

Regenerated Lignocellulose Beads Prepared with Wheat Straw

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The conversion of lignocellulosic biomass into fine chemicals and polymers has been gaining attention recently. Regenerated lignocellulose beads (RLBs) were prepared by an emulsification/precipitation technique, using wheat straw as a raw material and [Bmim]Cl as a solvent. The morphology and properties of the obtained beads were characterized. The RLBs were perfectly spherical, with a porous microstructure, and had a huge specific surface area (142.4 m²/g). Their components were similar to that of wheat straw; however some chemical and crystal changes of these components occurred during the preparation process. Eighty percent of the beads were in the size range between 24.4 to 149.6 μm, and the mean particle size was 84.7 μm. Furthermore, the beads possessed good thermostability in the temperature range between ambient temperature and 200 °C. This work demonstrated the feasibility of the production of RLBs using lignocellulosic biomass and provided a new direction for high-valued utilization of lignocellulosic agricultural residues.

Keywords: Ionic liquid; [Bmim]Cl; Wheat straw; Beads; Lignocellulose; Biomass

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INTRODUCTION

Lignocelluloses, such as wood and some agricultural residues, are abundant, low-cost, and renewable bioresources. To take full advantage of these lignocelluloses, various polymers and chemicals can be developed that reduce dependence on fossil fuel. Hence, the conversion of lignocellulosic biomass into high-valued fine chemicals and materials has been rapidly gaining attention (Iqbal *et al.* 2013; Cai *et al.* 2014).

Regenerated cellulose beads are a wide class of important cellulose-based materials with diameters in the micro- to millimeter scale. They are currently used in many advanced applications, such as chromatography, metal ion adsorption, protein immobilization, and retarded drug release (Gericke *et al.* 2013; Luo and Zhang 2013; Zhang *et al.* 2015). However, the production of cellulose beads is costly and not environmentally friendly, despite the fact that the raw material, cellulose, comes from cotton or is separated from lignocelluloses. Cotton is a relatively costly feedstock, and the separation of cellulose from lignocellulose (wood or straw) is tedious and causes pollution.

Lignocellulosic resources consist of three main components: cellulose, hemicelluloses, and lignin. Both cellulose and hemicellulose are hydroxyl-group-rich carbohydrates. Compared with lignin, cellulose and hemicelluloses account for a larger proportion in the cell walls of wood and grain straws. If lignocellulosic materials could be directly converted into regenerated lignocellulose beads (RLBs) without removing any components, the obtained beads might replace the more costly cellulose-based spheres.

Fortunately, certain types of ionic liquids (ILs), which are good solvents for lignocellulose, allow for the preparation of RLBs. ILs are organic electrolytes that exist in a liquid state around ambient temperatures. Owing to their negligible vapor pressures and high thermal stability, they can be regarded as green solvents having many potential applications (Wasserscheid and Stark 2014). Some ILs dissolve lignocellulosic materials or their components (cellulose, hemicellulose, and lignin), which greatly promotes the utilization of lignocellulosic resources (Chowdhury *et al.* 2014; Morais *et al.* 2015; Peleteiro *et al.* 2015; Silveira *et al.* 2015). After dissolution in ILs, lignocellulosic materials can be converted into various products, such as furfural (Carvalho *et al.* 2015), cellulosic aerogels (Demilecamps *et al.* 2015), lignocellulosic aerogels (Li *et al.* 2011), and modified regenerated bamboo that removes Cd^{2+} and Pb^{2+} (Zhong *et al.* 2012).

Based on the dissolution of lignocellulosic material in ILs, RLBs have been generated using the emulsification/precipitation method (Zhang 2013), which is the most commonly used technique for preparing regenerated cellulose beads (Chen *et al.* 2013). First, lignocellulosic materials were dissolved in an IL, and the solution was dispersed in oil with the help of a surfactant, which was immiscible with the type of IL used. RLBs were obtained by adding water (regenerant) to the emulsion. Because no component in wheat straw was separated and “green solvent” was used, the process was simpler and more eco-friendly compared with traditional processes for producing cellulose beads.

