Biomass and Bioenergy 95 (2016) 388–404

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Using pyrolytic acid leaching as a pretreatment step in a biomass fast pyrolysis plant: Process design and economic evaluation

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ARTICLE INFO

Article history:
Received 27 January 2016
Received in revised form
1 July 2016
Accepted 2 July 2016
Available online 30 July 2016

Keywords:
Fast pyrolysis
Acid leaching
Alkali and alkaline earth metals
Pyrolytic sugars
Process design
Techno-economic evaluation

ABSTRACT

Removing alkali and alkaline earth metals (AAEMs) from biomass, with pyrolytic acids, before pyrolysis leads to increased organic oil and sugar yields. These pyrolytic acids are produced and concentrated within the pyrolysis process itself. The purpose of this paper was to evaluate under which conditions acid leaching of pinewood, bagasse and straw can improve the technical and economic feasibility of a pyrolysis process. Therefore, a preliminary process design for the implementation of acid leaching at a pyrolysis plant, with a biomass capacity of 5 and 50 t h^{-1}, was made and compared with a pyrolysis plant using the untreated biomass. Target products were heating oil and/or additional pyrolytic sugars.

It has been calculated that with the leaching step the heat for pyrolysis and drying of the biomass can still be supplied by the combustion of the char and gases, but insufficient excess heat is available to produce electricity for the process. Critical for the economics of the acid leaching pyrolysis process are the amount of extractives in the biomass (organics ending up in the waste water) but not its moisture content. Mechanical dewatering before thermal drying turns out to be very important. The economics of the presented approach turned out to be very sensitive to the plant scale, CAPEX and obviously to the biomass price. At the current market scenario and state of proven techniques the production of sugars and heating oil from bagasse at 50 t h^{-1} is the most economic option (IRR 15.4%).

1. Introduction

Fast pyrolysis of lignocellulosic biomass is a promising conversion process to depolymerize the biomass building blocks, hemicellulose, cellulose and lignin, into a liquid termed bio or pyrolysis oil. This oil, a mixture of oxygenates and water, can be used directly for heat and power production or further refined to liquid fuels [1–3] and/or chemicals [4]. In this process dry biomass particles are quickly heated to temperatures around 450 °C–550 °C in the absence of oxygen causing the biomass to decompose into gases, vapors (condensed to obtain oil) and char. The oil yield and composition varies largely between different biomass feedstocks [5]. These differences are mainly caused by the varying alkali and alkaline earth metal (AAEM) contents [6], which have been reported to catalyze dehydration reactions leading to increased water and char production [7,8]. The increased water production often leads to phase separation of the oil, which complicates further processing [9]. Moreover potassium and sodium reduce the melting temperature of ash leading to problems in the char combustor [10–12]. Typical AAEM concentrations of "clean" debarked wood are around 5 g kg^{-1} while herbaceous and agricultural waste streams, like straw, contain around 15 g kg^{-1} [13]. In the authors opinion, the lower organic oil yield and phase separation of the obtained oils from many biomass residue steams high in AAEMs makes these biomass streams not suitable as feedstock for conventional pyrolysis.

Recently we proposed and validated that the majority of AAEMs can be removed from biomass via leaching with organic acids, produced and concentrated within the same pyrolysis process [14]. The different functional blocks required for the proposed process are shown in Fig. 1 [14]. Size reduction of the biomass is required to achieve reasonable AAEM removal rates during acid leaching (discussed in section 3.2). After acid leaching and rinsing the biomass will contain around 75% of moisture by weight, which has to be removed before pyrolysis. The drying is done by a combination of mechanical and thermal treatment. The pyrolytic acids are separated from the majority of the oil (including sugars and phenolics) by applying fractional condensation of the pyrolysis vapors using at least two condensers operated at different temperatures [15]. The

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http://dx.doi.org/10.1016/j.biombioe.2016.07.003

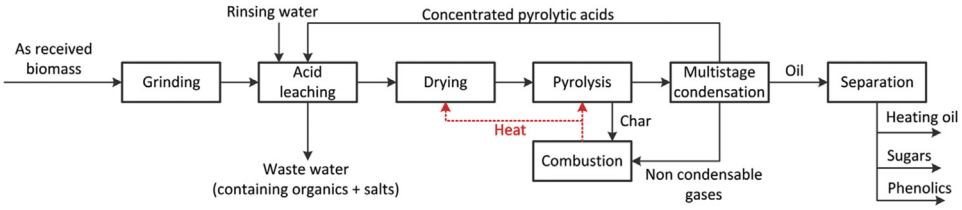

Fig. 1. Function block diagram for the pyrolysis of pyrolytic acid leached biomass.

char and gases are combusted to provide the heat required for pyrolysis and drying.

