

## Reactivity of main components and substituent distribution in esterified sugarcane bagasse prepared by effective solid phase reaction



Tao Gan<sup>a</sup>, Yanjuan Zhang<sup>a,\*</sup>, Yane Chen<sup>a</sup>, Huayu Hu<sup>a</sup>, Mei Yang<sup>a</sup>, Zuqiang Huang<sup>a,\*</sup>, Dong Chen<sup>b</sup>, Aimin Huang<sup>a</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Guangxi University, Nanning, 530004, China

<sup>b</sup> State Key Laboratory of Non-Food Biomass and Enzyme Technology, Guangxi Academy of Sciences, Nanning, 530007, China

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### ABSTRACT

Three main components of lignocellulose (cellulose, hemicellulose, and lignin isolated from sugarcane bagasse (SCB)) as well as holocellulose and SCB were modified with maleic acid by mechanical activation (MA)-assisted solid phase reaction (MASPR) technology. The order of reactivity was found to be lignin > hemicellulose > cellulose. The amorphous structure of lignin and hemicellulose mainly attributed to their better reactivity, and the modified lignin could reach a maximum degree of esterification (DE) of 93.45%. MA improved the accessibility and reactivity of cellulose, as the DE of modified cellulose gradually increased with milling time and reached the maximum value of 57.30% at 120 min, which had significant effect on structure changes and DE of modified holocellulose and SCB. MA enhanced the esterification of all three components in lignocellulose with relatively high substituent distribution in them, and maleated SCB with a maximum DE of 64.17% was successfully prepared by this simple, green, and effective MASPR technology.

### 1. Introduction

Sugarcane, a main sugar crop, is widely cultivated in tropical and subtropical regions. Sugarcane bagasse (SCB) is the fibrous residue of cane stalks left over after the crushing and extraction of the juice from sugarcane (Pandey, Soccol, Nigam, & Soccol, 2000). Therefore, SCB is an abundant, inexpensive and readily available source of lignocellulosic biomass (Zhang & Wu, 2014), which can be considered as an almost inexhaustible source of raw material for the preparation of environmentally friendly and biocompatible products (Leibbrandt, Knoetze, & Görgens, 2011; Nakasone, Ikematsu, & Kobayashi, 2016; Sakdaronnarong et al., 2016). In order to improve the properties of lignocellulose, including dimensional stability, resistance to fungal attack, and mechanical properties, chemical modification with dicarboxylic acids or anhydrides is an effective and promising approach to satisfy the above mentioned demands (Doczekalska, Bartkowiak, & Zakrzewski, 2014; Hundhausen, Kloeser, & Mai, 2015; Iwamoto & Itoh, 2005; Vaidya et al., 2016).

Lignocellulose mainly consists of cellulose (~50%), hemicellulose (~25%), and lignin (~25%), which associate with each other to form a supermolecular structure by hydrogen bonds and some other covalent bonds. Cellulose is a linear natural polymer of anhydroglucose units linked by  $\beta$ -1,4-glycosidic bonds. The three hydroxyl groups with

different acidity/reactivity in anhydroglucose units form strong inter- and intramolecular hydrogen bonds, leading to the formation of highly-ordered and stable crystal structure of cellulose (Sun, Sun, Zhao, & Sun, 2004). Hemicellulose, branches with short lateral chains that usually composed of easy hydrolyzable polymers (including xylose, arabinose, galactose, glucose, and mannose), is an amorphous polymer and has a lower molecular weight than cellulose (Hendriks & Zeeman, 2009; Ren et al., 2007). Lignin is composed of three phenyl propane units called *p*-hydroxyl phenyl propane (H), guaiacyl (G), and syringyl (S) units, which are connected in a disorderly manner with C–C and C–O bonds and form a three-dimensional network. Lignin also contains a lot of functional groups, such as aliphatic hydroxyls, phenolic hydroxyls, carboxyls, carbonyls, and methoxyls (Kai et al., 2016). Lignocellulose can be chemically modified by the substitution reactions of the hydroxyl groups in cellulose, hemicelluloses, and lignin. However, these three main components in lignocellulose have characteristic chemical and crystal structures, contributing to different reactivity of their hydroxyl groups.

Generally, chemical modification of cellulosic materials is performed in organic solvents in either heterogeneous or homogeneous reaction system (Boufi & Belgacem, 2006; Chen, Chen, Liu, & Sun, 2013; Crépy, Miri, Joly, Martin, & Lefebvre, 2011; Freire et al., 2008). In these reactions, it is necessary to separate and properly dispose or

\* Corresponding authors.

E-mail addresses: [zhangyj@gxu.edu.cn](mailto:zhangyj@gxu.edu.cn) (Y. Zhang), [huangzq@gxu.edu.cn](mailto:huangzq@gxu.edu.cn) (Z. Huang).

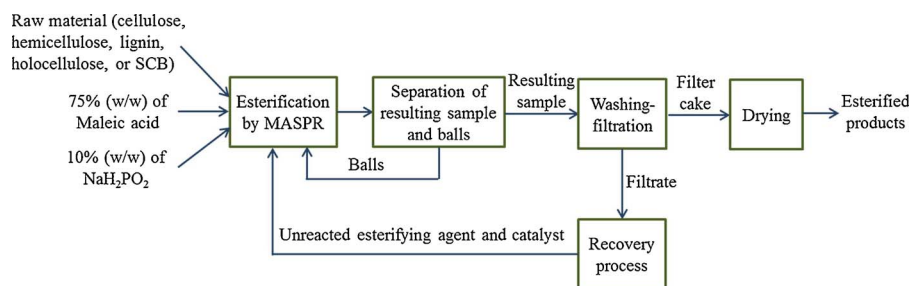


Fig. 1. Flow diagram of the esterification of different samples by MASPR.

