragments with low heterogeneity (Avelino et al., 2018). In addition, the weight-average molecular weights of the lignin powders in this work were all smaller (M_w < 1500) than those of alkali lignin (Mw $\geq$ 2330) and organosolv lignin (Mw $\geq$ 2170) reported in literature (Wen et al., 2013; Yuan et al., 2013; Tolvert et al., 2015). The lower molecular weights of lignin powders may have resulted from the excellent solvency and protective effects of EG on the lignin fragments during the fractionation process, limiting repolymerization reactions (Schuerch, 1952; Deuss et al., 2017). Regarding the slight differences of the molecular weights and PDI in the three lignin powder samples, the largest PDI was obtained with the PMFS followed by LMF and then LCF (Table 2); the molecular weight data showed the same trend. It has been reported in the literature that there are two competing lignin reactions, fragmentation and repolymerization, both occurring in biomass pretreatment processes with acid catalysts (Pu et al., 2013). Since repolymerization can be promoted by higher fractionation temperatures and/or longer fractionation times, we cannot exclude the possibility that the higher lignin molecular weight of PMFS may have resulted from its long effective fractionation time.

The thermal stability of a lignin product is extremely important for high temperature applications, especially in polymer chemistry (Cheng et al., 2018). Thermogravimetric analyses were conducted on the lignin powders to analyze their thermal stabilities and ash contents. It can be seen from Fig. 5 that the degradation of lignins extended over a wide range of temperatures (175–800 °C), with several overlapping decomposition steps similar to those reported in the literature (Cheng et al., 2018; Monteil-Rivera et al., 2013). Pyrolytic degradation of lignin between 200 and 400 °C has been reported to involve fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase, and at higher temperatures (400–600 °C), the decomposition and/or condensation of the aromatic rings (Sun et al., 2001). It can be observed that two peaks of weight loss rate appeared at between 200 °C and 400 °C in the LCF-lignin DTG curve (Fig. 5). In contrast, the LMF and PMFS lignin only presented a shoulder at 275 °C. According to (Jakab et al., 1995), the degradation curves in the range 200–300 °C correspond to the decomposition of aliphatic alcohols, acids, and esters. It can therefore be concluded that lignins obtained by fractionation processes with microwave heating have fewer side-chains than that obtained by conventional heating. Interestingly, the temperature corresponding to the maximum degradation rate of PMFS lignin (500 °C) is different from both the LMF and LCF lignins (550 °C). This may be attributed to the

Table 2
Yields, molecular weights, elemental analyses and ash contents of lignin powders from the lab-scale and pilot-scale fractionation processes.

Fractionation process[a]	Lignin powder yield (%)	Molecular weight analysis			Elemental analysis					Ash (%)
		Mn	Mw	PDI[b]	C	H	S	N	O	
LCF	21.1 (1.48)[c]	645	1050	1.63	61.37	5.94	0	0.33	32.13	1.56
LMF	19.2 (1.63)	691	1299	1.88	63.11	5.75	0	0	31.06	1.10
PMFS	20.5	705	1451	2.06	62.78	5.76	0	0	31.30	1.77

[a] Lab-scale fractionation processes with conventional heating (LCF) and microwave heating (LMF); PMFS = pilot scale microwave fractionation system
[b] PDI = polydispersity index
[c] Standard deviations shown in parentheses.

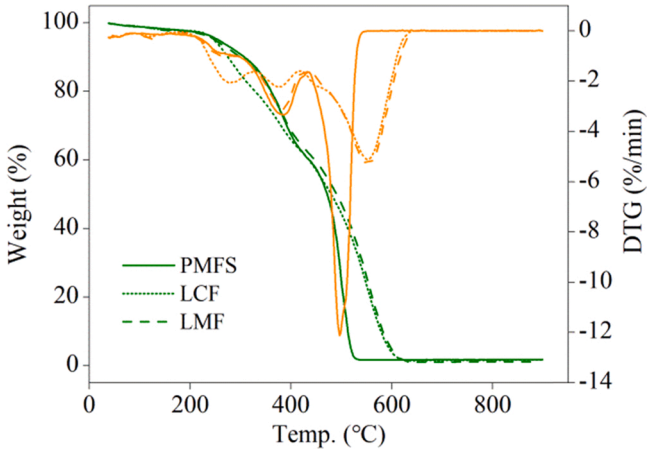

Fig. 5. TGA and DTG curves of lignin powders from the lab-scale (LMF, LCF) and pilot-scale (PMFS) fractionation processes.

