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Full Length Article

Supercritical water gasification of lignin solution produced by steam explosion process on Arundo Donax after alkaline extraction

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ABSTRACT

In this paper the lignin gasification by using water in supercritical was studied. The employed lignin was produced via steam explosion of Arundo Donax after alkaline extraction and filtration. The lignin, with a total solid content of about 4 wt% in a solution of sodium hydroxide which confers to the solution a pH of about 11, was fed in a continuous PFR bench scale reactor able to operate at supercritical water conditions. The experiments were carried out at 550 °C and 250 bar by varying the feed flow rate from 10 mL/min to 60 mL/min in order to understand the effect of the residence time on the liquid and solid phases in terms of volume composition, liquid phase composition, carbon and global gasification efficiency. The main results showed that by using lignin after alkaline extraction, syngas with a higher heating value (HHV) greater than 40 MJ/kg without CO_2, mainly composed by hydrogen and methane, was obtained. At the same time, in the liquid phase the presence of some compounds, such as glucose, syringaldehyde, formic acid, acetic acid and xylose, was revealed, and all these species are included in the main building block group for the green chemistry or for the development of bioprocess for high added value intermedia production.

1. Introduction

The rapid depletion of natural sources and the increase of greenhouse gas emissions have promoted the increase in the interest for the lignin energetic valorization. Lignin is a natural biomass component and is classified as substitute of petroleum for several energetic applications [1]. It is one of the main components of the biomasses and, depending on the vegetable specie, is in weight percentage in the range of 15–35 wt%. Lignin in the biomass plays a role for binding and cementing the fibers together, allowing their compactness and resistance. From the chemical point of view, it is a three-dimensional irregular biopolymer, with a relatively complex structure [2]. In the industrial sector, it represents a byproduct of the paper production process and over the 95% is burned to recovery the additives, which are often used for the same process [3,4].

In the last decade, the development of renewable biofuels, and in particular the second-generation sugars production using lignocellulosic as raw material, highlighted as lignin represents an important and undervalued stream [5–9]. Generally a lot of lignocellulose residues like wheat and maize straws contain 40–60 wt% of carbohydrates (cellulose and hemicellulose) and about 20–30 wt% of lignin. Sugars can be exploited in several material production (biofuels, biopolymers, etc.) with almost assessed processes, while lignin is a material currently studied for new and more interesting applications (fuels, nanocomposites, polymer mixtures) [10–22]. Steam Explosion (SE) [23,24] is the main process used for the valorization of the lignocellulosic biomass by fractionating it into hemicellulose, lignin and cellulose, the last could be used in fermentative processes for bioethanol production [25]. The Fig. 1 shows the scheme of the steam treatment and the sequential fractionation of lignocellulosics.

This process is based on the use of pressurized steam at temperature between 180 °C and 230 °C for a period of about 2–10 min. In these operative conditions biomass, and, in particular hemicellulose, are hydrolyzed and solubilized. After this residence time, the pressure is quickly brought back to the atmospheric value [26–29]. Decompression stage causes the spillage from the biomass's cellular membrane which is further amplified by the mechanical effect [30]. Lignin used in this work has been extracted via SE treatment followed by alkaline

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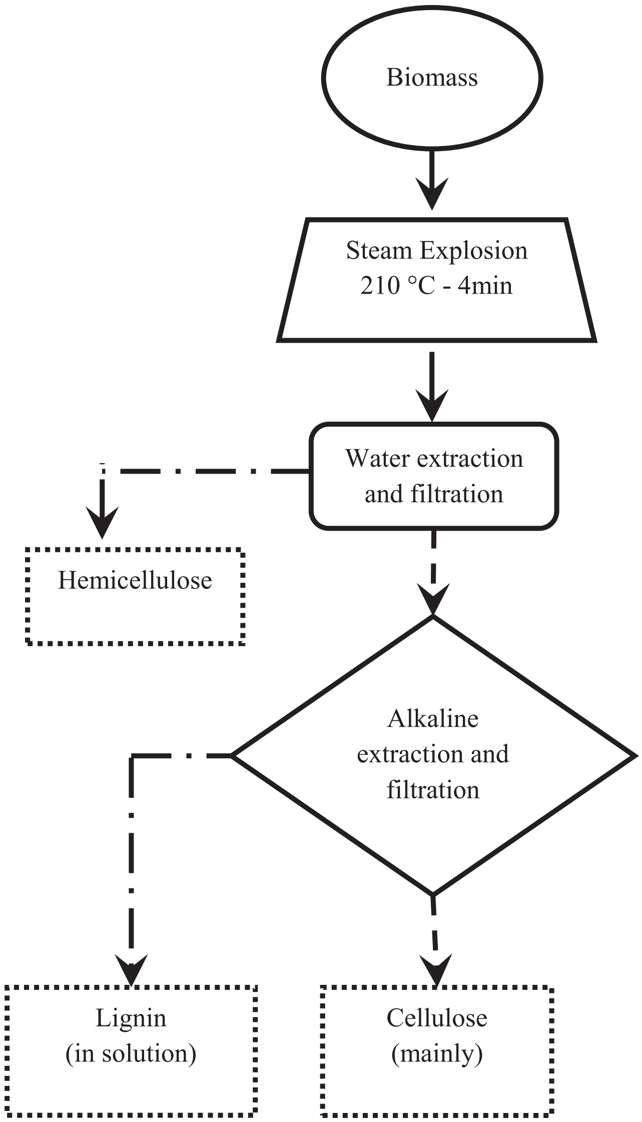

