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Design, synthesis and evaluation of novel glycosyl surfactant—lignocellulosic hydrolysate esters from shrub willow

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ABSTRACT

To meet the demands for environmental benign and food safety of surfactant industry, a green process for conversion of agriculture and forest residues into high-value added carbohydrate products has been presented in this work. The process was conducted with ultrasonic assistant and carbon-based solid alkali catalysts, and the maxim yield of lignocelulosic hydrolysate esters (LHE) could reach 88.5%, with 81.3% content of monoester. The as-prepared LHE were characterized and evaluated using FT-IR, 2D-NMR and TLC, indicated that the as-prepared LHE mainly compose of lignocellulosic monose esters and lignocellulosic oligose esters. Significantly, the LHE exhibited remarkable surfactant capacity as a glycosyl surfactant with the surface tension of 33.0 mN/m, CMC value of 0.514 g/L, emulsifying power value of 11.63 min and HLB number of 13.9, respectively. This process could offer a promising strategy for effective conversion of lignocellulosic biomass into high-value added carbohydrate products.

1. Introduction

Along with the development of society, the rapid consumption of fossil resources, as well as global environmental pollution, sustainability and safety issues regarding the existing surfactant industry based on fossil resources attract great attention (Foley et al., 2012; Jiang et al., 2013). To obtain more environmental benign and food safety surfactant has motivated the use of renewable natural resources as replacements for the non biodegradable fossil resources. Until now, various forms of renewable surfactant feedstock have been developed as excellent alternatives such as starch (Masia et al., 2014), sucrose (Van Kempen et al., 2013), chitosan (Richardson et al., 2013), rosin (Gupta and Washburn, 2014), phosphatide (Ausborn et al., 2012) and peptide (Koutsopoulos et al., 2012). Among these natural surfactant feedstocks, sugars are considered as the most promising feedstock for its abundant capacity and excellent hydrophilic performance (Nichifor et al., 2014; Van ben Broek and Boeriu, 2013; Neta et al., 2015). For example, sucrose laurate esters (SE), with sucrose and long chain-fatty acid as hydrophilic and hydrophobic group, exhibits remarkable performance as food additive with outstanding biodegradability and nontoxic, which has been widely applied in worldwide food industry. However, concerns raise about the utilization of these sugars (sucrose, starch, glucose) competed with food for feedstock. Moreover, their potential availability of such components is limited by the amount of fertile soil.

To overcome the limitations mentioned above, here we designed a green process for preparation of novel glycosyl surfactant derived from lignocellulosic biomass. Each year in China, 1.6 billion dry tons of forest waste and crop straw are generated (Tan et al., 2015), and lignocellulose forms are about 80–95% of it. Lignocellulose could be grown in combination with food or on barren land, which is composed of mainly holocellulose (70–85%) and lignin (15–30%) Rabemanolontsoa et al., 2011). The comprehensive utilization of lignocellulose is shown in Fig. 1. The sugars derived from hydrolysis of holocellulose in lignocellulosic biomass, which mainly composed of oligose (72.2 wt%) and monose (26.8 wt%), were applied as feedstock for synthesis of lignocellulosic hydrolysate sugar esters (LHE). With long chain fatty acid esters (FAE) as hydrophobic group, LHE are considered to be synthesized by transesterification between hydrolysate (mixture of monose and oligose) and FAE using mesoporous carbon as catalyst which could be derived from hydrolysis residues. By com-

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Abbreviations: LHE, lignocellulosic hydrolysate esters; SE, sucrose laurate esters; FAE, fatty acid esters; LME, lignocellulosic monose esters; LOE, lignocellulosic oligose esters; CMC, critical micelle concentration; EP, emulsifying power.

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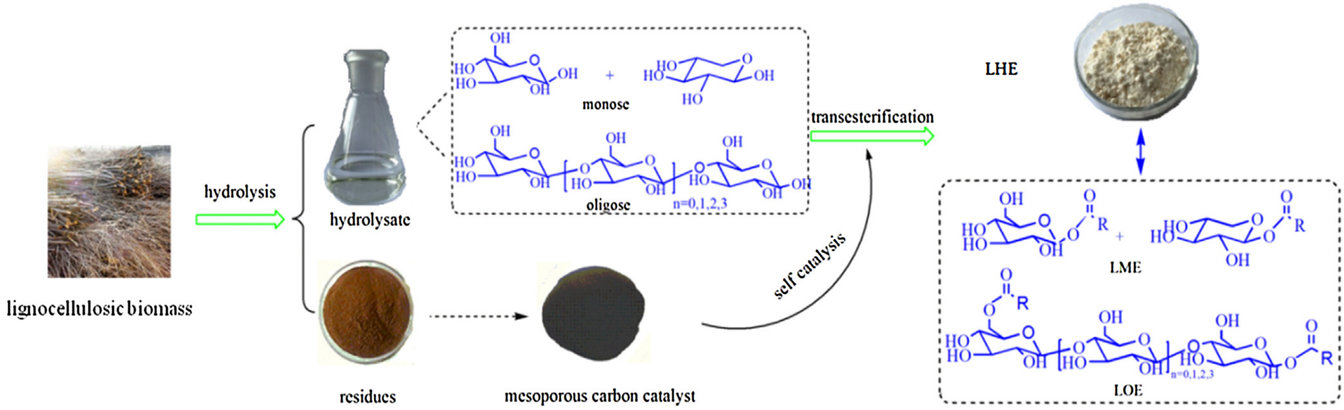

Fig. 1. A green process for preparation of novel glycosyl surfactant from lignocellulosic biomass.

parison, lignocellulosic monose esters (LME) and lignocellulosic oligose esters (LOE) were also prepared using the same method with monose and oilgose as carbohydrate sources, respectively. The performance of LHE, LME and LOE as the glycosyl surfactant were evaluated in our study according to the standard methods.

