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Study of Different Bio-Processing Pathways in a Lignocellulosic Biorefinery by Process Simulation

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In the present study, different bio-transformation stages were simulated by Aspen Plus® for the obtaining of different bio-products (ethanol, lactic acid, xylitol and citric acid) from a pretreated lignocellulosic feedstock. For this purpose, experimental and literature data were used for proper design of involved treatments and operations. As common starting point of all the proposed bio-processing scenarios, the solid fraction resulted from the delignification pretreatment of the lignocellulosic feedstock was hydrolyzed, in order to dissolve lignocellulose and enhance bio-transformation of carbohydrates. The resulting fractions were subsequently treated with different microorganisms depending on the required final bio-product. Finally, separation and product recovery stages were simulated.

1. Introduction

The Biorefinery processes include different stages for biomass treatment, such as its fractionation or dissociation into its main constituent components (cellulose, hemicelluloses and lignin), and the transformation of these components into bio-fuels and bio-products. In general, and as many other industrial processes do, the biomass transformation requires several stages involving different processing and conversion steps. The bio-conversion of biomass uses microorganisms and enzymes in aerobic-anaerobic conditions to transform the biomass into biofuels (bio-ethanol, bio-butanol, etc) and chemical precursors (acids such as lactic, oxalic, citric, etc). In the present work four proposed bio-processing scenarios were techno-economically evaluated and compared, by using process simulation tools, in terms of product yield, energy-water requirement and chemicals demand, allowing the assessment of multiple approaches for the suitable and profitable exploitation of lignocellulosic biomass within the biorefinery concept.

2. Design of bio-conversion processes in Aspen Plus

Aspen Plus was used to design and simulate different carbohydrate transformation processes on the basis of experimental and literature data. A pretreated lignocellulosic material was used as feedstock for this purpose (45 % cellulose, 20 % hemicelluloses, 30 % lignin, 5 % acetate groups, in weith). Lignin, cellulose and hemicelluloses were defined by their chemical structure and physical properties, which were obtained from the National Renewable Energy Laboratory (NREL) database (Wooley and Putsche, 1996), whereas other conventional components were selected from the ASPEN PLUS data bank. The biological process was designed to evaluate the lignocellulose microbial transformation pathways considering only the most critical production parameters found in literature.

2.1 Hydrolysis and microorganisms culture steps

Different pathways for the biomass hydrolysis can be found in literature (Conde-Mejía et al., 2012), covering mild or strong acidic hydrolysis, as well as enzymatic treatments for the saccharification of cellulose to glucose (Barta et al., 2010).

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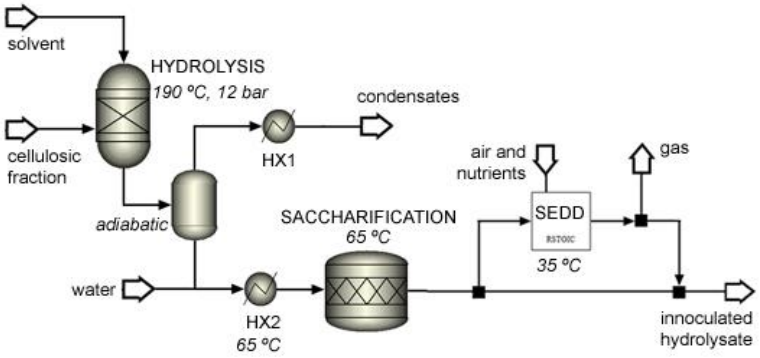

Figure 1: Flowsheet of the hydrolysis-saccharification-culture process. The values next to the reactions are the conversion factors; s: solid, d: dissolved