recycle the used organic solvents due to toxic, corrosive nature and unpleasant odour of the effluents. In addition, the products need extraction and purification steps. These treatments decrease the economic feasibility of the whole process (Vaidya et al., 2016). Recent years, solid phase reaction (SPR) has been attracting more and more attentions for the advantages of nonuse of organic solvent, high selectivity and efficiency, and simple operation of reaction and purification processes. However, mass transfer and heat transfer in SPR system are very poor, especially the reactants with stable and compact structure. Therefore, SPR is difficult to carry out under common reaction conditions, and assisted means is necessary to improve the contacting state between reactants and promote the reactivity of the solid materials with stable and recalcitrant structure. In our laboratory, we have applied mechanical activation (MA) to enhance the chemical modification of natural polymers by SPR, and this technology is defined as MA-assisted SPR (MASPR) (Zhang, Gan, Hu et al., 2014; Zhang, Gan, Luo et al., 2014). For the chemical modification of cellulosic materials by MASPR, the general problem is to accomplish as a sufficient penetration of the chemical agents into cellulosic materials. Cellulose, hemicelluloses, and lignin possess their special chemical and crystal structures, so it is interesting and significant to investigate the reaction characteristics of these three main components in lignocellulose.

For these reasons, the present work was to comparatively study the reactivity of monocomponents and multicomponents in SCB, including cellulose, hemicellulose, lignin, holocellulose (cellulose + hemicellulose), and lignocellulose (SCB itself), with maleic acid as esterifying agent by MASPR. Moreover, in order to comprehensively study the strengthening mechanism of MA for enhancing the reactivity of cellulosic materials during the process of MASPR, these materials were also treated by MA without any chemical reagent to accurately measure the structure changes induced by MA. The degree of esterification (DE) of different components was determined by measuring the content of carboxylic groups ( $C_{COOH}$ ), and Fourier transform infrared spectroscopy (FTIR), solid state CP/MAS  $^{13}C$  NMR, X-ray diffractometry (XRD), and scanning electron microscopy (SEM) were applied to measure the changes in chemical, crystal, and morphological structures after MA treatment and MASPR modification. It is expected that these data can efficiently analyze the reactivity of different components in lignocellulose and understand the substituent distribution in esterified lignocellulose prepared by MASPR.

## 2. Materials and methods

### 2.1. Materials

SCB was used as lignocellulose material and was obtained from a local sugar factory (Nanning, China), which was sieved through a standard sieve of 60 mesh size (250  $\mu$ m). It contained 44.04% cellulose, 30.77% hemicellulose, 22.80% lignin, and 2.39% ash and others. All chemical reagents were obtained commercially and were analytical grade without further purification.

### 2.2. Isolation of different components from SCB

Cellulose, hemicellulose, lignin, and holocellulose were isolated from SCB. Cellulose, hemicellulose, and holocellulose were prepared according to the reported procedure (Rowell et al., 1994; Vaidya et al., 2014). Lignin was prepared following the method of Xiao, Sun, & Sun (2001). All these samples were dried in an oven at 105  $^{\circ}C$  for 12 h before use.

### 2.3. Esterification of different samples by MASPR

Esterification of cellulose, hemicellulose, lignin, holocellulose, and SCB was performed by MASPR procedure in a customized stirring ball mill (Zhao et al., 2016). A fixed amount of milling balls (300 mL, 5 mm diameter) was first put in a jacketed stainless steel tank (1200 mL). Then, dry sample (10 g) was mixed with 75% w/w esterifying agent (maleic acid) and 10% w/w catalyst (sodium hypophosphite). The mixture was put into the tank and was subjected to dry milling at a fixed stirring speed of 300 rpm, and the reaction temperature was fixed at 80  $^{\circ}C$  by circulating the thermostatic water in the jacket of tank. When the mixture was milled for desired reaction time (milling time), the balls were removed from the resulting sample by a sieve. The crude product was purified by a repeated washing-filtration process with deionized water (maleated hemicellulose was washed by alcohol) until the filtrate was neutral to remove unreacted reagents, and the filtrate was collected for analysis by high performance liquid chromatography (HPLC, LC-6AD, SHIMADZU, Japan). The filter cake was vacuum-dried at 55  $^{\circ}C$  for 48 h, and then the resulting product was obtained. The flow diagram of the esterification of different samples by MASPR is illustrated in Fig. 1.

### 2.4. MA treatment

MA treatment of the samples was operated in the same way as in MASPR, except for the non-addition of chemical reagents (maleic acid, sodium hypophosphite). The resulting sample was oven-dried at 55  $^{\circ}C$  for 12 h and then sealed for characterization.

### 2.5. Determination of DE

DE of the chemical modified samples was calculated by measuring the  $C_{COOH}$  in them, and DE value was the ratio of the measured  $C_{COOH}$  value to the theoretical maximum  $C_{COOH}$  value. The  $C_{COOH}$  of modified cellulose, hemicellulose, holocellulose, and SCB was measured by the acid-base titration method as follows (Gurgel, Júnior, Gil, & Gil, 2008): 0.1 g of the sample was precisely weighed and was mixed with 100 mL of 0.01 mol  $L^{-1}$  NaOH solution in a 250 mL conical flask. The solution was stirred at a constant temperature of 30  $^{\circ}C$  for 1 h, and then was filtered. Finally, 25 mL of filtrate was titrated with 0.01 mol  $L^{-1}$  standard HCl solution. The  $C_{COOH}$  of modified lignin was measured by the potentiometric titration method as follows (Gosselink et al., 2004): 1.0 g of the sample was accurately weighed and then was added in 10 mL NaOH solution. After stirred for 1 h, the pH was adjusted to 12 with NaOH solution. After another 2 h stirring, the solution was

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