SEMI-CONTINUOUS LAB-SCALE PLANT FOR HYDROTHERMAL OR ORGANOSOLV TREATMENT OF LIGNOCELLULOSIC BIOMASS

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ABSTRACT: Lignocellulosic biomass is increasingly being considered as a potential alternative source for both fuels and goods production. In order to better address the starting material to higher conversion and selectivity in the desired products, the possibility to selectively control the dissolution of the three main constituents of the matrix (hemicellulose, cellulose and lignin) should be pursued. As the three biopolymers are intimately connected one another, a suitable pretreatment step could help the effectiveness of the whole process, by producing cleavage of the biomacromolecules interconnecting bonds and by starting their depolymerization . In this frame, we developed a semi-continuous lab-scale plant in which a fixed bed of comminuted biomass can be contacted in flow-through configuration with specific fluid streams at suitable temperature and pressure conditions This versatile plant allows performing different treatments, such as liquid hot water (LHW) or organosolv processes, and extractives recovery as well. Additional possible configurations, already implemented, allow the addition of CO_2 as acid catalyst to the aqueous process stream, or performing steam explosion procedure. Together with the plant description, an overview of the first experimental results will be presented.
Keywords: lignocellulosic sources, biomass, biorefinery, treatment.

1 INTRODUCTION

Lignocellulose biomasses are mainly constituted by the three biopolymers hemicellulose (20-40%), cellulose (30-50%) and lignin (15-25%) [1] and another 3-35% consisting in lower amounts of ashes, waxes, oils, proteins and other minor components. The relative concentration of the constituents strongly depends on the type of the biomass and, for the same species, in a minor but not negligible way, also from the cultivation crops conditions (temperature, irrigation, soil, insolation, humidity, etc..). In principle, polysaccharides constituting the matrix could be converted into intermediates or end products, such as fuels and chemicals, through integrated chemico-physical and/or biotechnological processes of variable complexity.

Sugar cane, cereal (wheat, rye, corn) straw and stover have been up to now the most investigated and used biomasses for ethanol production, especially in Brazil (cane) and U.S (corn) where about the 87% of the world's ethanol is produced [2]. In order to avoid food competitive use, and according to the concept of the new (third) generation biorefineries [3], other lignocellulosic materials are being considered both for chemical and fuels synthesis. In particular, efforts are addressed to exploit widespread and no food crops, inherently present in the territory, or easy to be grown in disadvantaged (i.e. partially polluted) soils, or to sustain their traditional use (like oils or woods). Among these biomasses, Arundo Donax (giant reed), Panicum Virgatum (switchgrass) and Miscanthus Gigantus are often considered, especially for bioethanol production, due to their spontaneous grown, high productivity per acre and their high cellulose content [4]. However, woody biomass (above all, eucalyptus and poplar) pruning can also be considered as raw material for biorefineries. In general, the main hurdle for biomass conversion into desired chemical products lies in the limited availability of the biopolymers to selective chemico-physical transformations, owing to their microscopic structuration and interconnection. Whatever the type of the target products, the material processing is aimed to the dissolution of the main constituents in the reaction medium. Dissolution of the two polysaccharides (hemicellulose and cellulose) can be achieved through hydrolysis process in a aqueous medium or ionic liquid [5] and in this case the solid residue at the end of the process is a substance enriched in lignin. Reversely, organosolv type processes use mixture of organic solvents and water to dissolve both acid soluble lignin (ASL) and acid insoluble lignin (AIL) [6]; for this type of process the solid residue is enriched in cellulose. For processes in aqueous media, the hydrolysis of polysaccharides can be activated thermally, enzymatically, or by the addition of acid species. A particular thermal treatment is the stem explosion, by which, a fast depressurization of the steam in contact with the biomass bed causes mechanical stresses in addition to hydrolytic reactions. Currently, respect with the biological and mechanical methods, thermochemical fractionation with pressurized low polarity water (PLPW) seems to be a promising approach to optimize processing time and products yields [7]. For bioethanol production, high yields in fermentable sugars should be pursued. However, the operative conditions (high temperature and acidity) which promote biopolymers depolymerization, also promote sugars degradation towards substances, among which weak acids, furan derivatives, and phenolic compounds [8] that can also inhibit fermentation processes. Then, an effective pretreatment step should break the interconnections among the biopolymers, and possibly also affecting microstructure of crystalline domains, and initiate depolymerization of polysaccharides at operative conditions in which follow-up reactions to sugars degradation products are kinetically controlled. Prompted by these considerations, we have built a semi-continuous lab-scale plant to study the possibility of using as adjustable parameters the inlet flowrate and the operative temperature, to match suitable control of the product evolution with good depolymerization efficiency and acceptable product concentration in the outlet streams, thus limiting energetic costs in the further steps of the process.