The chosen conditioning operations consisted of a hydrolysis step (190 °C, 12 bar) in which the cellulosic solid fraction was treated with aqueous acid (1% w/w of H_2SO_4), in a solid to liquid ratio of 1:6, in order to sterilize the stream and almost totally dissolve the contained hemicelluloses. The resulting flow was then expanded in a flash separator (1 bar) resulting in a slurry stream, containing the dissolved and solid lignocellulosic components and a vapour fraction that contained the furfural and acetic acid formed during hydrolysis process, respectively.
The slurry was then mixed with a water stream in order to adjust the total solid content of the flow to 30 ± 0.1% w/w (water flow calculated by DesignSpec). After temperature conditioning (up to 65 °C in HX2), the slurry was submitted to the saccharification unit in order to dissolve most of the contained cellulose into glucose. This treatment is usually enzymatically performed (Galbe and Zacchi, 1992). However, for its simulation no enzymatic load was considered. In Figure 1 the flowsheet of the described process and the occurred dissolving reactions and used conversion rates (Aden et al., 2002) are displayed.
After saccharification process, a portion of the resulted hydrolysate was treated in order to grow microorganism cells (Aden et al., 2002). The microorganism growth required carbon, nitrogen and oxygen sources. The carbon source was the sugar load contained in the hydrolysate. For the simulation, all hexoses were depicted as glucose ($C_6H_{12}O_6$) and pentoses were represented as xylose ($C_5H_{10}O_5$). The NH_3 was selected as nitrogen source, and the oxygen source was provided as an input stream of air in excess. The molecular formula of microorganisms was assumed as $CH_{1.8}O_{0.5}N_{0.2}$ (24.6264 g/mol), representing a bacterium form as described in the Aspen Plus physical property database (Wooley and Putsche, 1996). Thus, the microorganism growth was simulated according to stoichiometric coefficients, mathematically determined on the basis of 1 mol of substrate, taking into account the C, H, O y N balances and assuming a microorganism growth mass yield of 0.5 g microorganism/g substrate.

$$C_6H_{12}O_6 + a\ NH_3 + b\ O_2 \rightarrow c\ CH_{1.8}O_{0.5}N_{0.2} + d\ CO_2 + e\ H_2O \quad (1)$$

Analogously, when xylose was used as substrate the balanced molar stoichiometric reaction resulted:

$$C_5H_{10}O_5 + a\ NH_3 + b\ O_2 \rightarrow c\ CH_{1.8}O_{0.5}N_{0.2} + d\ CO_2 + e\ H_2O \quad (2)$$

These reactions were exothermic and a reaction heat of 187,300 kJ/kmol was considered (reference conditions 25 °C, 1 bar, liquid phase). In this way, the bioreactor (SEED, RStoic module) operated at 35 °C and 1 bar. The amount of hydrolysate used as growing broth was calculated by using the DesignSpec tool of Aspen Plus, in order to fulfil the requirement of a 0.3 ± 0.01 % w/w of microorganisms in the final inoculated hydrolysate.

2.2 Carbohydrate bio-transformation processes
Four different transformation processes, extensively experimentally studied, were designed and simulated with Aspen Plus (Galbe and Zacchi, 1992) on the basis of different literature data (Barta et al., 2010).

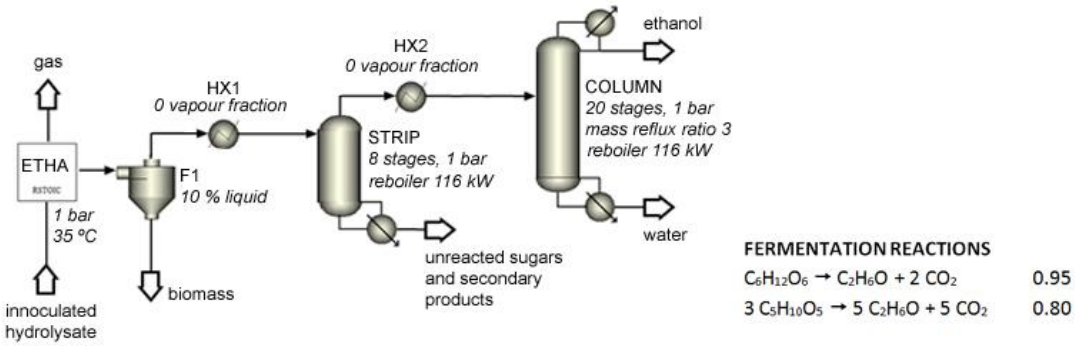

Figure 2: Flowsheet of the ethanol production process. The values next to the reactions are the conversion factors