2. Material and methods

2.1. Material and chemicals

For this study, shrub willow was used as the lignocellulosic biomass, which is one kind of fast growing shrub and was collected from Dafeng Forest of Jiangsu province. In a typical procedure, the shrub willow was ground into powders to pass through a 60 mesh sieve, followed by oven drying at 105 °C overnight. According to our previous work (Wang et al., 2016), the dried powders were then hydrolyzed in water under microwave irradiation for 1 h. After the typical run, the clarified hydrolysate could be obtained with brown residues left, which mainly containing 26.8 wt% of monose and 72.2 wt% of oligose according to the analysis of ion chromatography (ICS5000, Thermo Fisher). The as-prepared hydrolysate was applied as the feedstock for synthesis of LHE without further purification. On the other hand, the brown residues were dried at 105 °C overnight and then analyzed to determine the main composition using the standard method (Sluiter et al., 2012), which composed of 68.5 wt% of lignin, 23.3 wt% of cellulose and 8.2 wt% of others. Other chemicals, including glucose and cellobiose as model compounds, were all of analytical grade, commercially available (Sigma-Aldrich, Inc.), and used as received.

2.2. Catalyst preparation

According to previous literature (Bhatnagar et al., 2013), the mesoporous carbon support was prepared via impregnated pre-activating and high temperature activating process. In a typical run, 10 g of residues were mixed with 30 g of phosphoric acid (80 wt%), followed by stirring at 140 °C for 1 h, then the mixture were removed into muffle furnace for temperature programmed activate (10 °C/min) at 450 °C for 1 h. Then washing by concentrated hydrochloric acid (37.5 wt%) and hot water till neutral, the obtained carbon material was dried at 60 °C for 12 h under vacuum condition and then applied as the mesoporous carbon support. The composition and structure of as-prepared mesoporous carbon support were analyzed using element analysis (Thermo Scientific Flash 2000 CHNS/O) and BET specific surface area analyzer (Micromeritics ASAP 2020M), respectively. In a typical run, the element analysis of sample (2 mg) was conducted under furnace temperature of 950 °C, column temperature of 65 °C and oxygen flow of 250 mL/min with nitrogen as carrier gas (140 mL/min) and reference gas (100 mL/min), respectively. The specific surface area and pore size of the sulfonated char were obtained by Brunauer Emmett Teller surface analyzer using N_2 as the adsorbent at liquid nitrogen temperature. Whereafter, 5 g of prepared mesoporous carbon support were mixed with certain amount of potassium carbonate solution under vacuum condition, followed by stirring at room temperature for 3 h and filtration. The filter cake was then dried at 110 °C for 12 h, and activated at 450 °C for 2 h to finally obtain black powders, that of so-called K_2O/C catalysts. Fourier transform infrared spectroscopy (FT-IR, Nicolet I80) and X-ray photoelectron spectroscopy (XPS, Ultra AXIS^{DLD}) were applied to analyze the change of functional group and active site in K_2O/C catalysts. FTIR Spectrum was recorded on a Fourier transform infrared spectroscopy using the standard KBr disc method. The samples were scanned between 400–4000 cm^{-1} with a resolution of 0.4 cm^{-1}. XPS analysis was done using the Kratos Ultra^{DLD} (Al Kα peak) with 150W power and an Ar^+ ion bean etch at 1000 eV was used to qualitatively analyze the depth profile of the elemental composition and chemical states.

2.3. Synthesis of LHE

Due to the immiscible phase between the hydrolysate and ethyl laurate, ultrasonic assistant were introduced to promote the heterogeneous transesterification. With the mixture of ethyl laurate (50 mL, 99.5 wt%) and hydrolysate solution (100 mL, 25.0 wt%), light yellow emulsion were formed by magnetic stirring under ultrasonic assistant at room temperature. After slow heating to 60 °C, most of water in the emulsion was removed under vacuum condition, followed by the addition of K2O/C catalysts. The reaction was then conducted in the emulsion at certain temperature (more than 100 °C) until no more ethanol could be removed under vacuum condition. The reactants were centrifuged for 5 min, followed by separation of the upper layer liquid which was subsequently neutralized and washed by 60 °C of sodium chloride solution (10 wt%). With purification by ethanol and ethyl acetate, respectively, and vacuum drying, LHE was finally obtained from the crude oil phase. The yield of LHE was calculated according to the formula: $m_{LHE}/[m_{hydrolysate} + n_{hydrolysate} \times D_E \times (M_{laurate}\text{-}18)]$, where m_{LHE} is the weight of as-synthesized LHE, $m_{hydrolysate}$ and $n_{hydrolysate}$ refer to the mass and mole of hydrolysate, respectively, D_E is the coded of degree of esterification, and $M_{laurate}$ is molecular weight of lauric acid. By using this method, LME and LOE were also prepared with glucose and cellubiose as the initial materials. In addition, we also carried out the control experiment using ethyl myristate, ethyl palmitate and ethyl stearate instead of ethyl