



Research paper

Comparative study: Furfural production from two types of pre-hydrolysates produced using aspen and maple chips



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ABSTRACT

During the production of kraft dissolving pulp a pre-hydrolysate stream is generated prior to pulping. This pre-hydrolysate is a potential feedstock for the production of high value-added bioproducts. It contains a considerable amount of dissolved organics such as hemicelluloses, lignin and acetic acid. The purpose of this study was to investigate the effect of sulfur dioxide (SO₂) used during the pre-hydrolysis step on furfural production. The production of furfural from two types of simulated kraft dissolving pulp mill pre-hydrolysates was investigated. The first pre-hydrolysate was generated using hot water (PHLW) while the second one (PHLS) was generated using an aqueous solution containing sulfur dioxide (SO₂). The effect of temperature and sulfuric acid concentration on furfural yield from both pre-hydrolysates was investigated. A maximum furfural yield of 83.3% was obtained at 240 °C and with no sulfuric acid addition when PHLS was employed. For PHLW, a maximum furfural yield of 75.7% was obtained at 240 °C and with 3.6 kg m⁻³ of sulfuric acid. The higher furfural yield obtained after SO₂ pre-hydrolysis step was a result of lignin sulfonation that rendered the lignin less reactive towards intermediate molecules, sugars or furfural during the course of furfural production.

1. Introduction

During the production of kraft dissolving pulp a pre-hydrolysis step prior to pulping is performed, as shown in Fig. 1 [1]. This step allows the hydrolysis of hemicelluloses present in the wood chips [1] and the production of a pulp with high cellulose content after subsequent kraft pulping [2,3]. This solution is mixed with black liquor generated at the end of the cooking process. The combined liquor obtained is burnt in the recovery boiler to produce energy, steam and to recycle chemicals used throughout the process to meet the internal needs of the pulp mill. However, it is known that the energy produced by hemicelluloses represents only ¼ of the total energy produced in the recovery boiler [4]. This is mainly due to its low calorific value compared to that of lignin. Thus, the use of the pre-hydrolysate as an energy source cannot be considered an efficient utilization of hemicelluloses [5–8]. In addition, the level of solids in the pre-hydrolysate is very low (a mass fraction of 4%) compared to that in black liquor recovered after the cooking step (a mass fraction of 15–20%) [9]. Therefore, a large amount of energy would be required during evaporation to concentrate this pre-hydrolysate solution before burning it.

Condezo and his co-authors [10] evaluated several scenarios: 1) burning the mixture of black liquor and pre-hydrolysate as a source of

energy in the recovery boiler; 2) fractionating the pre-hydrolysate and burning the concentrate obtained with the black liquor in the recovery boiler; and 3) burning only black liquor in the recovery boiler to generate energy. The study showed that the solids content of the mixture was reduced significantly when black liquor (a mass fraction of 15% of solid) was mixed with the pre-hydrolysate (a mass fraction of only 2.8% of solid). As a result, the calorific value of the mixture decreased. When the pre-hydrolysate was mixed with the black liquor, 14.1 m³ of water per Mg of dry pulp were sent to the evaporators as opposed to only 7.55 m³ per Mg of the dry pulp otherwise. This represents 87% of additional water volume that must be evaporated.

In another study carried out by Paleologou et al. [11] on the valorization of the sugars present in the pre-hydrolysate, different options were proposed such as: production of ethanol, methane, butanol, furfural and incineration in recovery boilers. They estimated that for a pulp mill processing 2 Gg of wood chips per day, burning the pre-hydrolysate would be the least favorable choice. This option would generate an annual revenue of only 1.4 M\$ y⁻¹ compared to the pre-hydrolysate utilization that would generate additional revenues of 11.6 M\$ y⁻¹, 5 M\$ y⁻¹ to 8 M\$ y⁻¹, 15.4 M\$ y⁻¹ to 33 M\$ y⁻¹ and 28 M\$ y⁻¹ for the production of methane, ethanol, furfural and butanol, respectively. In addition, the pre-hydrolysate contains other high value-

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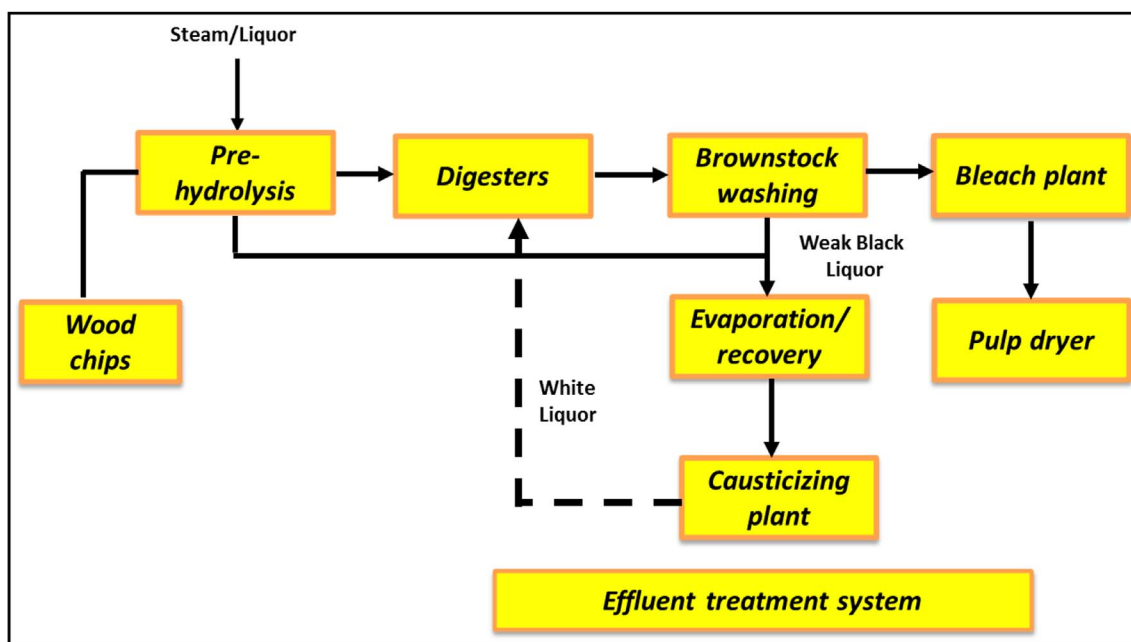