The designed **ethanol production process** started with the transformation in the ETHA fermentor into ethanol of the sugars contained in the hydrolysate inoculated in the previous microbial culture step (see Figure 2). After separation of undissolved lignocellulose and grown cell, the fermentation liquid was treated for the recovery of the produced ethanol. The resulting liquid fraction, containing 20-30 % w/w of ethanol, was heated up to its boiling point and subsequently distillated in a stripping column (STRIP). Most of the ethanol was recovered as overhead vapour (with 60-70 % w/w of water vapour), which was then condensed in a second heat exchanger (HX2) before the rectification operation (COLUMN). The obtained distillate contained up to 92 % w/w ethanol. As bottom products from both distillation columns, an aqueous sugar-enriched stream (from STRIP) and a stream containing more than 99 % w/w of water (from COLUMN) were obtained.

The proposed **xylitol production process** began with a fermentation unit similar to the one used for the ethanol production (see Figure 3). After the solid-liquid separation (in F1), the fermentation liquid was conducted to the xylitol recovery process. The xylitol was recovered by evaporation of the fermentation liquid followed by a crystalization step (De Faveri et al., 2002). Thus, the liquid was first heated by using low pressure steam in the EX1 heat exchanger and then adiabatically expanded in order to recover the products at 50 °C (avoiding xylitol degradation). This evaporation operation unit was controlled by a DesignSpec, acting under the required low pressure stream in order to reach a 50 % of solids in the concentrate. The concentrated stream was conditioned to 25 °C and then the water was removed in the CRYS module.

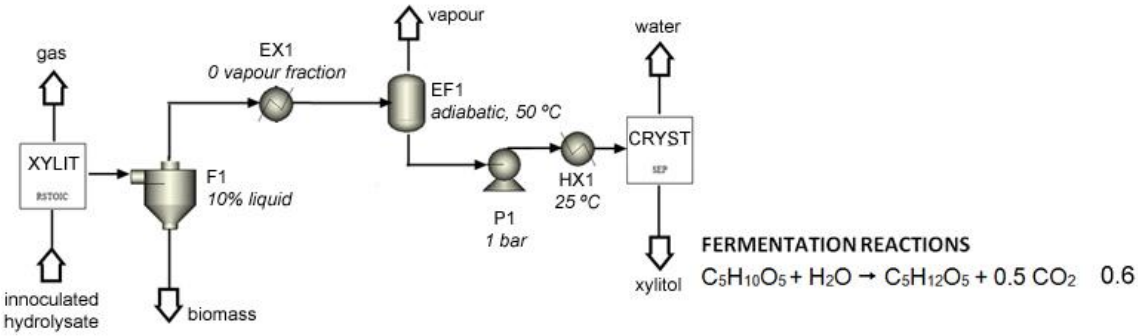

Figure 3: Flowsheet of the xylitol production process. The value next to the reactions is the conversion factor

The citric acid production process was designed for the transformation of C6 and C5 sugars (see Figure 4). After the separation of the fermentation liquid, this fraction was treated with calcium hydroxide in order to precipitate the produced citric acid as calcium citrate. This compound was defined in Aspen Plus according to its molecular formula $Ca_3(C_6H_5O_7)_2$ with the properties of gypsum, which is defined in the NREL database (Wooley and Putsche, 1996). A DesignSpec was used for the calculation of the 15:85 w/w lime-water stream (common industrial conditions). The produced citrate was then separated by filtration and subsequently washed in a two-steps operation. A DesignSpec was defined to control the amount of water necessary to achieve a solid content less than 1 % w/w in the liquid part. In the DISOL equipment,

the acidification of this slurry was carried out in order to obtain citric acid in solution and to remove the calcium salt. For this purpose, an aqueous H2SO4 stream (15:85 w/w sulphuric acid-water) was added (calculated by DesignSpec). The calcium sulphate formed was separated by filtration and the citric acetic containing liquid was submitted to the vacuum evaporation step (EX1 and EF1 equipments) for the obtaining of a concentrate stream with 50 % w/w of solids at 40 °C. Finally, the concentrated stream was crystallized at 25 °C (HX2 and CRYS equipments), removing all the contained water and obtaining a solid citric acid-enriched stream.

