



Furfural formation from the pre-hydrolysis liquor of a hardwood kraft-based dissolving pulp production process



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HIGHLIGHTS

- ▶ Furfural was produced from the pentose sugar present in the pre-hydrolysis liquor without using external acid.
- ▶ Both monophasic and biphasic experiments were carried out.
- ▶ Biphasic significantly increased furfural yield.
- ▶ Mass balance of furfural production from the pre-hydrolysis liquor was done.
- ▶ Xylose, furfural, syringaldehyde were used in model experiment.

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ABSTRACT

This study aimed to produce furfural from the PHL. Results showed best furfural yield of 32.8% and the furfural selectivity of 37.7% in the monophasic system (170 °C, 100 min), while they were 60.1% and 69.8%, respectively in the biphasic system. The lower furfural selectivity in the monophasic system was explained by more side reactions, such as fragmentation, condensation reactions, resinification and others. Model compounds such as: xylose, furfural, syringaldehyde, were used to confirm/identify these side reactions. The addition of dilute sulfuric acid/acetic acid in the system under the same conditions decreased the recovery of furfural. The addition of syringaldehyde into the PHL also led to a decrease in the furfural yield, supporting the conclusion that lignin structures in the PHL may also be involved in the side reactions, thus decreasing the furfural yield.

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1. Introduction

The successful exploitation of biomass to produce value-added chemicals may lead to a stepwise move of the present global economy towards a sustainable bio-based economy. For lignocellulosic materials, pre-extraction of lignocellulosic materials prior to pulping has been considered as an important aspect for the implementation of integrated forest biorefinery (van Heiningen, 2006). In this context, the commercial pre-hydrolysis kraft-based dissolving pulp production process fits well into the biorefinery concept (Li et al., 2010; Shen et al., 2011). For such a process, the removal of hemicelluloses prior to pulping by steam (or hot water) pre-hydrolysis technology is a critical step for producing high-quality dissolving pulp (Sixta, 2006). In the pre-hydrolysis liquor (PHL),

hemicelluloses, acetic acid, lignin, and furfural are present (Saeed et al., 2012; Liu et al., 2012), while xylose/xylooligosaccharides (C-5 sugars) are the main hemicelluloses. Furfural may be one of the possible products from the hemicelluloses. Furfural is presently produced from agricultural lignocellulosic materials based on the traditional acid hydrolysis/dehydration technology. Today commercially, furfural is produced using batch or continuous reactors using a mineral acid (i.e. sulfuric acid) as the reaction catalyst (Kottke, 2000).

The application of various catalysts in the furfural conversion has been well documented in the literature, including mineral acids (such as H₂SO₄, H₃PO₄, and HCl) (Kuster and Van der baan, 1977; Moye and Goldsack, 1966), organic acids (Szmant and Chundury, 1981), solid acids (Moreau et al., 1994). The presence of acetic acid in PHL is about 1% (Saeed et al., 2012), which may act as the catalyst for the dehydration during the furfural production. The first objective of this work was to study the potential of furfural formation from the PHL, using acetic acid as the catalyst, which is already present.

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A monophasic system, which uses an aqueous medium, in the production of furfural from the lignocellulosics, has been widely reported. However, such a process is not very selective, so the furfural yield is very low. The biphasic system, which includes an organic phase so that the generated furfural can be transferred to, with other compounds still remaining in the water phase, was advantageous in improving the furfural yield (Zhang et al., 2012). Different solvents, such as methyl isobutyl ketone (MIBK) (Weingarten et al., 2010), butanol (Zhang et al., 2012), may be used. The second objective of this study was to use methyl isobutyl ketone (MIBK) as a solvent to extract furfural in the biphasic system to improve the furfural yield from the PHL. MIBK has similar polarity to ethyl acetate, its water immiscibility is good in reference to other ketone solvents like acetone; MIBK can be produced via the fermentation of biomass derived carbohydrates (Jones and Woods, 1986).

In addition, model systems, including xylose, furfural and syringaldehyde, were studied to gain further insights of the side reactions during the furfural formation process.

2. Experimental

2.1. Methods

The industrially produced PHL of the kraft-based dissolving pulp production process was collected from a mill located in Eastern Canada. To remove large particles and impurities, the PHLs were filtered by filter paper followed by membrane. The PHL contains 4.91% hemicelluloses, 1.02% lignin, 1.04% acetic acid and 0.15% furfural. Xylose and syringaldehyde were purchased from Sigma–Aldrich. Methyl isobutyl ketone (MIBK) was purchased from Fisher Scientific and used as received.