2 EXPERIMENTAL

2.1 Plant description

In Figure 1 a schematic description of the lab-scale plant for lignocellulosic biomass (pre)treatments is depicted. The semi-continuous layout was chosen in the perspective of an industrial scale-up, since the process should be characterized by large enough production scales to become competitive with oil based conversion routes. Moreover, differently from what happens in the batch reactors, the fixed bed of comminuted biomass inside the reactor is continuously contacted with a "fresh" stream, which performs a continuous biomass washing, together with the treatment at the set conditions. This fact has noticeable effects on the products yields, as it will be discussed later.

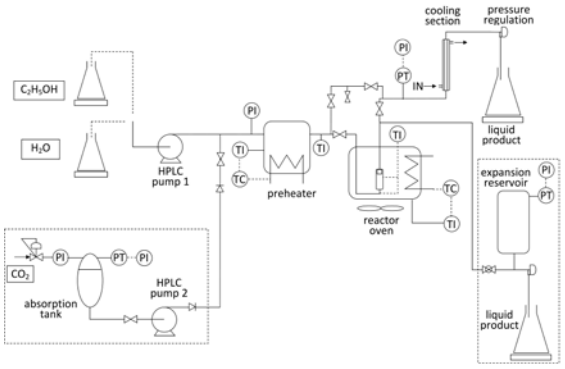

Figure 1: Schematic description of the semi-continuous plant for lignocellulosic biomass treatment.

The biomass fixed bed is charged inside an AISI 316 reactor of 30 mL volume, before starting the treatment. A quaternary HPLC pump (1), Varian Inert 9012, is used to feed the liquid stream. This pump allows the mixing of different liquid streams (up to 3) with an adjustable volumetric ratio. The process stream is sent to a preheater where it reaches the desired process temperature, and then it is directed toward the reactor where it passes through the biomass bed. The preheater coil and the reactor are inserted inside two respective ovens, where hot ceramic heating elements (from Watlow) provide heat transfer primarily by irradiation. The reactor outlet stream is cooled down in tube-in-tube heat exchanger, using liquid water as cooling stream. The cooled process stream reaches a pressure relief valve, set at the desired pressure for the experiment. The liquid coming out from the valve is collected in a sample flask.

Both feeding and sample collection flasks are put on a respective electronic scale and masses of pumped and collected liquid streams are recorded.

2.1 Temperature control

The temperature of the preheater and reactor ovens is regulated by using two temperature controllers (Eurotherm 2216e series) with a PID control algorithm. Before reaching the temperature set for the test, the preheated stream is conveyed to the reactor bypass, thus avoiding any contact with the biomass bed. For the temperature control of the reactor, together with the ceramic heating elements, a fan is also used as air-cooling system. In addition, the oven of the reactor can be vertically translated at any time and this allows fast heating up and quenching of the reactor at the beginning and at the end of the treatment, respectively. The use of the reactor by-pass and the possibility of insert and extract the reactor in/from the oven minimize the transient time (about 3 min) necessary for the biomass in contact with the process stream to reach its steady processing temperature. Actually, these features seems to be advantageous peculiarity with respect to other flow-through lab-scale plants described in the literature [9][10].

