



## Research paper

## Furfural production from a pre-hydrolysate generated using aspen and maple chips

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## ABSTRACT

This paper focuses on the production of furfural from a simulated kraft dissolving pulp mill pre-hydrolysate solution that is rich in pentoses. Presently, this stream at the mill is mixed with the black liquor and then burned to recover some of the energy needed for the process. However, this pre-hydrolysate would have a higher potential if used as a feedstock for furfural production. This work demonstrates a novel approach to produce furfural in high yields by adding the catalyst only when the desired reaction temperature is reached, and by removing the furfural as soon as it is generated in the reactor. By applying this concept on the pre-hydrolysate, a furfural yield of 76% can be obtained at 240 °C and 2.5 kg m<sup>-3</sup> of sulfuric acid. In other approaches where the acid is initially mixed with the pre-hydrolysate, furfural yield varies between 54 and 65% depending on whether furfural is left in the reaction medium or removed as it is formed, respectively.

Maximization of furfural production has also been studied in this work by varying the sulfuric acid dosage (1–5 kg m<sup>-3</sup>) and the reactor temperature (160–260 °C). The highest furfural yield of 77.6% can be obtained when a sulfuric acid concentration of 3.6 kg m<sup>-3</sup> and a temperature of 240 °C are used for the pre-hydrolysate solution. When lignin is removed from the pre-hydrolysate prior to furfural production, the highest furfural yield is 72.6% at 220 °C and 3.6 kg m<sup>-3</sup> of sulfuric acid.

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## 1. Introduction

In the dissolving kraft pulp process, a pre-hydrolysis step is used to remove the hemicelluloses prior to production of pulp with high cellulose content. In addition to lignin, the pre-hydrolysate generated in this step is rich in monomeric and oligomeric sugars [1]. This stream is usually mixed with black liquor and is used as a fuel to produce energy in the recovery boiler [2,3]. However, its calorific value is low because it contains more hemicelluloses than lignin [3,4]. The conversion of the sugars to other bio-chemicals would therefore be an interesting option that would allow pulp mills to diversify their product portfolio and increase their revenues. This stream is rich in pentoses (C5 sugars) since hardwood is employed in most dissolving kraft pulp mills. The conversion of the sugars to

furfural by an acid hydrolysis step, for example, was earlier proposed [3] and is still worth investigating.

Furfural is one of the important platform chemicals considered in the forest biorefinery. It is used as a solvent to separate saturated compounds from unsaturated ones in oil refineries [4]. Furfural is employed in the synthesis of a considerable number of chemicals in the pharmaceutical, agrochemical, and plastic industries [5]. Furfural is also used to synthesize second-generation biofuels such as methylfuran. Methyltetrahydrofuran (MTHF) which is one of the most important components of P-series fuels (a mixture of ethanol, methyltetrahydrofuran, pentane, and butane) is also produced from furfural [6,7].

Currently, furfural is produced from lignocellulosic biomass such as corn and sugarcane bagasse by dehydration of pentoses present in lignocellulosic raw materials [8–10]. No considerable changes have been made in relation to the industrial furfural production processes during the last 90 years [8]. Quaker Oats was the first industrial furfural producer that used oat hulls as raw material and sulfuric acid as a catalyst. The process consists mainly of mixing

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the raw material with sulfuric acid and then injecting steam in order to reach high temperature levels necessary to produce furfural [11]. The furfural produced is simultaneously stripped by the injected steam. However, the process presents several disadvantages [11,12] such as:

- Low yield that does not exceed 50%;
- Long residence time (about 5 h);
- Losses of about 16% of the total furfural produced in the residue;
- High steam consumption.

Recently, furfural attracted the attention of several researchers. Numerous studies were published in relation to the production of furfural from biomass and several pathways were also developed in order to improve the furfural yield. The evaluation of different types of catalysts such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, maleic acid, acetic acid, formic acid, zeolite, metallic oxide (ZnO, TiO<sub>2</sub>...) was investigated in various studies. The effect of the dehydration of sugars in one step or two steps on furfural yield was also studied [13–15].

Several researchers have been interested in the production of furfural from biomass using metal chlorides since chloride ions significantly improve the yield of furfural production [16–20]. Rong et al. [21] investigated the effect of sodium chloride NaCl and iron trichloride (FeCl<sub>3</sub>) on the yield of furfural from xylose in a biphasic system. The authors showed that the concentration and type of salt directly affected the yield of furfural. Marcotullio and De Jong [22] studied the conversion kinetics of acid-catalysed D-xylose. The aim was to improve the yield by the addition of halide ions such as chloride, bromide and iodide. The results of this study showed that the presence of metal halides in an acid solution of xylose improved the kinetics of the reaction by promoting the formation of the 1,2-endiol structure and consequently the formation of furfural. In the presence of a mass fraction of 5% NaCl in 2.92 kg m<sup>-3</sup> HCl, the authors obtained a maximum furfural yield of 81.3%. The same observation was done by Mandalika and Runge [23] who reported that salt addition facilitated the furfural formation reaction and resulted in increased yield, possibly via promotion of the 1,2-endiol form of sugar. Using xylose mass fraction of 17.6%, a maximum yield of 58% was obtained in the presence of 100 kg m<sup>-3</sup> chloride, whereas the yield which was obtained under similar conditions but in the absence of chloride was only 41%, which demonstrates, according to the authors, the favorable effect of metal halides on the yields of furfural. The use of halides has shown its positive effect on improving the yield of furfural in several investigations. However, their use is not acceptable in pulp and paper mills because they are not compatible with the recovery systems.