Fig. 1. Main steps of the Steam Explosion process.

extraction (as reported in Fig. 1) and used as fed in a Supercritical Water Gasification (SCWG) process. The aim of the study is the lignin valorization for pressurized biofuels production (bio-hydrogen & Synthetic Natural gas) as well as for liquids bio-products production. Lignin solution, derived by steam explosion treatment of Arundo Donax and alkaline extraction by using sodium hydroxide, was employed in the supercritical water gasification process allow in tar free syngas and liquid phase composed mainly of glucose and aldehydes and others chemical species that could be used as biobased in the green chemistry for chemicals production [31–34].

2. Materials and methods

The lignin solution was produced by the following procedure: about 1 kg of Arundo was treated by a steam-explosion batch plant (10 L capacity), at 210 °C, 10 min; the product was extracted with water at 60 °C, then filtered to separate the hemicellulose liquid fraction; the solid was extracted two time with 5 L of soda solution (pH 11.5 and 80 °C for 1 h) [35], then the liquid fraction, containing the solute lignin (40 g/L), was separated from the solid (mainly cellulose) by filtration. About 1 L of lignin solution was used for SCWG tests. Bench scale plant used for the experimental tests was realized by Parr Instrument Co® using stainless steel T316 not only for the achievement of the

Fig. 2. Bench scale SCWG reactor.

supercritical water condition but for operating till to 350 bar and 600 °C. The reactor is characterized by a tubular geometry with an internal diameter of 25 mm, an external diameter of 48 mm and with a total length of 1120 mm.

Fig. 2 shows the bench scale reactor that was used for experimental tests using water in supercritical conditions. The internal volume of the reactor was of about 450 mL and the heat was provided on the external side of the tubular system by power for a length of 900 mm. The process parameters were monitored and controlled by using Distributed Control System (DCS).

Fig. 3 shows the Piping and instrumentation diagram (P&ID) of the SCWG reactor. It is possible to see that the feed was pressurized using syringe pump (Teledyne Isco® Pump 500D) and for its monitoring was employed a digital manometer while the temperature was controlled with a multiple thermocouple. Regarding the lignin composition, proximate and elemental analysis were carried out, and the results are showed in the Tables 1 and 2.

Table 1 shows the proximate analysis of lignin derived by steam explosion experimental tests where it is possible to observe as, the total solids composed by only lignin, was of about 4 wt%. At the same time, volatile solids, residual carbon and ashes were analysed as percentage of total solids. Results showed that about 91 wt% of TS was composed by volatile substances, while only 2 wt% was made up by residual carbon. At the same time, based on the dry solids, the elemental analysis allowed to understand the CHN composition of this lignin used for SCWG process.

Table 2 shows the ash free elemental analysis of lignin used for the SCWG tests which evidenced a high carbon content that contribute to increase the higher heating value of dry lignin.

Experimental tests in supercritical condition were carried out using dilute lignin fixing the temperature at 550 °C, the pressure at 250 bar and varying the flow rate from 10 mL/min to 60 mL/min. The produced syngas was separated from water in a condense, quantified by using a GILMONT Instruments flow meter and analysed in terms of composition every 3 min, through the gas chromatograph on-line HP 6890 equipped with a conductivity detector. At the same time the obtained liquid condensate was analysed for several time ranges for each test. Aldehydes, sugars and carboxylic acids were detected using high performance liquid chromatography (HPLC) model 1100 equipped with photodiode array detector and Phenomenex Idro RP 80 as column by Agilent.

3. Results and discussions

Experimental results carried out in SCWG by using lignin as feed