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Intensification of the 2G Bioethanol Production Process

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The main objective of the present study is to propose a methodology to evaluate alternatives for the synthesis of the second-generation bioethanol production process from lignocellulosic feedstock, in order to reduce amount of waste, energy consumption and production costs. The methodology is based on modelling, synthesis, design and simulation, where the heat integration in the 2G bioethanol production process is a key tool to evaluate the process in technical, economic and environmental terms. As a case study, wheat straw is considered as raw material, and the simulations are performed using a modular process simulator. For the assessment and comparison of the biorefinery alternatives, the selected evaluation criteria are ethanol yield, unit production cost, energy consumption, CO_2 emissions and water consumption. The results show the best process alternatives that can lead to greater sustainable ethanol production, supporting better decision making in the synthesis and design of biorefineries.

1. Introduction

First-generation (1G) biofuels can be produced from crops; however, they are competitive with the production of food for humans and cause environmental damage. Therefore, research has focused on second-generation (2G) and third-generation (3G) biofuels, whose raw materials are generally not food crops (e.g. agro-industrial wastes) and microalgae, respectively; and both of them are environmentally friendly (Lakatos et al., 2019).
Recently in Process Systems Engineering, process intensification techniques are being developed and implemented to: obtain safer processes with greater equipment efficiency, reduce their size and operating costs, incorporate retrofitting, consume a minimum of energy, generate the least possible amount of waste and obtain as many products with the least possible amount of raw material (Vaghari et al., 2015). Under this perspective, the 2G ethanol production process has not been extensively investigated. Generally, the reported studies on the design of 2G ethanol production plants have focused on the determination of efficient pretreatments for lignin removal, the improvement of enzymes and strains to increase the efficiency of the saccharification and fermentation stages, respectively; and the recovery of waste such as fermentation residues (Kumar et al., 2016). However, to achieve sustainable designs, it is necessary to analyse aspects of energy integration, waste management and its environmental impact. Hence, the objective of this work is to propose a methodology to evaluate alternatives for the synthesis of the 2G bioethanol production process from agro-industrial wastes (i.e., lignocellulosic raw material), with the incorporation of different processing technologies, to obtain data that support the eligibility of a sequence of most appropriate operation in technical, economic and environmental terms.
The methodology is based on modelling, synthesis, design and simulation, where the heat integration (Gonzalez-Contreras et al., 2017) in the 2G bioethanol production process is a key tool to evaluate the process in technical, economic and environmental terms. Detailed process flow diagrams are used with various alternatives for the 2G ethanol production plant: (a) the first option corresponds to a standard design (Sanchez et al., 2016) that includes traditional technologies for the pretreatment, saccharification, fermentation, separation and purification, and additionally options for wastewater treatment and energy cogeneration; and (b) other alternatives consider for two different modules for pretreatment (dilute acid

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process or steam explosion) and two different modules for the purification of anhydrous ethanol (molecular sieves or extractive distillation). These alternatives have been selected since they are two bottleneck processes with direct effect on the final bioethanol yield and further economic competitiveness of the process. On one hand, pretreatment processes of lignocellulosic biomass plays an important role in the productivity and performance of saccharification and fermentation (da Silva et al., 2017), and in the other hand, dehydration of ethanol determines the quality of the final product to be use as a fuel (Lara-Montaño et al., 2019).
The proposed methodology is shown with a case study, where wheat straw is considered as raw material. Simulations of the different design alternatives are made using a modular process simulator (*SuperPro Designer*) and process alternatives are compared by evaluating technical, economic and environmental criteria (such as overall ethanol yield, unit production cost, CO_2 emission, overall energy required and water consumption). The results show the process alternatives that can lead to greater sustainable ethanol production, supporting better decision-making in the synthesis and design of biorefineries and pointing to where research should be directed to obtain integrated and intensified processes.