The effect of using a bi-phasic system (aqueous phase and organic phase) on furfural yield was also investigated. The aqueous phase usually contains an acid (HCl or H<sub>2</sub>SO<sub>4</sub>) and water or a mixture of water and dimethyl sulphoxide (DMSO) [15]. The organic phase is composed of organic solvents having a great potential to absorb furfural such as methylisobutylketone (MIBK), MIBK-2-butanol, tetrahydrofuran (THF) or dichloromethane (DCM) [24]. In this system, furfural is produced in the aqueous phase and simultaneously transferred to an organic phase [15,25]. In this case, the reaction medium (aqueous phase) contains only a limited amount of furfural because the latter, once formed, it is transferred spontaneously to the other phase. Since furfural is captured by the organic phase, it is protected against the attack of hydronium ions, thereby minimizing the formation of degradation products and improving the yield of furfural production [15,25].

Even though the use of a biphasic system leads in most cases to improvement in furfural yield [6,7,15,18,21,25–28], it is still far from being the best technique to be implemented on an industrial level.

Indeed, the presence of acid, salt and the use of two phases (the aqueous phase and the organic phase) in a single process is difficult from an operational standpoint. In addition, the solvent, acid and salt must be recovered to obtain an economically viable process [15]. Thus, this recovery process could be done on a laboratory scale, but would be complex and costly on an industrial scale [15]. Liquid-liquid extraction may not be the most cost-effective way to produce furfural on an industrial scale. The use of solvents poses cost problems and requires the installation of additional recovery systems. In addition, many industrial solvents are known to be hazardous to human health, so concerns related to flammability and environmental aspects (because of their processing) may prevent their use in modern bio-refineries [23].

Typically, in most industrial furfural production processes, reactors are heated with steam [11]. By passing through the raw material, the steam increases the reaction medium's temperature and at the same time entrain the furfural produced. Compared to the analytical process, this technique is incapable of bringing the reaction medium to its boiling point since the presence of pentoses and other dissolved materials causes boiling point elevation [11]. As a result, most of the furfural produced remains in the aqueous phase, which leads to the formation of undesirable products due to side reactions such as condensation and polymerization reactions that depend on, the residence time of furfural in the solution [11], composition of the reaction medium, its temperature, and the type and concentration of acid used. These side reactions can only take place in the aqueous phase [11] characterized by its hot temperature and acidity (two important parameters that favor side reactions). Thus, the longer the residence time of the furfural in the aqueous phase, the higher the chance of secondary reactions taking place and resulting in low furfural yield [11].

In order to reduce this high level of secondary reactions and to achieve high yield, we propose a system that avoids prolonged exposure of furfural molecules to other active species in the hot liquid phase. This can be done in two steps. The first step is to add the acid (catalyst) after the desired reaction temperature has been reached (novel approach). Consequently, this will minimize any secondary reactions of furfural with other species during the heating up stage. The second step consists of removing the furfural from the liquid phase as soon as it is produced by rapidly cooling down the vapor phase, thus avoiding losses due to the secondary reactions (polymerization and condensation). To carry out this work, we used a Parr reactor which we modified to produce and simultaneously separate furfural. By increasing the temperature above the boiling temperature of the reaction medium, two phases (an aqueous phase and a vapor phase) are instated inside the closed reactor. When the pressure increases, the extraction of the furfural formed in the system is facilitated. Moreover, a novel acid injection system is added to the Parr reactor. It is a system that allows us to add acid when the desired reaction temperature is reached (from 160 °C to 260 °C). As the pressure inside the reactor is higher than the atmospheric pressure, a much higher pressure is applied using nitrogen gas to inject the acid.

## 2. Materials and methods

### 2.1. Wood chips

The wood chips mixture used in this study was a combination of maple (a mass fraction of 65%) and aspen (a mass fraction of 35%) from 30 year old trees (without bark) available in New Brunswick (Canada). They were provided by a Canadian dissolving pulp mill. The chips were screened on disc screen using a thickness fraction between 2 and 8 mm. The mass fractions of their solids content were 60.5 and 37.3% for maple and aspen, respectively. The composition of the wood species in terms of cellulose,

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