In the present study, RLBs were prepared using the emulsification/precipitation method. The morphology and properties of the obtained beads were characterized. Wheat straw was used as the raw material, and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), a frequently-used solvent of lignocellulosic material (Chowdhury *et al.* 2014; Badgujar and Bhanage 2015), was selected as the solvent.

EXPERIMENTAL

Materials

Wheat straw was harvested from a local farmer in a suburb of Jinzhong city, Shanxi Province, China. The straw was ground to about 40 mesh size with a plant disintegrator, extracted with ethanol/benzene (1:2, v/v) for 8 h using a Soxhlet apparatus, and ground to powder with a ball grinder. The powder was dried for 4 h at 105 °C before use.

[Bmim]Cl was purchased from Linzhou Keneng Material Technology Co., Ltd. Its purity was 98%. Other reagents such as liquid paraffin, Span 80, and ethyl ether was supplied by Beijing Chemical Works and have been of analytical purity.

Preparation of RLBs

Figure 1 shows a schematic diagram of the RLB preparation process. Briefly, 0.1 g of wheat straw-powder was mixed with 2.5 g of [Bmim]Cl in a 50-mL boiling flask at 130 °C for 50 min to prepare a 4 wt% solution. Then, 0.75 g of Span 80 and 25 mL of liquid paraffin were added to the solution with stirring at 110 °C for 15 min, after which the emulsion was poured into the same volume of deionized water and stirred for 15 min. The regenerated beads were isolated by centrifugation and washed with ether three times to remove liquid paraffin. The resulting beads were stored in water or freeze-dried.

Characterization of RLBs

Morphological observation

The micro surface morphology of the RLBs was observed using a JSM-6700F field emission scanning electron microscope (JEOL, Tokyo, Japan). The macro surface morphology was observed with an optical microscope (UB203i, UOP, Chongqing, China) and a Nikon 600D microscope (Tokyo, Japan).

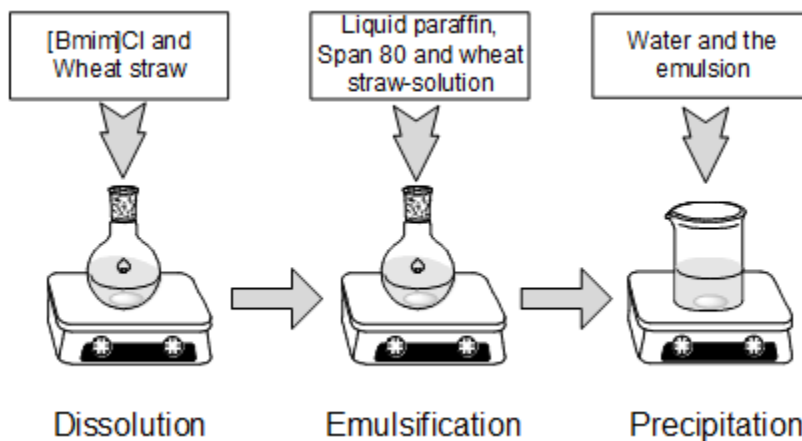


Fig. 1. Schematic diagram of the preparation of regenerated lignocellulose beads

Measurement of the physical properties

The wet density (ρ_w , g/mL) of wet samples was measured using a 5-mL gravity bottle. The porosity (P , %) and the pore volume (V_p , cm³/g of dry particles) were described according to Eqs. 1 and 2, which expressed the pore volume per volume of wet particles and the volume per gram of dried sample, respectively,

$$P = \frac{\rho_w \omega}{\rho_0} \times 100\% \quad (1)$$

$$V_p = \frac{\omega}{(1 - \omega) \rho_0} \quad (2)$$

where ρ_0 is the density of water and ω is the water content calculated using dehydration at 105 °C to a constant mass (Shi *et al.* 2011).

The specific surface area (S , m²/mL) was measured using the Brunauer Emmet Teller (BET) method on a Gemini V2380 surface analyzer (Micromeritics, Norcross, GA, USA).