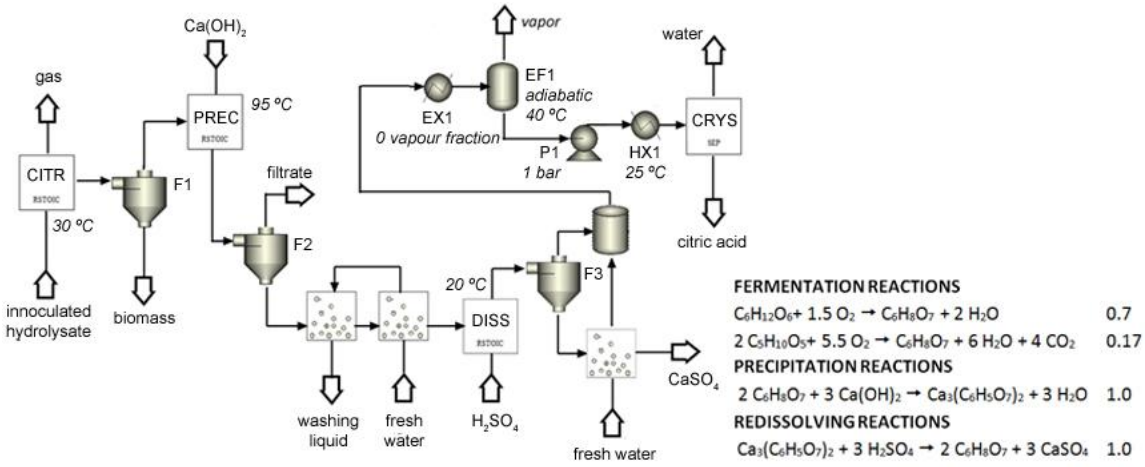

Figure 4: Flowsheet of the citric acid production process. The values next to the reactions are the conversion factors

The proposed **lactic acid production process** started in the fermentor LACT, where glucose and xylose were transformed into lactic acid (see Figure 5). The formed lactic acid was precipitated from the fermentation liquid as calcium lactate in the block PREC. Similarly to the above described citric acid production process, $Ca(OH)_2$ was added in aqueous form (in a ratio lime-water of 15:85 w/w). The recovery of the produced lactic acid was carried out by the same method designed for the citric acid recovery. A low temperature evaporation process was conducted for the obtaining of a 50 % concentrated stream (low pressure stream controlled by DesignSpec) that was subsequently crystallized.

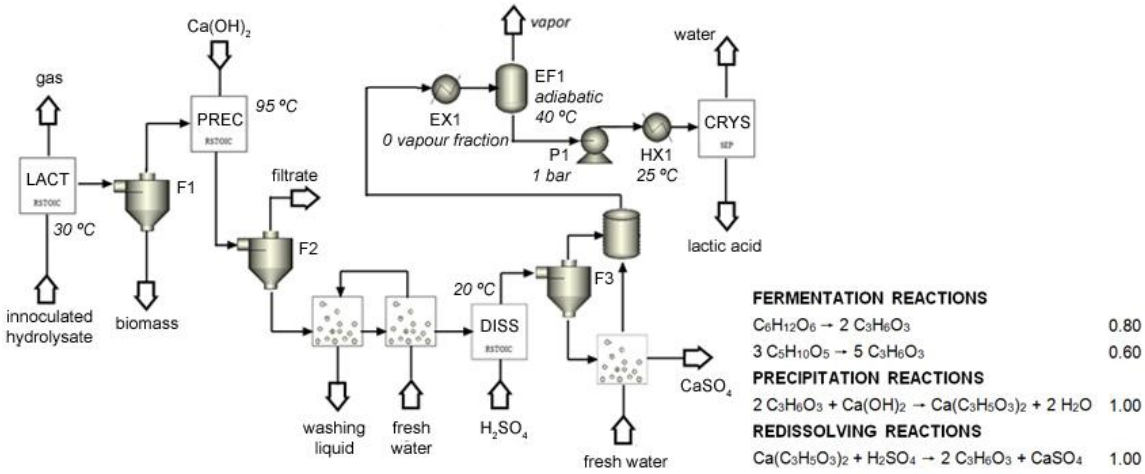

Figure 5: Flowsheet of the lactic acid production process. The values next to the reactions are the conversion factors