2. Methodology

2.1 Biorefinery conceptual design

The conceptual design of the 2G ethanol biorefinery is shown in Figure 1, which consists of five main section: pretreatment, saccharification, fermentation, separation and purification. First, the lignocellulosic raw material is conditioned (triturated and soaked) and then is fed to the pretreatment section, which will be briefly described in next subsection. Subsequently, separate saccharification and fermentation are used to convert the biomass into sugars (mainly glucose and xylose) and then into ethanol. Saccharification is carried out by hydrolysis using cellulase enzymes, while sugar fermentation is carried using *Zymomonas mobilis*. The fermentation broth (that contains around 3.5% w/w) is sent to the separation section, where two distillation columns are used to concentrate the ethanol near its azeotropic point. The first beer column separates the fermentation broth in two main streams: the distillate stream that is mainly composed of diluted ethanol beer (around 30% w/w) and the bottom stream that contains unconverted biomass, inorganic impurities and water. The bottom stream is centrifuged, so that the solids are sent to the cogeneration section (where heat and electricity are produced by the solid combustion), and the centrifuged liquid is sent to the wastewater treatment section (where the recovered water is recycled back to the process). The distillate stream is then sent to the second (rectifying) column where the overhead contains concentrated ethanol (around 90% w/w of ethanol). Finally, the distillate product from the rectifying column is sent to the purification section for the ethanol dehydration, which will be briefly described in next subsection, to reach the fuel grade category (99.98% w/w of ethanol). The bottom stream from the rectifying column contains pure water that is also recycled back to the process.

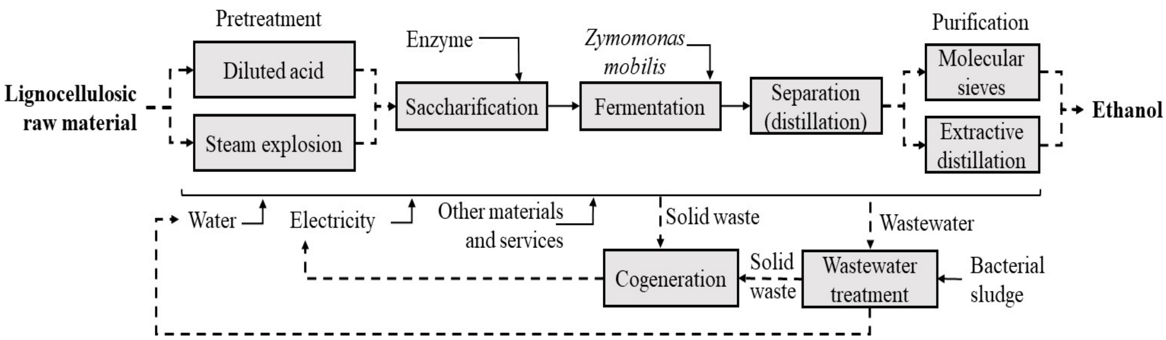

Figure 1: Conceptual design for the production process of 2G bioethanol.

2.2 Process design alternatives

The main objective of pretreatments is to break the lignin structure and interrupt the crystalline structure of cellulose to improve the accessibility of enzymes to cellulose during the saccharification stage. There are many types of pretreatments, such as physical, chemical, physicochemical and biological processes. The two most efficient pretreatments reported in literature (Kumar et al., 2016) have been selected in this work:

(a) Dilute acid pretreatment (DAP) is a chemical process (see Figure 2), performed with dilute sulphuric acid at 190°C. Once the reaction is over, the hydrolysate mixture is separated using a filter. The solids are sent to the saccharification section, and the liquid hydrolysate is neutralised followed by a reacidification to adjust the pH. The liquid stream is also sent to the saccharification section.

(b) Steam explosion pretreatment (SEP) is a physicochemical process (see Figure 3), which is modelled assuming a steam explosion unit that uses high pressure steam at 200°C. Subsequently, the material is expanded adiabatically to atmospheric pressure in a flash unit. Then, the hydrolysed biomass is sent to the saccharification section.

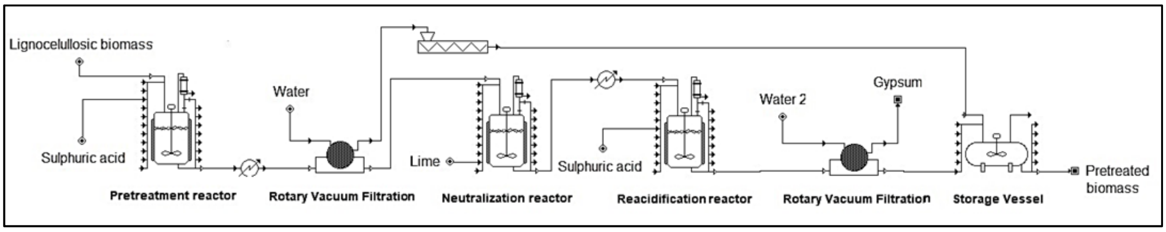

Figure 2: Flowsheet for the dilute acid pretreatment (DAP).