Particle size distribution

The particle size distribution and mean particle diameter were determined using a laser particle size analyser (Winner 2000E, Winner Particle Instruments Joint Stock Co. Ltd., Jinan, China).

Compositional analysis

The sample components were determined based on a standard NREL procedure (Sluiter *et al.* 2008; Zhang *et al.* 2010).

The samples were immersed in 72% (v/v) sulfuric acid at 30 °C for 1 h and then treated with 4% dilute sulfuric acid (w/w) at 121 °C for 45 min. The cellulose and hemicellulose contents were estimated from the obtained glucose and xylose contents multiplied by conversion factors of 0.90 and 0.88, respectively (Zhang *et al.* 2010).

The glucose and xylose in the hydrolysate were estimated using HPLC (1220 Infinity HPLC system, Agilent, Santa Clara, CA, USA) equipped with a refractive index detector (RID) and an Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA). H₂SO₄ (5 mmol/L) was the mobile phase. The flow rate of the mobile phase and the column temperature were 0.6 mL/min and 65 °C, respectively.

The residual solid after sulfuric acid treatment was filtered using a sand core filter (G3) and washed with deionized water three times. The obtained solid was dried at 105 °C for 4 h and burned at 575 °C for another 4 h in a muffle furnace. The lignin content was estimated from the difference in weight before and after burning.

Fourier-transform infrared spectroscopy (FT-IR)

FT-IR spectroscopy was used to study the changes in the chemical structure between the straw powder and the RLBs. The spectra of each sample were obtained using a Vertex 70 spectrometer (Bruker, Ettlingen, Germany). A total of 2 mg of wheat straw powder or RLBs was mixed with 250 mg of KBr and ground completely. The mixture was pressed into thin pellets, and 32 scans were obtained from each sample at a resolution of 4 cm⁻¹. All spectra were conducted in the range of 4000 to 400 cm⁻¹.

X-ray diffraction (XRD)

The X-ray diffractions were measured using a XD-3 diffractometer (Persee, Beijing, China). Scans were collected from $2\theta = 10$ to 60°, with a scanning speed of 2° per minute.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed from room temperature to 600 °C under steady nitrogen using a Q600 SDT thermal analysis machine (TA Instruments, New Castle, DE, USA). The sample weight used was 5 mg, and the heating rate was 10 °C min⁻¹.

RESULTS AND DISCUSSION

Macro and Micro Morphology of the RLBs

In principle, the RLBs were produced in three steps: (i) dissolving wheat straw powder with [Bmim]Cl, (ii) shaping the solution into spherical particles, and (iii) solidifying the solution particles into beads. As previously reported (Gericke *et al.* 2013), there are several techniques used to shape a solution of polymer into spherical particles, such as dropping and emulsification (Gericke *et al.* 2013). In this study, emulsification was selected to shape the wheat straw solution into spheres because of its high efficiency.

The morphology of the RLBs was observed using optical and electron microscopy. The optical microscope image of the beads immersed in water shows the macro morphology (Fig. 2).

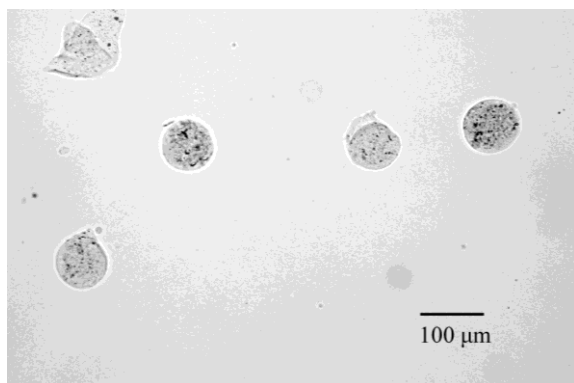


Fig. 2. Photo of the regenerated lignocellulose beads in water

Figure 3a is the electron micrograph after the beads were freeze-dried. Both figures clearly show that the RLBs were perfectly spherical, which indicates that emulsification was the appropriate method for shaping the RLBs. Figure 3b shows that the micro surface structure of the RLBs contained a fibrillar network, which was analogous to that of aerogels made from cellulose or wood (Sescousse *et al.* 2010; Li *et al.* 2011).