2.2. Additional features

As already mentioned, the effectiveness of the biomass pretreatment depends on the adopted operative conditions. Together with the nature of the process fluid, the kinetic severity, i.e. a combination of temperature and fluid-biomass contact time, determines the obtained products [11]. In addition, polysaccharides hydrolysis reactions can be acid catalyzed. In this regards, Overend and Chornet extended their previous definition of process severity [12] to the additional contribution of the acidity, by definition of a combined severity parameter [13].
For hydrolysis, carbonated water can be used in place of other acids solution [14] to reduce the system pH with the advantage of easily separating the acid additive at the end of the process by expansion, and thus not needing any alkaline chemical addition to perform catalyst neutralization.

To test the effect of CO_2 addition we have implemented in the plant a section (dashed frame on the left side of Figure 1) to introduce carbon dioxide as solute inside the process stream. The concentration of the gas can be tuned by changing the pressure inside the supply tank.

In addition to flow-through experiments, the experimental setup allows one to perform steam explosion batch treatments. In this case, the reactor can be filled with steam by holding the pressure at values below water vapor pressure at the desired process temperature; then the steam volume can be quickly expanded by connecting the reactor with a large volume (dashed box on the right side of Figure 1). Then the system can be cooled down and washed with fresh water to recover the soluble hydrolysis products.

2.3 Other equipment and materials

Culms and leaves of Arundo Donax (giant reed), grown in two different Italian sites have been used. The material was received already ground and sifted to a size of 0.5 mm, then dried and kept inside airtight plastic bags. Deionized water and 96% pure grade ethanol from *Carlo Erba* have been used as solvents. *Whatman* grade 42 filter paper has been used to collect the solid residue. Centrifugation at 3000 rpm for 10 min has been used to separate suspended residue inside half-filled vials of 15 mL volume. Liquid chromatography analyses have been performed with an Agilent 1100 series HPLC, using a column Rezex ROA-OrganicAcid H+ 8% cross-linkage, size 300 x 7.8 mm (equivalent to Bio-Rad Aminex HPX-87H), with a security guard coloumn Carbo-H, size 4x3.0 mm. A refractive index detector with 8 µl flow cell has been used for substances identification. The operative conditions to perform analyses (mobile phase, flowrate, injection volume, column and detector temperatures) were fixed according to NREL procedures [15]. Quantitative determinations were performed referring to a standard external calibration method.

3 FIRST EXPERIMENTAL RESULTS

We started an experimental campaign to study the optimization of process parameters to maximize, since the pretreatment step, the sugars and oligosaccharides yields, while keeping sugar degradation products at the lowest possible concentration. Liquid hot water (LHW) treatment was performed at different temperatures (150, 180, 200 °C), different treatment time (20 and 60 min) and different water flowrates (2.5 and 5 mL/min), on 13 g of comminuted biomass. For all the experiments the process pressure was kept at about 70 bar.

3.1 Extractives recovery

Extractives contain substances which can affect the pretreatment effects. For this reason, a preliminary stage of extractives removal from the matrix has been performed. In fact, the described layout of the experimental plant allows performing a sequence of different treatments on the same biomass, once this has been charged inside the reactor. For all the matrices extraction was performed using in sequence:

- pressurized water at 100 °C for 20 min with a flowrate of 5 mL/min, to extract polar substances;
- pressurized ethanol at 80°C for 20 min with a flowrate of 5 mL/min, for the nonpolar substance recovery.

Then, pure water at 10 mL/min for 20 min was used to wash the system at lower temperature. By this approach, the amount of recovered extractives was 7.7 wt% of the initial biomass.

3.2 Hydrolysis

HPLC analysis of the hydrolysate obtained with the tests in different conditions highlighted the influence of the three different considered parameters. As a reference of the process severity, the definition of the severity parameter R0 given by Overend and Chornet [12] was considered, according to the following equation:

$$R0 = t * \exp[(T-100/14.75] \quad (1)$$

In equation 1 T is the temperature in Celsius degrees, while t is expressed in min and represents the treatment time that for our flow-throw configuration was calculated as V/Q (where V is the reactor volume and Q is the volumetric flowrate).