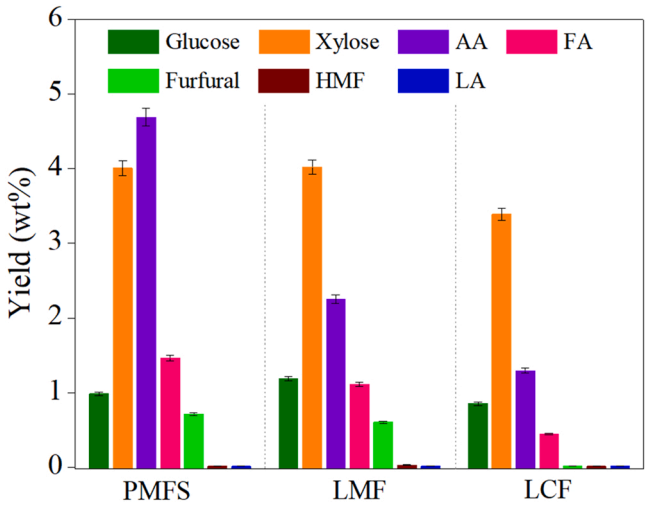

Fig. 6. The contents of sugars and derivatives in DDS from pilot-scale (LMF, LCF) and lab-scale (PMFS) fractionation processes.

thermal degradation of humins, furan-rich structures formed during the acid catalyzed dehydration of carbohydrates (Van Zandvoort et al., 2015), that may be more abundant in the PMFS lignin given its longer effective fractionation time. Finally, the TGA data demonstrated that the ash contents were all less than 2% (Table 2); it should also be noted that sulfur was not detected in any of the lignin powders.

To confirm our assessment of structural characteristics for the PMFS lignin being different from the LMF lignin, both lignin powders were analyzed by 2D-HSQC NMR to characterize and compare their monolignol compositions and inter-unit linkages. The NMR spectra depicting the side chain (δ_C/δ_H 50–90/3–5.5) and aromatic (δ_C/δ_H 100–135/5.5–8.5) regions were shown in Fig. S7. The detailed ^{1}H–^{13}C correlations signals were assigned according to literature (Rinaldi et al., 2016; Wen et al., 2015, 2013) and the results shown in Table S1. Compared to LMF lignin, PMFS lignin has a weaker A_β (G) signal, and no A_β' (G) or A_β (S), all corresponding to ß-O-4 substructures, the main bonding environment between the monolignols. In addition, humins in the PMFS lignin may be contributing to the stronger signals of $G_{condensed}$ and $S_{condensed}$ units in the 2D NMR spectra of the PMFS lignin.

3.3.3. Degradation derivatives solution

During the organosolv fractionation processing of biomass with acid catalysts, hemicellulose, and part of the cellulose, are hydrolyzed into monosaccharides and/or further degraded to FA, AA, LA, HMF, and furfural. These sugar derivatives are important industrial chemicals and can be obtained from the DDS by means of extraction. Therefore, the content of these chemicals in the DDS reflects the utility of the fractionation process and can be used to evaluate the valorization potential of the DDS. With that in mind, the contents of sugars and their derivatives in the DDS were analyzed. As shown in Fig. 6, the content of xylose in the PMFS sample is comparable of that in the LMF sample (around 4%); the content of glucose is slightly lower than that in LMF sample (0.98% vs. 1.18%). These results were consistent with the data of cellulose retention and hemicellulose removal displayed in Table 1. Regarding the degradation products, the AA content of PMFS sample is nearly twice as that for the LMF sample. That may be due to the greater degradation of the monosaccharides caused by the longer fractionation time of PMFS (Gürbüz et al., 2013). The content of xylose, glucose and their derivatives in LCF sample were all the lowest among the three DDS samples. That may be explained by milder reaction conditions of conventional heating compared to microwave heating. It is worth noting that furfural was not detected in the LCF sample of DDS. In addition, little HMF and LA were detected in all of the three DDS samples. Generally, the conversion of monosaccharide to HMF and LA needs harsher reaction conditions, for example, more than 150 °C under microwave irradiation (Yu and Tsang, 2017; Kassaye et al., 2016); the fractionation conditions used in this paper were not so severe as to convert the monosaccharides to HMF and LA.