3. Results and discussion

3.1 Dissolution of lignocellulose and inoculation of the resulting hydrolysate

In the first hydrolysis step, the lignocellulosic feedstock was treated with weak acid at high temperature, consuming 4,633 kW for heating. As a result of the expansion of the produced slurry, a flash vapour was obtained (6,413 kg/h) containing 98.9 % of the furfural, 98.8 % of the acetic acid and 20.1 % of the HMF produced during the hydrolysis of the raw material due to dissolution and degradation mechanisms. The condensation of this vapour stream required 4,063 kW of cooling utility. In order to maintain the solid concentration of the slurry stream at 30% w/w, 181 kg/h of water were added before temperature conditioning of the slurry (to 65 °C, consuming only 4 kW for the cooling of the stream). During the subsequent saccharification process, about 95% of the cellulose was dissolved into glucose, requiring less than 1 kW of heat to keep the operation at constant temperature. From the slurry stream obtained at the previous hydrolysis/saccharification process, 71 kg/h of the liquid substream were derived to the SEED module in order to obtain an inoculum and, therefore, to achieve a microorganism cell contain of 0.3 % w/w in the culture, which would be sent to the subsequent biological transformation operations (total inoculated stream of 753 kg/h, 2263 kW, 35 °C, 1 bar). In this way, 12.1 % of glucose and xylose were consumed during this process, in aerobic conditions (air in excess) and 8 kW of cooling utility were required in order to keep the microbial growth at 35 °C.

3.2 Bioproducts production processes

The simulation of the different proposed bioproducts production processes allowed the determination of the associated mass balances in order to evaluate chemicals and water requirements as well as generation of products and wastes streams.

As displayed in Figure 6, citric and lactic production processes required of different amounts of washing water and chemicals (sulphuric acid and lime), with the subsequent generation of solid waste stream (calcium sulphate) and liquid waste streams (filtrates and washing liquids). Except for ethanol production process, condensate vapours and water streams were generated in the recovery steps of the simulated bioprocesses (evaporation and crystallization, respectively). All the simulated processes generated a sub-stream of biomass, containing undissolved lignocellulosic material and the grown microorganisms' cells. Moreover, in the ethanol production process two waste streams were obtained from the two-step distillation process: one as residue of the strip column (containing 8 % w/w of unfermented sugars) and other aqueous one obtained from the rectification column.

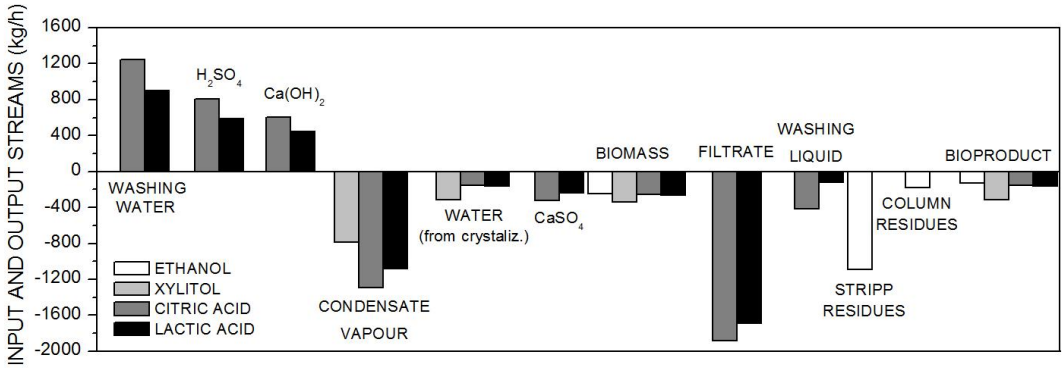

Figure 6: Mass balance results for the different simulated bioprocesses

The generation in the simulated ethanol, xylitol, citric and lactic acid production processes resulted in 133, 310, 157 and 162 kg/h of bioproduct outputs. However, the designed production and recovery processes led to different purity of these streams (92.5, 14.3, 94.3 and 94.1 % w/w) and, therefore, to different bioproduct yields (0.25, 0.09, 0.30 and 0.31 kg of product by kg of cellulosic feedstock), mainly due to the different substrates (C5 or C6 sugars) consumed in each bioprocess. In the specific case of ethanol production, the production yield resulted slightly higher than the obtained in other works (Porzio et al., 2011).

