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Synthesis and characterization of carboxymethylated xylan and its application as a dispersant

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ABSTRACT

In this study, carboxymethylated beechwood xylan was produced under alkali conditions using sodium chloroacetate. Taguchi orthogonal design was used to explore the influence of the process parameters, i.e. NaOH concentration, time, temperature, the molar ratio of sodium chloroacetate to xylan and the concentration of the reaction medium on the charge density and degree of substitution (DS) of xylan. Carboxymethylated xylan (CMX) with the maximum charge density of 1.62 meq/g and DS of 0.21 was produced under the optimal conditions of 0.75 M NaOH concentration, 1.0 mol/mol sodium chloroacetate (SCA)/xylan ratio, 2 h reaction time, 70 °C and 15 g/L xylan concentration. The carboxylate group of the product was 1.48 mmol/g. The attachment of the carboxymethylated group to xylan was confirmed by Fourier transform infrared spectroscopy (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The molecular weight of xylan increased and its thermal stability was improved via carboxymethylation. The dispersion performance of the carboxymethylated xylan in clay suspensions was determined by photometric dispersion analyzer (PDA). CMX showed better performance than sodium carbonate-polyacrylic acid (Na_2CO_3-PAA) in dispersing the clay suspension. The unmodified xylan did not show any dispersion performance.

1. Introduction

Today, there is a strong intensive for replacing oil-based chemicals with green chemicals (Hansen & Plackett, 2008). Xylan is a polysaccharide polymer with a similar structure to cellulose. It constitutes 25–35 wt.% of woody biomass and approximately 50 wt.% of non-woody plants (Sjostrom, 1993, chap. 1). The polymeric backbone of xylan is made of xylose repeating units that are linked by β-1-4 linkage (Mueller-Harvey & Hartley, 1986). Recently, xylan gained interests as a functional biopolymeric material because of its abundant hydroxyl group and broad availability of hardwood species (Adinugraha, Marseno, & Haryadi, 2005; Heinze, Liebert, Heinze, & Schwikal, 2004).

Xylan can be chemically modified to produce value-added products (Schmorak & Adams, 1957). These chemical modifications include carboxymethylation (Petzold, Schwikal, Gunther, & Heinze, 2006), cationization (Schwikal, Heinze, Ebringerova, & Petzold, 2006; Wang, Hou, Kong, & Fatehi, 2015), laurolyation (Ren, Xu, Sun, Peng, & Sun, 2008), acetylation (Ren, Sun, Liu, Cao, & Luo, 2007) and oleoylation (Sun, Sun, & Sun, 2004). Among these chemical modifications, carboxymethylation is the most versatile modification for producing biobased materials that can be used in the paper, textile, pharmaceutical and paint industries (Chen et al., 2009; Heinze & Koschella, 2005; Methacanon, Chaikumpollert, Thavorniti, & Suchiva, 2003). This is because carboxymethylation excludes the use of extreme modification conditions and solvents (e.g. ethanol), which makes it industrially attractive.

In the past, studies were conducted on the carboxymethylation of non-wood and wood based xylan in solvent media (Hebeish, Khalil, & Hasheem, 1990; Togrul & Aralan, 2003). In one study, arabinoxylan isolated from *Plantago ovata* seed husk was carboxymethylated using sodium mono chloroacetate (SMCA) in an ethanol medium (Saghir, Iqbal, Hussain, Koschella, & Heinze, 2008). In another study, xylan rich hemicelluloses extracted from wheat straw biomass was carboxymethylated using SMCA in an ethanol/water medium under microwave irradiation (Peng, Ren, Zhong, Cao, & Sun, 2011). Ren and coworkers produced a carboxymethylated product by modifying sugarcane bagasse xylan using mono chloroacetic acid in an isopropanol medium (Ren, Sun, & Peng, 2008). Xylan isolated from birchwood was converted into a carboxymethylated product using sodium mono chloroacetate in an isopropanol medium (Petzold-Welcke, Schwikal, Daus, & Heinze, 2014). However, there are very few studies reported on the carboxymethylation of hardwood xylan in aqueous conditions

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(Simkovic et al., 2014). The first objective of this study was to produce carboxymethylated xylan in aqueous media (under alkaline conditions).

Modified hemicelluloses were proposed to be used in various applications (Hansen & Plackett, 2008). In one study, carboxymethylated hemicelluloses were reported to be used as an emulsifying or binding agent in the pharmaceutical industry (Ogaji, Nep, & Audu-Peter, 2011), oil drilling, metal binding, papermaking and medicine (Goksu, Karamanlioglu, Bakir, Yilmaz, & Yilmazer, 2007) or packaging film (Alekhina, Mikkonen, Alen, Tenkanen, & Sixta, 2014). In another study, sugarcane-based carboxymethylated hemicellulose was used as a strength agent for papermaking (Ren, Peng, Sun, & Kennedy, 2009). However, the use of carboxymethylated xylan as a dispersant has not been reported and is, in fact, the second objective of this work.