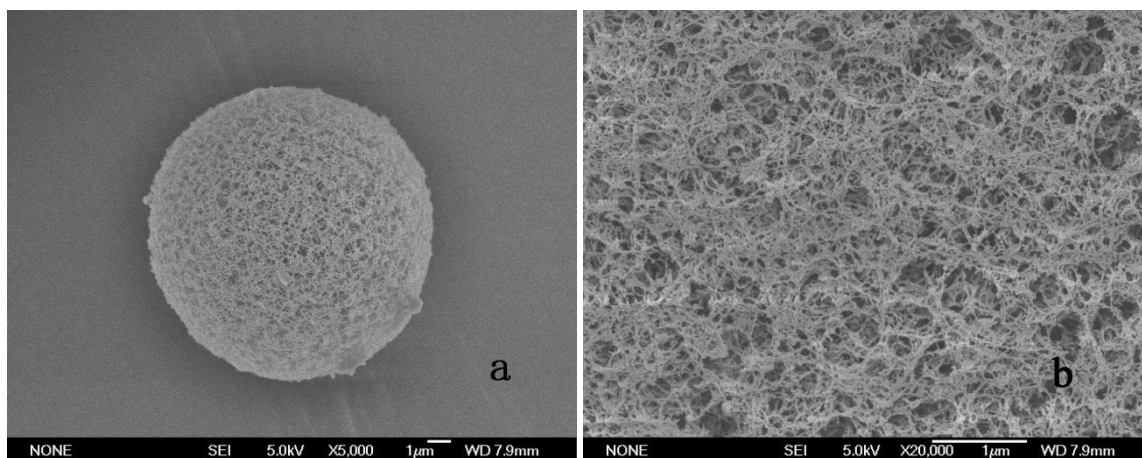


Fig. 3. SEM images of the regenerated lignocellulose beads, showing (a) bead morphology and (b) their micro surface structure

Bead Size Distribution

The size distribution of beads is important because it affects their applications. The size of RLBs was estimated using a laser particle size analyser (Fig. 4); 80% of the beads were between 24.4 and 149.6 μm, with a mean particle size of 84.7 μm. This data suggested that the beads were in the micro-millimeter scale. The range was comparable to cellulose beads used in protein separation, as previously reported by Li *et al.* (2014). These authors studied the protein separation and purification by expanded bead adsorption, and cellulose beads with a particle size distribution of 80 to 165 μm were used as the separation media.

The size distribution of RLBs is related to the emulsifying condition. In theory, the size is modulated by controlling parameters in the preparation process. To develop further applications for RLBs, methods to regulate their size should be studied.

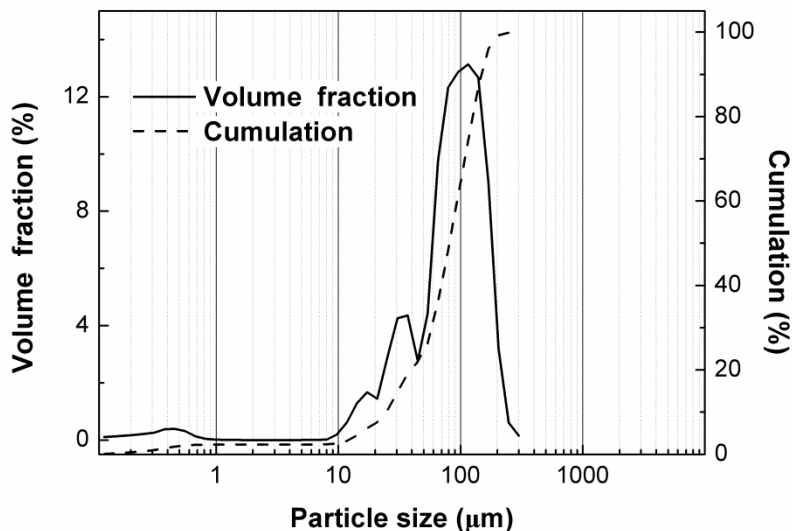


Fig. 4. Particle size distribution of the regenerated lignocellulose beads

Components of the RLBs

In addition to the morphology, size, and physical properties, the chemical composition of RLBs was estimated both qualitatively and quantitatively and compared with wheat straw to discover if changes occurred during the preparation of RLBs.