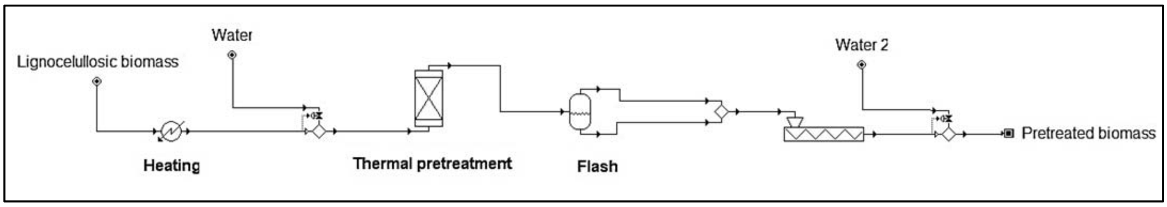

Figure 3: Flowsheet for the steam explosion pretreatment (SEP).

With regard to the purification section of ethanol, it is important to keep in mind that obtaining anhydrous ethanol is not a simple process since it requires the separation of the azeotropic ethanol-water mixture. For this purpose, there are different processes of ethanol dehydration, among which are: vacuum distillation, azeotropic distillation, extractive distillation, adsorption with molecular sieves, pervaporation, and hybrid processes. It has been reported that lower energy consumption has been achieved with molecular sieve and distillation technologies extractive (Gil et al., 2008). Therefore, these two ethanol dehydration processes have been selected:

(a) Adsorption with molecular sieves (AMS) (see Figure 4) uses a bed of zeolite in which water molecules are strongly retained within the pores, while ethanol molecules pass through the bed (because the water molecules have a diameter of 2.8 Å and the pores of 3 Å, while the ethanol molecules have a diameter of 4.4 Å). The process consists of combined cycles of ethanol dehydration and molecular sieve regeneration. For the regeneration of the bed, a hot inert gas is passed to remove the accumulated moisture. The final product reaches an ethanol purity of 99.98% w/w.

(b) In the extractive distillation with solvents (EDS) (see Figure 5), a separation agent that does not form azeotropes with water or with ethanol is added. In this work, glycerol is used as solvent, since it has recently been tested experimentally successfully (Lara-Montaño et al., 2019). The conventional process consists of two columns, but other intensified configurations could be implemented (Errico and Rong, 2012). In the first extractive column, the distillate from the rectifying column (from the separation section) and glycerol are fed. Dehydrated ethanol (with a purity of 99.98%) is obtained as a distillate and the solvent-water mixture obtained as bottom stream is transferred to a second solvent recovery column. The solvent is recovered in the bottom stream, cooled and recycled back to the first extractive column. Additionally, a stream of pure water is obtained as distillate, which is recycled into the process.

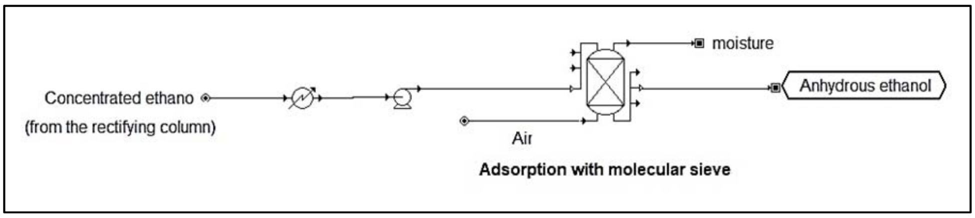

Figure 4: Flowsheet for the adsorption with molecular sieves (AMS).

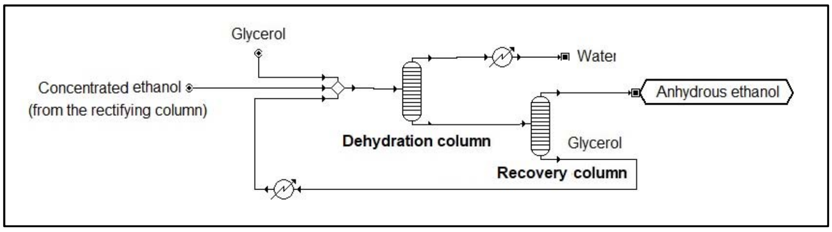

Figure 5: Flowsheet for the extractive distillation with a solvent (EDS).