The stabilization of clay suspensions with minimum water loss is critical to the drilling process, and this study intends to produce a biobased dispersant for this application (Zhoumei, Xhuexin, Zhiming, & Yuhui 1990). Natural polyelectrolytes, e.g. starch, cellulose, guar gum, are considered to be used as dispersants. These polyelectrolytes adsorb onto clay particles and introduce steric and electrostatic repulsions between the particles resulting in the stabilization of colloidal suspensions (Bimal, Menchavez, Takai, Fujy, & Takahaschi, 2005). The availability of guar gum is limited; starch is mainly used as a food product and cellulose is widely used in the paper production. However, xylan is not presently utilized effectively, and therefore, can be converted to a dispersant for clay suspensions.

The main novelties of this work were the production of carboxymethylated xylan in an aqueous medium and the use of the product as a dispersant for clay suspensions. The impact of carboxymethylation on the charge density of xylan was also discussed for the first time in this work. In the present work, the carboxymethylation of beechwood xylan was conducted using sodium chloroacetate in order to obtain carboxymethylated xylan with a high charge density and degree of substitution. The chemical, physical and structural properties of carboxymethylated xylan were also determined. The application of carboxymethylated xylan as a dispersant in clay suspensions was also discussed for the first time in this study.

2. Experimental

2.1. Materials

Beechwood xylan, sodium hydroxide, sodium chloroacetate (SCA), 3-(trimethylsilyl)propionic-2,2,3,4-d_4 acid sodium salt (TSP), sodium nitrate, acrylic acid (99%), sodium carbonate, potassium persulphate ($K_2S_2O_8$) and kaolin clay were obtained from Sigma-Aldrich Company and used as received. Acetic acid (99%) was obtained from Sigma-Aldrich Company and diluted to 80 wt.% prior to use. Ethanol (99%) obtained from Sigma-Aldrich Company and was used as received or diluted to 80 wt.% prior to use. Sulphuric acid was obtained from Sigma-Aldrich Company and diluted to 0.1 M prior to use. Cellulose acetate dialysis membrane (molecular weight cut-off of 1000 g/mol) was purchased from Spectrum Labs. Inc., USA. Polydiallyldimethylammonium chloride (PDADMAC) was obtained from Sigma-Aldrich Company and diluted to 0.005 M prior to use. Potassium polyvinyl sulfate (PVSK) was obtained from Wako Pure Chemical Industries Ltd., Japan.

2.2. Carboxymethylation

The carboxymethylation of xylan was conducted as described in the literature on the carboxymethylation of alkali lignin extracted from sugarcane bagasse (Ren, Sun et al., 2008). In this study, 1 g sample of xylan was dissolved in 50 mL of NaOH solution (0.25–1.25 M) by stirring at 200 rpm for 15 min at room temperature. Different amounts of sodium chloroacetate solution (2 mol/L) were added to xylan to generate various sodium chloroacetate/xylan ratios of 0.25–2 mol/mol, and the reactions were carried out at designated times and temperatures under a constant stirring at 200 rpm. After completion, the solution was cooled to room temperature and its pH was adjusted to 7 using an 80 wt.% acetic acid solution. The polymer present in the solution was precipitated using 150 mL of 99.5% ethanol. Then, the precipitated polymer was washed thrice using an 80 wt.% ethanol solution and dried at room temperature overnight and then stored at 4 °C until further use.

Table 1
The Taguchi orthogonal parameters and levels (L_{16}).

Run	Time (A), h	Temperature (B), °C	NaOH concentration (C), M	Xylan concentration (D), g/L	SCA/xylan (E), mol/mol
1	1	50	0.5	10	0.5
2	1	60	0.75	15	1
3	1	70	1.0	20	1.5
4	1	80	1.25	25	2
5	2	50	0.75	20	2
6	2	60	0.5	25	1.5
7	2	70	1.25	10	1
8	2	80	1.0	15	0.5
9	3	50	1.0	20	1
10	3	60	1.25	20	0.5
11	3	70	0.5	15	2
12	3	80	0.75	10	1.5
13	4	50	1.25	15	1.5
14	4	60	1.0	10	2
15	4	70	0.75	25	0.5
16	4	80	0.5	20	1

2.3. Experimental design and statistical analysis

The effect of reaction parameters on the charge density and degree of substitution (DS) of carboxymethylated xylan were studied using Taguchi orthogonal design (Konduri & Fatehi, 2015). In this experiment, L_{16} orthogonal design with five factors (each at four levels) was used to investigate the effect of parameters on the carboxymethylation reaction. The factors and their levels were time (1, 2, 3 and 4 h), temperature (50, 60, 70 and 80 °C), NaOH concentration (0.5, 0.75, 1.0 and 1.25 M), xylan concentration (10, 15, 20 and 25 g/L) and SCA/xylan (0.5, 1.0, 1.5 and 2.0 mol/mol). The experiments were repeated three times, and the average values were reported in this work. The carboxymethylated xylan (CMX), which was produced under the conditions of 0.75 M NaOH, 1.0 mol/mol SCA/xylan ratio, xylan concentration of 15 g/L, 70 °C and 2 h reaction time, had the maximum charge density and DS, and thus was selected for further characterization with TGA, FTIR and ^{1}H NMR.

2.4. Orthogonal design

A total of 16 runs were conducted based on Taguchi orthogonal design (L_{16}) to determine the optimum conditions for producing carboxymethylated xylan with the maximum charge density and DS. The experimental conditions conducted in the orthogonal design are listed in Table 1. The models for producing maximum charge density and DS of carboxymethylated xylan are depicted in Eq. (1). The number of terms in the models depends on the main effects and their degrees of freedom.