The experimental conditions of the performed tests are reported in Table I.

Table I: Experimental conditions adopted to perform LHW tests.

test	log R0	t [min]	water flowrate [ml/min]	total fed water amount		T [°C]	end mass (net extractives)
				[ml]	[n.of reactor vol.]		
A	3,17	20	5	100	3	180	-28.2%
B	3,47	40	2,5	100	3	180	-32.7%
C	3,76	20	5	100	3	200	-41.8%
D	3,76	60	5	300	9	200	-46.2%

Figure 2 shows a comparison between the tests in which a single parameter has been changed, respectively. As it is noticeable, an increase in the process severity in general causes an increase in the concentration of simple sugars in the hydrolysate. Interestingly, the estimated amount are higher than those reported in a previous work for Arundo Donax treated at similar process severity conditions [16][17].

In addition, the detected amount of degradation products (essentially furfural) was quite low, even at the highest severity values used. On the other hand, it must be considered that, due to the flow-through layout of the process, high dilution of the final products occurs when high water flowrate and/or high treatment time are used. Tests are currently in progress to check whether higher final concentration in the final hydrolysate can be achieved, without penalizing the selectivity in simple sugars and oligomers.

Negligible glucose concentrations were detected by HPLC, suggesting that the obtained simple sugars come only from hemicellulose dissolution. However, global mass balance suggests that hydrolysis phenomena involved also cellulose too. An additional indication of this fact could be represented by the significant peak of oligomers that was detected by HPLC analysis, but whose quantification is still in progress.

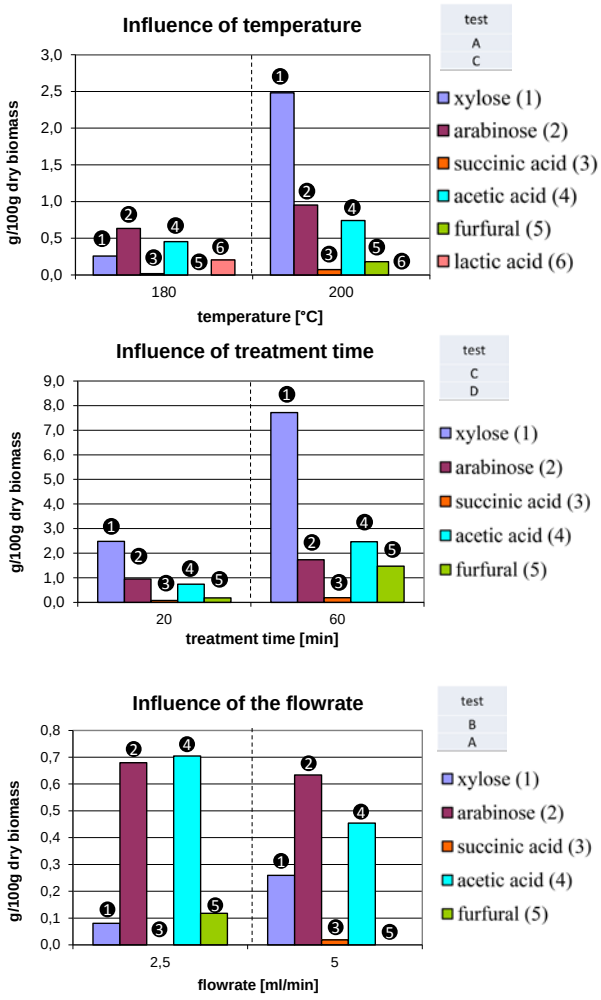

Figure 2: Influence of the three different parameters on the distribution of products in the hydrolysate.

4 CONCLUSIONS AND OUTLOOK

A lab-scale semi-continuous plant was assembled in order to be versatile in the execution of several kinds of lignocellulosic biomass pretreatment.

Preliminary tests were carried out using as initial process the LHW pretreatment of Arundo Donax and have given indication that by proper combination of temperature, flowrate and treatment time it is possible to modulate the concentration of hydrolysis products in the collected liquid samples.

