



Regeneration of cello-oligomers via selective depolymerization of cellulose fibers derived from printed paper wastes



Lee Ken Voon, Suh Cem Pang*, Suk Fun Chin

Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

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ABSTRACT

Cellulose extracted from printed paper wastes were selectively depolymerized under controlled conditions into cello-oligomers of controllable chain lengths via dissolution in an ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl), and in the presence of an acid catalyst, Amberlyst 15DRY. The depolymerization process was optimized against reaction temperature, concentration of acid catalyst, and reaction time. Despite rapid initial depolymerization process, the rate of cellulose depolymerization slowed down gradually upon prolonged reaction time, with 75.0 wt% yield of regenerated cello-oligomers (mean Viscosimetric Degree of Polymerization value of 81) obtained after 40 min. The depolymerization of cellulose fibers at 80 °C appeared to proceed via a second-order kinetic reaction with respect to the catalyst concentration of 0.23 mmol H₃O⁺. As such, the cellulose depolymerization process could afford some degree of control on the degree of polymerization or chain lengths of cello-oligomers formed.

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1. Introduction

Lignocellulosic biomass resources such as agricultural residues, forestry wastes, waste paper, and energy crops have long been recognized as potential sustainable feedstocks for the production of biofuels and other biomaterials (Himmel et al., 2007). Paper wastes are mostly originated from wood pulp or cotton which consists of 90–99% cellulose fibers (Sahin & Arslan, 2008). Cellulose is a linear biopolymer which consists of anhydroglucose units (C₆H₁₀O₅, AGU) bonded by 1,4-β-glycosidic linkages. Cellulose can be defined as a syndiotactic polymer of glucose with anhydroglucose units which are rotated by 180° against each other within the polymeric chain (Brodeur et al., 2011). Cellulose has been used as a renewable and biodegradable resource for the production of biofuels (Mascal et al., 2008; Li, Zhang, & Zhao, 2009), and others functional chemicals such as cellulose acetate (Cetin, Buduneli, Atlihan, & Kirilmaz, 2004; Meireles, Rodrigues Filho, Assunção, Zeni, & Mello, 2007; Rodrigues Filho et al., 2008) and cellulose ether (McCormick & Callais, 1987; Heinze & Pfeiffer, 1999; Pushpamalar, Langford, Ahmad, & Lim, 2006). The most crucial step in the conversion of paper cellulose into various value-added products involves hydrolysis or selective depolymerization of cellulose fibers into cellulosic

fragments, cello-oligomers or oligosaccharides. The depolymerization of cellulose can either occur in aqueous phase (Fan, Lee, & Beardmore, 1980; Philippidis, Smith, & Wyman, 1993), solution form (Sasaki, Fang, Fukushima, Adschiri, & Arai, 2000; Li & Zhao, 2007) or solid form (Meine, Rinaldi, & Schüth, 2012) in the presence of acid or alkali as catalyst. Basically, acid and enzymatic hydrolysis of cellulose gives high yields of monomeric glucose, whereas the alkaline hydrolysis produces mainly short chain carboxylic acids at low yields (Verendel, Church, & Andersson, 2011).

However, the depolymerization process was difficult to control due to the recalcitrance nature of cellulose attributed mainly to its extensive intra- and intermolecular hydrogen networks, the basicity of glycosidic bonds, and to a lesser extent, its high crystallinity (Rinaldi & Schüth, 2009; Rinaldi, Meine, vom Stein, Palkovits, & Schüth, 2010). Existing hydrolysis treatments require harsh conditions such as the use of acids at high temperature and pressures which lead to cello-oligomers degradation and generation of wastes (Mok, Antal, & Varhegyi, 1992; Kim, Lee, & Torget, 2001). Recent studies on the applications of ionic liquids have made great progress in providing a versatile platform for the utilization of cellulosic resources and the production of novel functional materials (Heinze, Schwikal, & Barthel, 2005; Cao et al., 2008; Feng & Chen, 2008). Due to their unique properties such as chemical and thermal stability, non-flammability and very low vapor pressure (Huddleston et al., 2001; Wang, Li, Cao, & Tang, 2011), ionic liquids are promising alternatives to conventional volatile organic solvents

* Corresponding author. Tel.: +60 82583017; fax: +60 82583160.

E-mail addresses: suhcem@gmail.com, scpang@frst.unimas.my (S.C. Pang).

for the dissolution, regeneration and derivatization of cellulose. As reported by Swatloski, Spear, Holbrey, and Rogers (2002), up to 25.0 wt% of cellulose could be dissolved in ionic liquid to form a homogeneous solution. Li and Zhao (2007) and Li, Wang, and Zhao (2008) reported that the combination of mineral acids and ionic liquids efficiently hydrolyzed lignocellulosic materials under mild conditions. In the presence of 1-butyl-3-methylimidazolium chloride (BMIMCl) and HCl, total reducing sugar yields of 66–81% were obtained from substrates such as corn stalk, rice straw, pine wood and bagasse.