Fig. 1. Kraft dissolving pulp process.

added products, such as acetic acid, with potential revenues of 10.6 M\$ y^{-1} when extracted.

In addition, in recent decades, and especially before the last recession, about 60–70% of the pulp and paper mills in North America have gradually increased their production to the point where they have reached the capacity threshold for their recovery boilers [12]. Therefore, to increase pulp production, plants must increase the capacity of their recovery boilers or install new boilers. This last option is unfortunately very expensive. One way to increase pulp production without having to invest millions of dollars in the installation of new boilers would be to reduce the heat load of these boilers by extracting: 1) part of the lignin from the black liquor and/or 2) the pre-hydrolysate solution, preferably before mixing it with the black liquor. This pre-hydrolysate solution contains a large amount of hemicelluloses (C5 and C6 sugars) and a considerable amount of lignin [1]. These products represent a great potential for use in high value-added products and would enable pulp and paper mills to diversify their product range [13–15].

Thus, in order to fully utilize the pre-hydrolysate, it would be advantageous to separate it from the cellulose-rich stream and to use it in other high value-added applications. Thus, valuing the pre-hydrolysate would be an alternative to increase revenues and diversify the product range of kraft plants. This option will allow mills to increase pulp production by increasing the amount of wood at the process entrance.

Furfural is considered to be an important platform chemical [16,17]. The global furfural market demand was about 300 Gg y^{-1} in 2013, and is expected to reach 652.5 Gg y^{-1} by 2020 according to Grand View Research (which is a U.S. based market research and consulting company) [18]. Corn cobs and sugarcane are the major feedstocks for furfural production. Furfural is mainly used as a solvent in petroleum refining to separate lubricating oils and diesel fuels [19]. It is also used as a feedstock to produce various resins in the agrochemical and pharmaceutical industries [19]. Currently, furfural is commercially produced from hemicelluloses. However, other constituents of biomass are generally used as a source of energy. Thus, the use of hemicelluloses alone in a process to produce furfural renders it costly and less effective in terms of waste generation [20]. At the industrial level, furfural is produced through a hydrolysis step where the raw material rich in pentoses (C5 sugars) is mixed with sulfuric acid at high temperature [21,22]. When the temperature of the mixture is

between 153 and 184 °C [23], the furfural is produced and transported by steam [22]. The vapor phase obtained is then condensed and an azeotropic distillation is performed to purify the furfural [22]. The overall theoretical yield (mass yield) for the production of furfural is 73%. On an industrial scale, the mass yield is generally around 33% [24] (or 46% on a molar basis). This low yield is usually due to several side reactions such as resinification, condensation and degradation reactions [22].

To improve the yield of furfural produced from xylose and biomass containing pentosans, different approaches have been proposed. These methods focused on developing ways to reduce losses from side reactions [25].

Biender et al. and Yang et al. [26,27] demonstrated that the use of chloride ions directs the reaction mechanism towards the isomerization of xylose to xylulose, which in its turn converted into furfural. In their study, they suggested that the dehydration of xylulose could be a more selective way to the furfural formation as compared to the dehydration of xylose, which explains the higher yield obtained when the chloride ions are added [26,27].

Xing et al. [16] reported that the yield of furfural production is strongly related to the amount of NaCl added in the aqueous phase. Indeed, the yield increases as a function of the concentration of NaCl since the yield reaches its maximum when the solution was saturated with NaCl. This was due, according to the authors, to decreased solubility of furfural in water from 84 to 39, then to 19 kg m^{-3} when the mass fraction of sodium chloride increases from 0 to 16 and then to 26%, respectively. Therefore, by decreasing the amount of furfural in the aqueous phase, its extraction into the organic phase was improved.

A yield of furfural production of 68% was obtained by Mao et al. [28] from corn cobs. Their idea was based on the use of a monophasic system that contains iron trichloride ($FeCl_3$) and acetic acid. A slightly higher yield (72%) was obtained by the same group in 2013 under better conditions using a mixture of $FeCl_3$, seawater and acetic acid. Contrary to what has been mentioned above, the authors report that increasing the concentration of $FeCl_3$ promotes the formation of furfural. However, excessive addition of this compound leads to a counter-effect by causing additional losses of furfural. This is consistent with the results obtained by Liu and Wyman [29]. The latter concluded that the effect of $FeCl_3$ was not just to catalyze conversion of xylose into furfural but also to accelerate the losses of the formed furfural, via resinification

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