Further research is ongoing to verify whether it is possible to obtain high selectivity in sugars with limited penalty in dilution of the collected liquid phase.

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6 REFERENCES

[1] B. Sluiter, R.O. Ruiz, C.J. Scarlata, A.D. Sluiter, D.W. Templeton, Compositional Analysis of Lignocellulosic Feedstrocks.1. Review and Description of Methods, J. Agric. Food Chem., (2010), 58, 16, pag.9043.

[2] U.S. Department of Energy – Energy and Renewable Energy - Alternative Fuels Data Center: Maps and Data, (2013).

[3] S. Fernando, S. Afhikari, C. Chandrapal, N. Murali, Biorefineries: Current Status, Challenges, and Future Direction, Energy and Fuels, (2006), 20, pag.1727.

[4] R.C. Brown, Biorenewable resources - Engineering new products from agriculture, Iowa State Press. Ames, (2003).

[5] D. Groff, A. George, N. Sun, N. Sathitsuksanoh, G. Bokinsky, B.A. Simmons, BM. Holmes, J.D. Keasling, Acid enhanced ionic liquid pretreatment of biomass, Green Chem., (2013), 15, pag. 1264.

[6] C. Ververis, K. Georghiou, N. Christodoulakis, P.Santas, R. Santas, Fiber dimensions, lignin and cellulose content of various plant materials and their suitability for paper production, Ind. Crop. Prod., (2004), 19, pag.245.

[7] C. Pronyk, G. Mazza, Kinetic Modeling of Hemicellulose Hydrolysis from Triticale Straw in a Pressurized Low Polarity Water Flow-Through Reactor, Ind. Eng. Chem. Res. (2010), 49, pag.6367.

[8] E. Pamqvist, B. Hahn-Hägerdal, Fermentation of lignocellulosic hydrolysates. II: inhibitors and mechanism of inhibition, Bioresour. Technol., (2000), 74, pag. 25.

[9] C. Liu, C. E. Wyman, The Effect of Flow Rate of Compressed Hot water on Xylan, Lignin, and Total Mass Removal from Corn Stover, Ind. Eng. Chem. Rees., (2003), 42, pag. 5409.

[10] T. Ingram, T. Rogalinski, V. Bockenmühl, G. antranikian, G. Brunner, J. Supercrit. Fluids, (2009), 48, pag. 238.

[11] J.E. Holladay, J.J. Bozell, J.F. White, D. Johnson, Top Value-Added Chemicals from Biomass Volume II—Results of Screening for Potential Candidates from Biorefinery Lignin, PNN, (2007), pag.16983.

[12] R.P. Overend, E. Chornet, Fractionation of lignocellulosics by steam-aqueouspretreatments, Phil. Trans. R. Soc. Lond., (1987), A321, pag. 523.

[13] H.L. Chum, D.K. Johnson, S.K. Black, R.P. Overend, Pretreatment-catalyst effects and the combined severity parameter, Appl. Biochem. Biotechnol., (1990), 24/25, pag.1.

[14] J.S. Luterbacher, Q. Chew, Y. Li, J.W. Tester, L.P. Walker, Producing concentrated solutions of monosaccharides using biphasic CO_2–H_2O mixtures, Energy Environ. Sci., (2012), 5, pag. 6990.

[15] A. Sluiter, B. Hames, R.Ruiz, C.Scarlata, J. Sluiter, D. Templeton, D. Crocker, Determination of Structural Carbohydrates and Lignin in Biomass – Laboratory Analytical Proedure, NREL, (2008).

[16] I. De Bari, Federico Liuzzi, Antonio Villone, Giacobbe Braccio, Hydrolysis of concentrated suspensions of steam pretreated Arundo donax, Appl. Energy, (2013),102, pag.179.

[17] S. Caparrós, G. Garrote, J. Ariza, M.J. Dí az, F. Ló pez, Xylooligosaccharides Production from Arundo donax, J. Agric. Food. Chem., (2007), 55, pag. 5536.