FT-IR spectroscopy is an analytical tool for qualitatively determining the chemical changes of lignocellulosic materials. The FT-IR spectra of the obtained RLBs and wheat straw-powder are shown in Fig. 5.

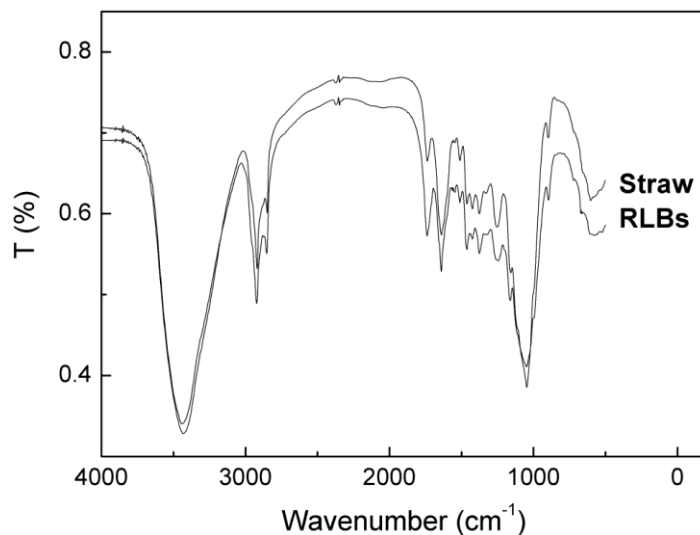


Fig. 5. FT-IR spectra of the regenerated lignocellulose beads and wheat straw-powder

The two spectra conformed to the typical characteristic of lignocelluloses. The bands between 3000 and 3700 cm^{-1} were assigned to OH stretching; the peaks at 2920 and 2850 cm^{-1} were attributed to asymmetric and symmetric CH stretching; the peaks at 1737 cm^{-1} represents the C=O stretching of ester; the peaks at 1047 cm^{-1} were attributed to C-O stretching in cellulose I and cellulose II; the peaks around 1463 and 1425 cm^{-1} was assigned to the C=C stretching of the aromatic ring (syringyl and guaiacyl); the peaks at

1161 cm^{-1} represents the C-O-C asymmetric stretching in cellulose I and cellulose II (Sun *et al.* 2005; Sain and Panthapulakkal 2006; Popescu *et al.* 2007; Alemdar and Sain 2008).

Compared with the spectrum of wheat straw powder, no supplementary bands appeared in that of RLBs, which suggested that the main interaction between [Bmim]Cl and wheat straw was of physical nature (Patachia *et al.* 2014). However, the changes of the intensity of some peaks indicated that some structural changes of the components (cellulose, hemicelluloses, and lignin) occurred.

The peak at 1737 cm^{-1} in the spectrum of RLBs was higher than the corresponding peak of wheat straw powder. It is generally recognized that the peak is related to certain ester bonds such as acetyl and uronic ester groups of hemicelluloses, or the ester linkage of carboxylic group of ferulic and *p*-coumeric acids of lignin and/or hemicelluloses. As Patachia *et al.* (2014) reported, when the cellulose was dissolved in ionic liquid without inert atmospheric, hydroxyl groups in cellulose molecular would be oxidised to carboxyl form. Hence, the intensification of the band around 1737 cm^{-1} might be because of the generation of carboxyl groups, or the generated carboxyl was converted to ester form.