Stainless steel tubes with screw cap were used as reactor in both monophasic and biphasic systems. For the production of furfural, sample and required chemical was placed in the stainless steel tube and cap was tightly fixed and placed in a Parr reactor (4843, Parr Instrument Company) for controlling the temperature. The Parr reactor is equipped with temperature limit controller and pressure transducer module. In the biphasic system, the ratio between aqueous phase (PHL) and organic phase (MIBK) was 1:1. A separatory funnel was used to separate the two phases.

2.2. Acetic acid and furfural analysis

The contents of acetic acid and furfural in aqueous phase were determined by following a nuclear magnetic resonance (NMR) method (Ni et al., 1996).

The concentration of furfural in the organic phase was also determined by NMR. The solvent suppression method was used using CDCl₃ to MIBK ratio of 1:1. Calibration curves were established for furfural using reagent furfural (Fisher Scientific) dissolved in MIBK, then mixed with CDCl₃ with the same ratio of 1:1.

The furfural yield and furfural selectivity were calculated based on the following formula,

$$F_y(\%) = W_f / W_{\text{theoretical}} * 100\% \quad (1)$$

$$F_s(\%) = F_y / C_c * 100\% \quad (2)$$

F_y : furfural yield; F_s : furfural selectivity; C_c : C-5 sugars conversion; W_f : the furfural weight that is generated during the reaction; $W_{\text{theoretical}}$: the theoretical amount of furfural produced.

2.3. Post-acid hydrolysis of the pre-hydrolysis liquor

To hydrolyze the oligomeric sugars in the pre-hydrolysis liquor into monomeric sugars, a vial containing 1 mL of the pre-hydrolysis liquor and 5 mL of 4% sulfuric acid was sealed in an autoclave (Yang et al., 2012), which was then put in an oil bath (Neslab Instruments, Inc., Portsmouth, NH, USA). The autoclave was kept in the oil bath at 121 °C for one hour. This post-acid hydrolysate was used to determine the total saccharides in the pre-hydrolysis liquor.

2.4. Sugar analysis

The monomeric sugar contents in the pre-hydrolysis liquor and the acid hydrolysate were determined by using an Ion Chromatography (Saeed et al., 2012; Shi et al., 2011) with a Pulse Amperometric Detector and CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada). De-ionized water was used as eluant with a flow rate of 1 mL/min. The regeneration agent used was 0.2 N NaOH with 1 mL/min flow rate and 0.5 N NaOH was used as the supporting electrolyte with 1 mL/min flow rate. The samples were filtered and diluted prior to analysis. The experimental error for the sugar analysis was within 6%. The monomeric sugar contents in the post-acid hydrolysate stood for the total saccharides in the pre-hydrolysis liquor. The sugar contents in oligomeric form in the pre-hydrolysis liquor were calculated from the difference of the monomeric sugar contents with and without the post-acid hydrolysis.

The total sugar conversion (S_c)/C-5 sugars conversion (C_c) was calculated as,

$$S_c(\%) = (S_1 - S_2) / S_1 * 100\% \quad (3)$$

$$C_c(\%) = (C_1 - C_2) / C_1 * 100\% \quad (4)$$

S_1 : total amount of sugars; S_2 : residual amount of sugars; C_1 : total amount of C-5 sugars; C_2 : residual amount of C-5 sugars.

2.5. FTIR spectroscopy

IR spectra of solid PHL and residues from mono and biphasic systems were recorded with a Nicolet 6700, Thermo Scientific, US. The dried samples were embedded in KBr pellets, at concentrations of about 1 mg/100 mg KBr. The spectra were recorded in the absorption band mode in the 4000 to 400 cm⁻¹ range.

2.6. Thermal gravimetric analysis (TGA)

Thermal gravimetric (TG) analysis of solid PHL (solid content in the PHL was 8.0%) and residues from the mono- and biphasic systems of about 5 mg (air-dried) were performed using a TA Q500 Thermogravimetry (TG) analyzer and a heating rate of 10 °C/min under helium atmosphere.

3. Results and discussion

3.1. Furfural formation from xylose in the monophasic system

In the literature the conversion of xylose to furfural has been well documented, many process parameters, including the acid used (as catalyst), temperature and time, xylose concentration, affect the furfural yield (Weingarten et al., 2010; Zhang et al., 2012). To benchmark the furfural formation from the pre-hydrolysis liquor (PHL), the conversion of xylose to furfural with and without addition of acid as the catalyst was studied first. According to literature, furfural can be formed via an autocatalytic mechanism involving organic acid produced in the process (Oefner et al.,

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