



Demineralization of wood using wood-derived acid: Towards a selective pyrolysis process for fuel and chemicals production

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ABSTRACT

A process concept for the pyrolysis of demineralized wood to obtain high organic and especially levoglucosan yields is proposed and tested experimentally. The wood is demineralized using organic acids, produced and concentrated within the same pyrolysis process.

Pine wood was pyrolyzed in a fluidized bed fast pyrolysis reactor (150 g feed per test) in which the produced vapors were condensed in two stages. The liquid obtained in the first condenser, operated at 80 °C (outgoing gas), contains the heavy compounds, like the lignin derived aromatic compounds and anhydro-sugars. In the second condenser, operated at –5 °C, most of the light compounds (including the acids) are collected. Pine wood was washed with this second condenser liquid at 90 °C for 2 h to remove the (alkali) minerals to increase the selectivity towards levoglucosan during pyrolysis.

Washing pine wood with the second condenser liquid prior to pyrolysis of the biomass, effectively removed the alkali ions initially present in biomass. No significant consumption of acetic acid during the washing step was observed. Rinsing of the biomass after acid washing is required for maximal levoglucosan production, to remove the washing liquid containing the dissolved minerals.

Fast pyrolysis of pine wood washed with second condenser liquid combined with rinsing resulted in an increase in organic oil yield and is accompanied with a decrease in water and char yield. The levoglucosan production increased strongly (up to 18 wt% on biomass intake) and was concentrated, by staged condensation, in a single fraction up to a concentration of 37 wt% in the first condenser oil. The obtained levoglucosan yield is comparable to yields reported in literature obtained by mineral acid washing.

The presented concept for demineralization wood, by washing with an aqueous pyrolysis fraction produced from the biomass itself, prior to pyrolysis is demonstrated to be an interesting sustainable process to increase both the organic oil yield and the production of levoglucosan.

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1. Introduction

Lignocellulosic biomass decomposes at elevated temperatures and in the absence of oxygen into gasses, vapors and char. This process is called pyrolysis. The vapors are condensed to obtain a liquid, called pyrolysis oil or bio oil. This liquid can be easier and more economically transported compared to the bulky solid biomass from which it originates. Pyrolysis oil is a complex mixture of water and a large variety of oxygenated organic compounds with different chemical functional groups. The exact composition of the pyrolysis oil depends on the biomass feedstock, process conditions and pyrolysis oil handling. It can be stated that the fast pyrolysis process of biomass lacks selectivity to single compounds. Improving the selectivity of compounds more readily

suitable for the production of fuels and chemicals would increase the value of the product slate. Conventional fast pyrolysis can be regarded as a process that converts biomass, with a high yield, into a single liquid. With this configuration the produced liquid may be (i) used as such as feed for turbines, boilers and engines or (ii) upgraded to serve as feed for fuels [1] and chemicals [2]. We are developing a pyrolysis process that produces several liquid streams which are concentrated in targeted compounds or groups of compounds. Concentration of the target compounds is achieved by, firstly, improvement of the selectivity of the pyrolysis reactions by demineralizing the biomass and, secondly, staged condensation of the pyrolysis vapors produced. The streams of interest, hence the products, are (fermentable) sugars, aromatics and light oxygenates. In this way, pyrolysis becomes a technology that produces precursors for the chemical, petrochemical and refinery industry. Based on a yield of 20 wt% for each stream the value of the product slate is in the range of 200–300 €/tonne feed.

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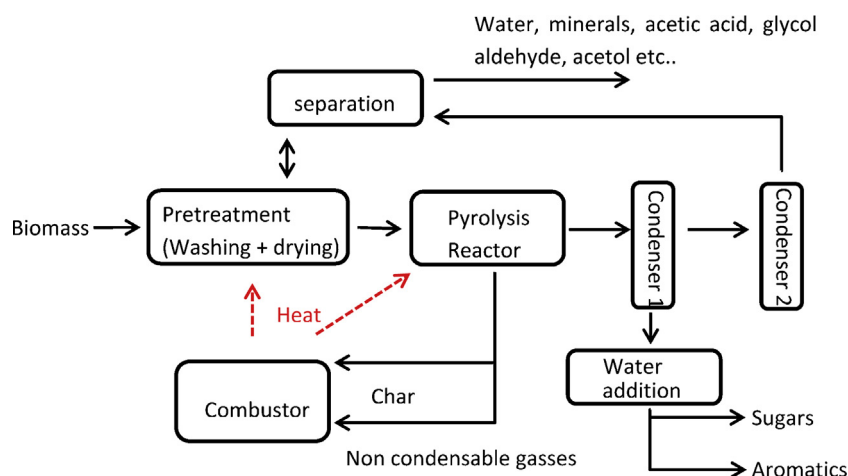


Fig. 1. Process layout for the production of sugars, aromatics and light oxygenates from lignocellulosic biomass via fast pyrolysis.