The broad peak around 1047 cm^{-1} decreased after the preparation of the RLBs. As previously reported (Patachia *et al.* 2014), when pure cellulose was dissolved in and then regenerated from [Bmim]Cl, similar change would take place. In addition, the proportions of cellulose plus hemicelluloses did not decrease in the present study (Fig. 7). Hence, the change of the intensity of the peak around 1047 cm^{-1} might be mainly because the change of crystallinity of cellulose decreased after the preparation of RLBs. Another proof of the change of crystallinity was that the peaks at 1161 cm^{-1} , which was attributed to C-O-C asymmetric stretching in cellulose I and cellulose II, decreased after the preparation process of RLBs.

Figure 5 also showed that the peak of wheat straw powder at 1425 cm^{-1} was significantly higher than that of the RLBs, while the heights of the peaks of the two spectra at 897 cm^{-1} were similar.

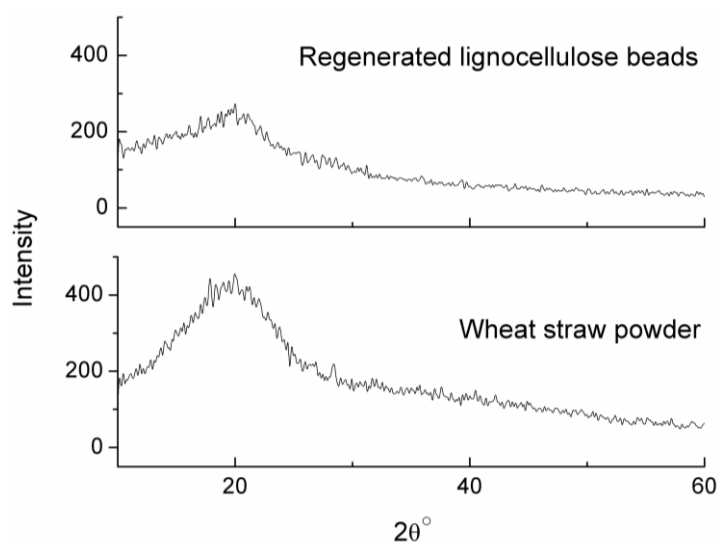


Fig. 6. X-ray diffractograms of regenerated lignocelluloses beads and wheat straw-powder

As previously reported (Åkerholm *et al.* 2004; Oh *et al.* 2005), the ratio of the peak heights at 1425 and 897 cm^{-1} is related to the proportion of cellulose I. Obviously, the ratio decreased after the wheat straw was converted to the beads. The change of the ratio

indicated that the proportion of cellulose I in the cellulosic component decreased after the preparation of RLBs.

The comparison of the FT-IR spectra between the RLBs and wheat straw-powder suggested that the obtained beads were composite spheres just like the raw material, wheat straw-powder. However, some chemical and crystal changes of the components in wheat straw occurred during the preparation process.

In order to confirm the crystal change in the components, XRD experiments were performed (Fig. 6). The main peak positions of both the RLBs and wheat straw-powder were at 19.9° , which is the characteristic diffraction peak of cellulose II (Croitoru and Patachia 2014). Obviously, the peak of the beads was much lower and broader than that of wheat straw-powder, which confirmed the decrease of the crystallinity after preparation process of RLBs. However, the change in the crystal structure from cellulose I to cellulose II was not confirmed by Fig. 6; such a change has been reported in the treatment of lignocellulose using ionic liquid (Çetinkol *et al.* 2010), since no apparent characteristic diffraction peaks of cellulose I (14.8° , 16.3° and 22.6°) (Croitoru and Patachia 2014) were found in the diffractogram of wheat straw-powder. This might be because the wheat straw-powder had undergone high intensity treatment (ball-milling), and some of crystalline region was destroyed.