The developed simulations also allowed to evaluate energy balances for each bioprocess (see Figure 7). Citric and lactic acid production processes appeared to be those that more cooling and heating utilities required (961-893 kW and 655-763 kW, respectively). However, according to the amount of bioproduct generated in each simulated process, the xylitol production process resulted to be the most energy

extensive (requiring 11.0 and 12.2 kW of cooling and heating utilities per generated kg of xylitol, respectively), followed by the lactic and citric production processes (4.3 and 6.5 kW of cooling utility/kg of bioproduct, 5.0 and 6.0 kW of heating utility/kg of bioproduct, respectively). In this sense, the ethanol production process resulted in the most energetically profitable, requiring 2.6 and 3.0 kW of cooling and heating utilities per produced kg of ethanol.

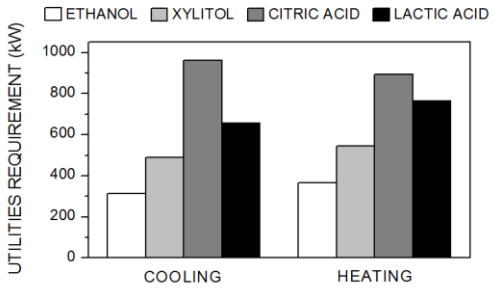

Figure 7: Energy balance results for the different simulated bioprocesses

4. Conclusions

In the present work different bioprocesses were designed and simulated for the evaluation of bioproducts from pretreated lignocellulosic materials. Ethanol, xylitol, citric acid and lactic acid obtaining processes were evaluated, resulting in yields of 0.25, 0.09, 0.30 and 0.31 kg of product by kg of cellulosic feedstock, respectively. Furthermore, the resulted mass and energy balances allowed assessing chemicals and water consumptions as well as energy requirements. In this regard, xylitol production process did not appear as an attractive biorefinery step, probably because a feedstock with higher xylose concentration would be required. An alternative to make these bio-transformation processes more effective might be the recycle of produced water streams and the reuse of carbohydrate-enriched liquid fractions resulted from previous biorefinery steps, increasing the bioproduct yields and minimizing water requirements.

Acknowledgements

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References

Aden A., Ruth M., Ibsen K., Jechura J., Neeves K., Sheehan J., Wallace B., Mongague L., Slayton A., Lukas J., 2002, Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL/TP-510-32438, National Renewable Energy Laboratory, Golden, Colorado, USA.

Barta Z., Kovacs K., Reczey K., Zacchi G., 2010a, Process Design and Economics of On-Site Cellulase Production on Various Carbon Sources in a Softwood-Based Ethanol Plant, Enzyme Research 2010, 3:21 doi: 10.1186/1754-6834-3-21.

Conde-Mejía C., Jiménez-Gutiérrez A., El-Halwagi M., 2012, A Comparison of Pretreatment Methods for Bioethanol Production from Lignocellulosic Materials, Process Safety and Environmental Protection 90, 189-202.

De Faveri D., Perego P., Converti A., Del Borghi M., 2002, Xylitol Recovery by Crystallization from Synthetic Solutions and Fermented Hemicellulose Hydrolyzates, Chemical Engineering Journal 90, 291-298.

Galbe M., Zacchi G., 1992, Simulation of Ethanol Production Processes Based on Enzymatic Hydrolysis of Lignocellulosic Materials Using Aspen Plus, Applied Biochemistry and Biotechnology 34, 93-104.

Porzio G.F., Prussi M., Chiaramonti D., 2011, Process Analysis and Modelling for 2nd Generation Lignocellulosic Bioethanol Production, Chemical Engineering Transactions 25, 869-874.

Wooley R.J., Putsche V., 1996, Development of an ASPEN PLUS Physical Property Database for Biofuels Components. NREL/MP-425-20685, National Renewable Energy Laboratory, Golden, Colorado, USA.