1.1. Process concept

Fig. 1 shows a first simplified process layout consisting of the following process steps:

- (i) Fast pyrolysis of the acid washed biomass where after the pyrolytic vapors are (fractional) condensed in two spray condensers in series. Operating the condensers at 80 and 20 °C (or lower), the lignin derived aromatic compounds together with the anhydro-sugars (mostly levoglucosan) are concentrated in the first condenser while an acidic aqueous fraction (containing up to 10 wt% of acetic acid) is recovered in the second condenser [3].
- (ii) Washing of the (wet) biomass with the acidic aqueous stream from the second condenser to remove the (alkali) minerals from the biomass feed, upfront to pyrolysis. By doing this the selectivity towards levoglucosan within the pyrolysis process is expected to increase, as suggested by Scott and co-workers [4]. To the best of our knowledge this has not been demonstrated experimentally so far. Washing with mineral acids followed by pyrolysis has already proven to result in higher levoglucosan yields [5]. After the washing step, the biomass is dried/dewatered to 0–20 wt% moisture content [6].
- (iii) Combustion of the char and combustible non condensable gases produced during pyrolysis in order to generate heat and energy for the drying, acid washing and pyrolysis process.

After washing, light oxygenates can be recovered, via e.g. a combination of extraction and distillation steps [7], from the washing solution (product of the 2nd condenser). The concentrations of the target compounds (e.g. acetic acid, acetol and glycolaldehyde) in the washing solution are significantly higher when compared to those in pyrolysis oil retrieved from a single condenser system [3], for more information on the composition of the 2nd condenser liquid is referred to Westerhof et al. [3]. Moreover, the washing solution is less “contaminated” with sugars and aromatics. The remaining washing liquid and the rinsing water can also be fermented to produce lipids [8] or digested to obtain bio-gas [9]. The liquid from the first condenser, rich in sugars and aromatic compounds, can be phase separated by water addition [10]. Doing so, the sugars and some mono aromatic compounds will be recovered in the aqueous phase, which can be used directly or after purification for fermentation to produce ethanol [11] or lipids [12]. Levoglucosan has also the potential to be chemically converted into e.g. medicines, biodegradable surfactants or polymers [5]. The lignin derived water insoluble fraction contains mainly aromatic compounds attractive for the

production of transportation fuels via hydro-deoxygenation (HDO) [13] or as feed for the aromatics industry.

Other reasons for removing the minerals, besides the increased selectivity towards levoglucosan, include: (i) increased oil yield at the expense of gas, char and water. (ii) No minerals in the pyrolysis oil and hence no mineral related problems in subsequent applications, as e.g. catalyst poisoning during catalytic upgrading of pyrolysis oil or ash deposition in engines/turbines during combustion. (iii) No low temperature melting ashes in the char: no agglomerates to be formed and less corrosion problems in the combustor section and (iv) no catalyst poisoning by ashes when applying a catalyst within the pyrolysis process itself, both inside the reactor or in the vapor phase between the reactor and condenser, or during regeneration of the catalyst (burning of coke).

Several review articles on removing minerals from biomass and the corresponding effect on the pyrolysis process have been published [5,14]. Here a short summary of the most important methods and observations is presented. Piskorz et al. [15] showed that the presence of alkali ions hampered the depolymerization of cellulose into anhydro-sugars and increased fragmentation reactions. It was shown that presence of relatively low concentrations of alkali ions (0.01 wt% NaCl added to cellulose) already reduced the levoglucosan yield (by 50%) to a large extent [16]. Minerals in biomass can be physically or chemically bounded to the biomass components [17]. Generally, it can be stated that the removal efficiency of the alkaline ions present in wood, e.g. Ca, K, Mg, Fe and Na, depends on the temperature, process time, acid type and the acid concentration. Washing with (hot) de-ionized water can effectively remove most of the Na, Mg and K, however Ca is only partly removed [17,18]. The acid washing methods can be employed at higher temperature as well as at (near) ambient temperature, both using strong acids. Washing at high temperatures (90–240 °C) with a strong acid is hereafter referred to as hydrolysis. With hydrolysis most of the hemicellulose and mineral content is removed from the biomass. The degree of polymerization of cellulose structure is lowered by hydrolysis reactions [19]. For washing with strong acids at relative low temperature Scott et al. showed that washing with 0,1 wt% HNO₃ at 30 °C for 60 min removed most of the alkaline ions present in the biomass [17]. When mineral acids remain in the biomass during pyrolysis, the produced levoglucosan could react further to levoglucosone [20,21]. Dobelet et al. showed that there is a maximum in the sum of the levoglucosan and levoglucosone yield at 2 wt% acid (H₃PO₄) before the yields started to drop due to intermolecular cross-linking reactions during pyrolysis [21].

Our approach is washing the biomass using organic acids produced within the pyrolysis process. This is beneficial because there

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