3.4. Mass balance of the bamboo fractionation process

Based on the analysis of the 3 fractions obtained by the organosolv fractionation of bamboo sawdust using the PMFS, the mass balance during the entire fractionation process was calculated based on 100 kg dry bamboo sawdust. As shown in Fig. 7, about 41.5 kg crude cellulose and 20.5 kg lignin powder can be obtained from 100 kg the feedstock. The yields of high-value chemicals, sugars and their derivatives in DDS were also listed in Fig. 7. The total biomass utilization was defined as the sum of the lignin powder, crude cellulose and chemicals detected in DDS. Other undetected compounds were defined as unknown and were excluded. The mass balance results shown that a high utilization rate (81.5%) of the bamboo feedstock could be obtained by the organosolv fractionation process in the PMFS.

4. Conclusions

A pilot scale microwave-assisted biomass fractionation system (PMFS) was developed and successfully applied for the organosolv fractionation of bamboo sawdust. More than 800 kg reactant can be heated at 65% energy efficiency with very uniform temperature distribution ($\Delta T_{max} \leq 4$ °C) and low (not more than 5%) microwave power loss. Higher lignin (93.2%) and hemicellulose (84.7%) removal rates were obtained in PMFS than in lab scale fractionation (both microwave and oil bath heating), without serious cellulose degradation (cellulose retention = 89.1%). Recovered lignin has relatively narrow molecular weight distributions. The mass balance results indicated 81.5% utilization of the bamboo feedstock can be obtained by the organosolv fractionation process in the PMFS.

CRediT authorship contribution statement

Yongjian Zhang: Conceptualization, Methodology, Writing – original draft. **Thomas L. Eberhardt:** Formal analysis, Validation, Writing – review & editing. **Bo Cai:** Investigation, Validation. **Mingqi Wu:** Data Curation, Software. **Xiangxin Xu:** Formal analysis, Resources. **Junfeng Feng:** Visualization, Supervision. **Hui Pan:** Project administration, Funding acquisition, Writing – review & editing.

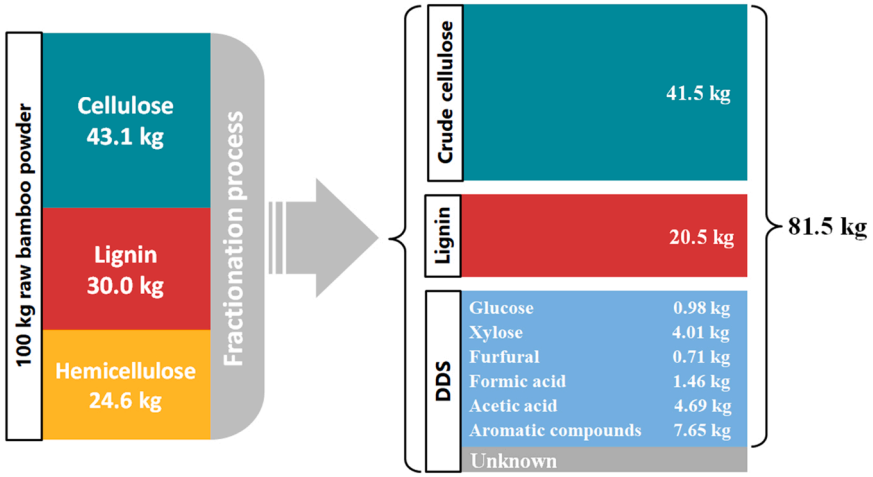

Fig. 7. The mass balance of the fractionation of bamboo in the PMFS.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.indcrop.2022.114700.

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