The depolymerization of cellulose fibers using ionic liquids to obtain high yield of glucose, total reducing sugar, 5-hydroxymethylfurfural, and levulinic acid have been reported (Li et al., 2009; Tao, Song, & Chou, 2011). However, study on controlled or selective depolymerization of cellulose fibers into cello-oligomers of varying chain-lengths is still lacking. Benoit et al. (2011) reported on the production of cello-oligomers with (DP = 120) from Avicel cellulose using the non-thermal atmospheric plasma, but the high energy demand of this process has limited its widespread applications. Macroreticulated styrene-divinylbenzene resins functionalized with sulfonic groups have been reported to be powerful catalysts for the selective depolymerization of cellulose dissolved in ionic liquid (Rinaldi, Palkovits, & Schüth, 2008). Cellulose chains were selective breakdown by solid acids and the resulting cellulosic oligomers could be precipitated by the addition of water. Cello-oligomers are useful for the manufacturing of methylcellulose and other platform chemicals with high potential applications as surfactants, thickening agents and glues (Monsan and Paul, 1995a,b; Boissou, De Oliveira Vigier, Estrine, Marinkovic, & Jérôme, 2014), and as rheology modifiers for food and home care applications (Zavrel, Bross, Funke, Büchs, & Spiess, 2008).

In this paper, we have reported the selective depolymerization of cellulose fibers derived from printed paper wastes into cello-oligomers of different degree of polymerization or chain lengths by using an ionic liquid, 1-allyl-3-methylimidazolium chloride (AMIMCl), as the solvent, and Amberlyst 15DRY as the acid catalyst. The effects of depolymerization parameters including reaction temperature, concentration of acid catalyst, and reaction time on the degree of polymerization of cello-oligomers formed and the composition of depolymerized products were investigated.

2. Methods

2.1. Materials

Printed paper wastes were collected from the Faculty of Resource and Science Technology, Universiti Malaysia Sarawak. Sodium hydroxide (NaOH), hydrochloric acid (HCl), Silver nitrate (AgNO_3), sulphuric acid (H_2SO_4) were purchased from Merck (American Pharmaceutical Company) whereas 1-methylimidazole, allyl-chloride, copper(II) ethylenediamine complex solution, (1.0 M) and dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich (American Life Science and High Technology Company). Both potassium sodium tartrate and phenol were purchased from JT Baker (Avantor Performance Materials). All chemicals were used without further purification.

2.2. Extraction of paper cellulose

Cellulose fibers were extracted from printed paper waste based on the method reported by Wang, Li, and Zhang (2013). Typically, printed paper wastes were grinded, dispersed by soaking in water and stirred continuously at 2000 rpm for 2 h, and subsequently filtered with a sieve. The resulting paper pulp sample was submerged

in 12.0 wt% NaOH solution overnight to remove ink residuals and hemicelluloses, and then treated with 3.0 wt% HCl solution at 80 °C for 2 h to remove any residual lignin. Cellulose fibers obtained were washed with deionized water and dried in an oven until constant weight at 80 °C. All cellulose fiber samples were dried in an oven at 80 °C for 48 h before each experiment to ensure that their water contents were consistently below 0.5 wt%.

2.3. Synthesis of AMIMCl

The room temperature ionic liquid, AMIMCl, was synthesized according to the method reported by Zhang, Wu, Zhang, and He (2005) with some modifications. Typically, 100 mL of 1-methylimidazole was placed into a 500 mL three neck round bottom flask, and then 120 mL of allyl chloride was being added dropwise to the flask at room temperature under inert condition. The reaction mixture was stirred magnetically under reflux at 55 °C for about 8 h. The unreacted allyl chloride was removed by rotary evaporator under reduced pressure, whereas the residual of 1-methylimidazole was eliminated by washing thrice with an excess amount of ether. The resulting ionic liquid was stored with molecular sieve in a vacuum desiccator.

2.4. Selective depolymerization of cellulose fibers

The depolymerization of cellulose fibers was conducted by dissolving 0.25 g cellulose fibers in 5.00 mL of AMIMCl at 80 °C under mechanical stirring. Upon complete dissolution of cellulose fibers, 0.10 mL of water was added into cellulose solution using a micropipette. The cellulose solution was mechanical stirred for 2 min and then 0.05 g of Amberlyst 15 DRY catalyst ($0.23 \text{ mmol H}_3\text{O}^+\text{g}^{-1}$) was added. Cello-oligomers formed after fixed reaction durations were regenerated by adding water dropwise into the reaction medium. Regenerated cello-oligomers were separated by centrifugation at 6000 rpm, and washed with ultrapure water until no chloride ions was detected using 0.1 M silver nitrate solution. Cello-oligomer samples were dried at 60 °C in an oven until constant weight, weighed and stored in a vacuum desiccators. The liquid fraction was collected and stored in a freezer for DNS assay and HPLC analysis. Experimental parameters such as reaction temperature (70–120 °C), equivalent H_3O^+ ions concentration (0.115–1.84 mmol), and reaction time (10–120 min) were varied for studying their effects on the yields and degree of polymerization (DP) or chain length of regenerated cello-oligomers, as well as yields of water-soluble oligosaccharides.

2.4.1. Determination of viscosimetric degree of polymerization (DP_v)

The degree of polymerization of cellulose was determined by measuring the intrinsic viscosity of cellulose in copper(II) ethylenediamine complex solution (CED) according to ISO 5351: 2012. Typically, 0.50 wt% of cellulose fibers was placed in bijou bottles and 10.0 mL of water was added. The mixture was stirred at room temperature for 30 min in order to swell the cellulose fibers. 10.0 mL of CED was then added to the bottle and purged with nitrogen gas for 5 min. The sample was stirred until complete dissolution of cellulose which was confirmed by examining 100 μL mixture solution on a microscope slide under an optical microscope. The intrinsic viscosity of cellulose solution was determined by measuring the efflux time of the cellulose solution using a viscometer (Canon Calibrated Ubbelohde) for at least 3 times. Mean DP_v values of the cellulose samples were calculated based on the following equation (Marx-Figini, 1978):

$$[\eta] = 0.42 \text{ DP}_v \quad (1)$$

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