In addition to FT-IR, the components of RLBs and wheat straw were compared quantitatively. Figure 7 shows the chemical analysis of the components of the RLBs and wheat straw-powder. The proportions of the three main components of RLBs were analogous to those of wheat straw. In previous studies (Bahrani *et al.* 2015), treatment with ionic liquid degraded some lignocellulose components. However, because the present study used mild conditions (lower temperatures and short handling times compared with those reported by Bahrain *et al.*), the amount of decomposition of the three components was minimal (Zhang and Chen 2012). In contrast, perhaps because some components other than cellulose, hemicellulose, and lignin were lost, the portion of these components increased slightly after the powder was converted into beads.

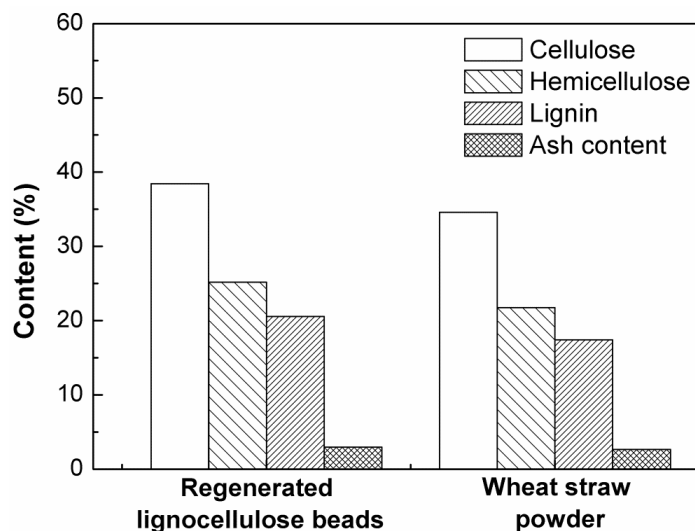


Fig. 7. Components of the regenerated lignocellulose beads and wheat straw-powder

Generally, because the main components of wheat straw were retained during the preparation of RLBs and the chemical structure changed little, it was concluded that the beads were a composite material with the same chemical constitution as wheat straw.

Physical Properties

Although the obtained RLBs contained the same components as wheat straw, their properties could have been different than those of the raw material. Thus, several of physical properties, such as wet density (ρ_w , g/cm³ of wet beads), porosity (P , %), pore volume (V_p , cm³/cm³), and specific surface area (S , m²/g), were measured and compared with those of wheat straw-powder (Table 1).

Table 1. Physical Properties of Regenerated Lignocellulose Beads

	Regenerated Lignocellulose Beads	Wheat Straw Powder
ρ_w (g/cm ³)	1.07	1.14
P (%)	94.8	83.4
V_p (cm ³ /cm ³)	7.70	2.74
S (m ² /g)	142.4	2.50

Both the RLBs and the wheat straw-powder had similar wet densities, which was due to the high proportions of water in both samples. However, the porosity, pore volume, and specific surface area of the RLBs were obviously higher than those of the powdered wheat straw. Especially, the specific surface area of the beads was much higher than that of wheat straw-powder at 142.4 m²/g. This value was analogous to that of the aerogel reported by Aaltonen and Jauhiainen (2009). These authors prepared a series of nanofibrillar aerogels using cellulose, spruce wood, and mixtures of cellulose, lignin, and xylan, which had specific surface areas of 108 to 539 m²/g. The value of the beads prepared herein was much higher than that of aerogels prepared from regenerated lignocellulose cellulose (Li *et al.* 2011) or porous cellulose (Liu *et al.* 2015).