Pyrolytic acid leaching of different biomasses (pinewood, straw, hay and bagasse) reduced the AAEM content to 90 mg kg^{-1} – 600 mg kg^{-1} [6]. Pyrolysis of these acid leached biomasses resulted in a large increase of the organic oil yield compared to the untreated biomasses (e.g. straw increased from 370 g kg^{-1} to 580 g kg^{-1}) [6]. In addition, the selectivity towards anhydrosugars (also referred to as pyrolytic sugars) was largely increased resulting in a high anhydrosugar content in the oils (e.g. bagasse, mass fraction anhydrosugar in 1st condenser increased from 10% to 48% by weight) [6]. These high anhydrosugar concentrations might allow the economic fractionation of the oil into higher economic value products. The sugars can be separated from the oil (including phenolics and furanics) by water extraction followed by ethyl acetate extraction (further discussed in section 3.7). The isolated sugars, obtained from acid leached pinewood, were successfully, after hydrolysis, fermented to bio-ethanol [16] or converted to lipids [17] with comparable yields as obtained from glucose. The residue after sugar separation is rich in phenolics. Tests at laboratory scale showed that this fraction can be used for the production of transportation fuel via hydro deoxygenation (lower H_2 consumption and higher C to oil compared to normal pyrolysis oil) [18,19]. To further improve the economic value of the pyrolysis oil, extraction of phenolics is proposed. The extracted phenolics (mainly oligomeric) can be used as feedstock for phenolic resins production [20] or cracked into mono phenolics [21], which would generate the highest value. The product slate including the purification steps, which are often overlooked, can be seen in Fig. 2.

Several studies have evaluated the economics of pyrolysis oil production using untreated biomass. Generally it is found that the biomass price has a large effect on the pyrolysis oil price (~50% for wood) [22,23]. The price of biomass varies a lot for different biomass types e.g. bagasse (~35 \$ t^{-1}), empty fruit bunches (15–35 \$ t^{-1}), mallee wood (~40 \$ t^{-1}) straw (~80 \$ t^{-1}) and pinewood (~80 \$ t^{-1}). It is worthwhile to mention that low cost biomass often has a high ash content. Techno economic studies involving acid leaching as pretreatment step to increase the oil yield and to improve the processability of the oil from high AAEM feedstocks have not been published so far. The economic potential of producing sugars (or ethanol) via pyrolysis has only been studied for two specific cases. In 1999 So and Brown showed that sugars (for fermentation to ethanol) produced from prehydrolysis, hydrolyzing the hemicellulose, followed by fast pyrolysis of the solid residue (cellulose and lignin) had a comparable production cost compared to sugars produced via dilute sulfuric acid hydrolysis or prehydrolysis combined with enzymatic saccharification [24]. In a later paper Brown compared the aforementioned methods for the production of ethanol also with syngas fermentation. It was found that the syngas fermentation route had the lowest ethanol production cost [25]. However, it should be noted that in this study only ethanol was taken as product whereby a large fraction (containing a significant amount of the energy) of the pyrolysis oil remains unused in case of pyrolysis. The second case, the pyrolysis of acid infused biomass (with H_2SO_4) producing d-glucose (via hydrolysis) and transportation fuels (via hydrogenation using hydrogen produced from the light organics), was evaluated by Zhang et al., in 2013 [26]. An IRR of 11.4% was calculated. It should be noted that the selected method for the production of expensive glucose (600 \$ t^{-1}) is rather optimistic, since the sugar stream after hydrolysis will contain next to glucose also sugars produced from the hemicellulose. In addition, the effectiveness of the described acid impregnation method, using sulfuric acid with a concentration of 50% on mass basis, can be questioned because: i) the low amount of liquid (acid) could lead to an uneven acid distribution and therefore not stabilizing all of the AAEMs; and ii) the low pH is expected to lead to dehydration of the biomass.

The objective of this paper is to identify under which conditions acid leaching can improve the technical and economic feasibility of a pyrolysis process. Therefore a process design of a pyrolysis plant with and without acid leaching processing 5 or 50 t of dry biomass per hour was made. The feedstocks studied were: i) pinewood, which has a low AAEM and moisture content and a high feedstock price; ii) straw, which has a high AAEM content, low moisture and a high feedstock price; and iii) bagasse, which has a low AAEM content, high moisture and a low feedstock price. Four different cases, as depicted in Fig. 2, were studied to evaluate the feasibility of producing multiple product streams, these were: i) pyrolysis of untreated biomass to produce heating oil (HO_U); ii) pyrolysis of acid leached biomass to produce heating oil (HU_{AL}); iii) pyrolysis of acid leached biomass to produce sugars and heating oil ($S\&HU_{AL}$); and iv) pyrolysis of acid leached biomass to produce sugars, phenolics

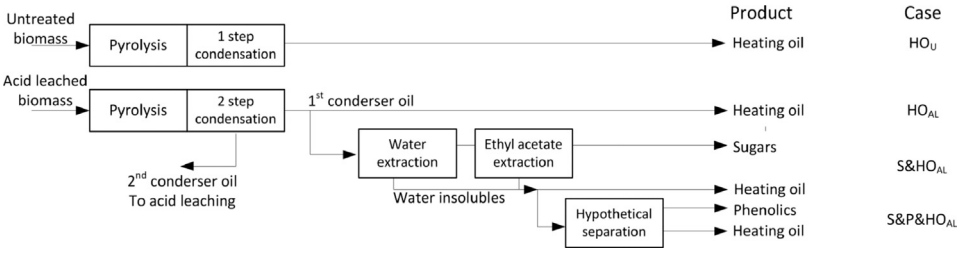

Fig. 2. Overview of the different cases studied.