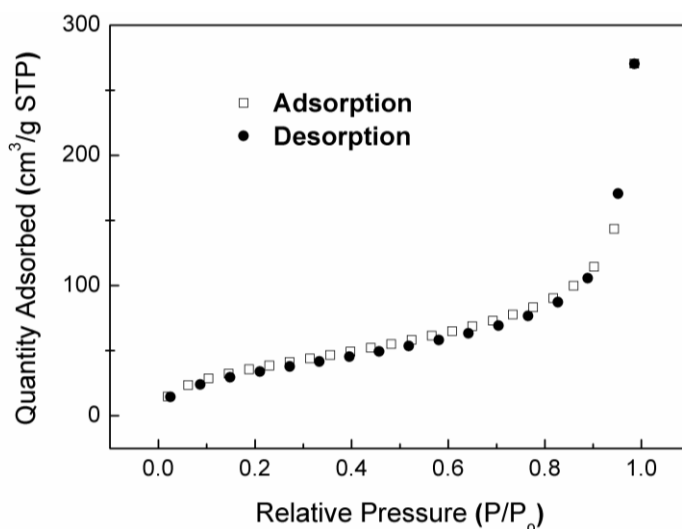


Fig. 8. N₂ adsorption-desorption isotherms for the regenerated lignocellulose beads

The huge specific surface area and the surface structure of the network mentioned above (Fig. 3b) suggested that the RLBs were an aerogel-like porous material. Because porous materials have many potential applications (Yue *et al.* 2012; Demilecamps *et al.* 2015; Rudaz *et al.* 2015), the RLBs had much better physical properties than the raw material. In other words, the properties of the lignocellulosic material were greatly improved by converting powder into beads.

In addition to the parameters mentioned above (ρ_w , P , V_p , and S), the type of pores in the beads were characterized. As described previously (Sing *et al.* 1985), pores in porous material are classified on the basis of their diameters as micropores (below 2 nm), mesopores (between 2 and 50 nm), and macropores (above 50 nm). In the present work, the adsorption-desorption curves were detected using a surface analyser (Fig. 8). The shape of the adsorption curve conformed to the characteristics of macropores (above 50 nm) (Kruk and Jaroniec 2001). The adsorption and desorption curves coincided almost completely, which also suggested that the pores were macropores (Kruk and Jaroniec 2001).

TGA Analysis

The thermostability of the RLBs—one of their most important properties—was evaluated by a TGA curve (Fig. 9). There was no weight loss when the temperature was below 200 °C, which coincides with the curve of cellulose in previous studies (Chen *et al.* 2011). Hence, the obtained beads had good thermal stability within the temperature range, which was similar to that of cellulose material. Between 200 °C and 380 °C, a drastic weight loss of about 60% occurred. Above 380 °C, the curve became flat. The two weight loss steps were analogous to the TGA curve of straw reported by Xiao *et al.* (2001), which may be because the beads were multi-compositional.

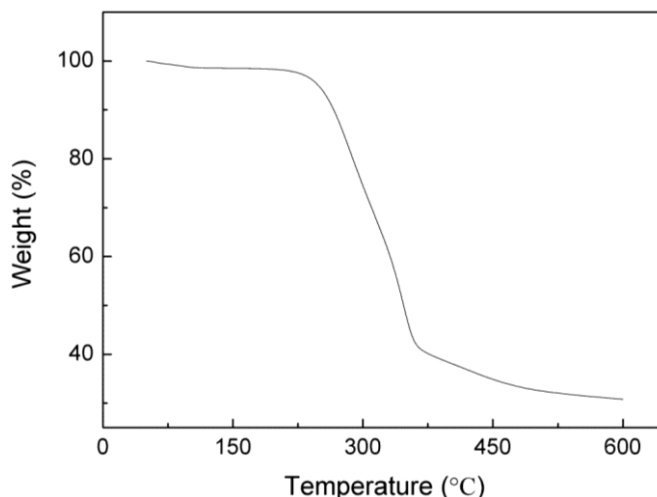


Fig. 9. TGA curves of the regenerated lignocellulose beads

CONCLUSIONS

1. This report is the first to create micro-millimeter-sized RLBs from wheat straw. The beads were prepared using the emulsification/precipitation process, and their resulting physical and chemical properties showed the feasibility of RLB production.

2. Like their raw material, wheat straw, RLBs are composite spheres made of cellulose, hemicelluloses, and lignin. However, some chemical and crystal changes of the components in wheat straw occurred during the preparation process.
3. RLBs are a kind of aerogel-like material, which has a porous microstructure.
4. The beads had good thermo-stability between ambient temperature and 200 °C.

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