It is important to note that, to our knowledge, the study of pretreatment technologies has been carried out independently of purification technologies. Therefore, the objective of this work is to analyse the effect of the synthesis of a 2G ethanol biorefinery, considering the following case studies that include the sections described in Figure 1 and the indicated pretreatment/purification alternatives:

- Case 1: DAP – AMS
- Case 2: SEP – AMS
- Case 3: DAP - EDS
- Case 4: SEP - EDS

2.3 Process evaluation

First, mass and energy balances are evaluated using *SuperPro Designer* commercial software, which is a modular process simulator that includes databases for component properties, equipment, resources, costs, unit operation models, kinetic models, thermodynamic models, etc. Then, the Pinch method for heat integration is implemented, in order to reduce the input of external energy and reduce operating costs. Afterwards, for comparative purposes of the case studies, various parameters are evaluated. The ethanol yield (*Y*, L ethanol / kg raw material) is calculated as a technical criterion. As economic criteria, the unit production cost (UPC) of ethanol that includes the discount for the credits of the electricity production in the cogeneration section, and the net unit production cost (NUPC) that includes the deduction due to the energy integration according the pinch analysis are calculated using the net present value method equal to zero (NPV = 0). As an energy criterion, the total energy consumption (TEC) is calculated taking into account the demand and generation of both electrical and thermal energies. In addition, as environmental criteria, CO2 emissions (ECO2) and freshwater consumption (FWC) are calculated. The first is obtained from the fermentation reactions and from combustion in the energy cogeneration section, while the latter takes into account the required process water less the treated water recovered and recycled to the process.

3. Simulation Results

In the present study, wheat straw was used as lignocellulosic biomass, which has a dry-based composition (w/w) of 48.4% cellulose, 18.3% hemicellulose, 6.5% lignin and 26.8% inert solids. The plant capacity was designed for processing 330 t/y of dry biomass, producing between 73.5-78.4 million L/y of ethanol (depending on the case study).
For the economic analysis, the following parameters were taken into account: all costs (of raw materials, products, consumables, labour, equipment and services) in US dollars, an annual production time of 330 days, a depreciation of 15-year term and 30% business tax. As mentioned earlier, UPC is calculated using the VPN = 0 method and without considering heat integration. Then, the pinch analysis is performed and the energy requirements are adjusted, so that the NUPC is reduced as shown in Figure 6. As it can be seen, the values of

NUPC for all case studies are smaller than UPC. Which means that the heat integration in the process is decisive for the profitability of the biorefinery.

The techno-economic-environmental assessment is summarised in Table 1. The ethanol production differs slightly for each case study, due to the efficiency of each technology selected for pretreatment and purification. As a result, the ethanol yields are slightly higher for Cases 2 and 4, which can be attributed to the good reaction conversions of the SEP process. Regarding the cost of operation, similar values are obtained for cases 1 and 3, as well as for cases 2 and 4. Achieving the highest capital returns for cases 2 and 4, indicating indicates that the AMS and EDS processes have similar costs of operation, while the SEP process is more profitable than the DAP process. The TEC values do not show a favourable systematic trend towards a particular technology. Case 4 requires the lowest TEC, followed by Case 1, and both cases use different pretreatments and different dehydration processes as well. This indicates that energy balances and heat integration are compensated in a different way for each case. Regarding the FWC, this is significantly lower for Case 1 and Case 3, which means that the DAP process is more environmentally friendly. Finally, CO_2 emissions are very similar for the four cases, although they are slightly lower for Cases 2 and 4 that correspond to the processes that use SEP.

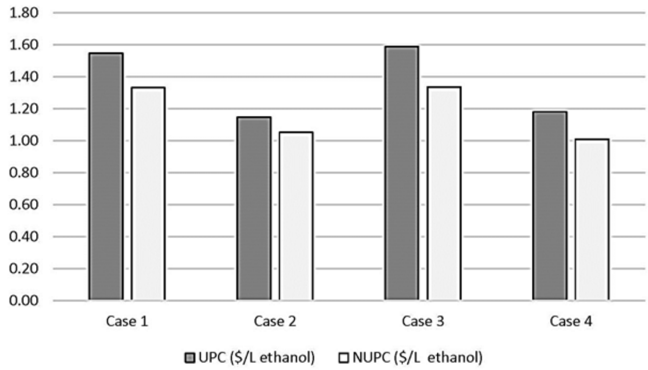

Figure 6: Comparison of the unit production cost of ethanol without heat integration (UPC) and with heat integration (NUPC).

In general, the results in Table 1 show that the selection of the ethanol purification process (either AMS or EDS) is not significant for the sustainability of 2G ethanol production, which is in accordance with some reports (Gil et al., 2008). Although the technical-economic criteria (ethanol production, Y and NUPC) and an environmental criterion (E_{CO2}) were favourable for the SEP process, the other two criteria (TEC and FWC) were not. For comparative purposes, the values of 1/Y, NUPC, TEC, FWC, and ECO2 were standardised taking as reference the highest value of each case study. These values are required to be as small as possible for a sustainable process. Figure 7 shows the comparison of these standardised parameters, where it is observed that the best cases correspond to Cases 1 and 3. This allows us to conclude that if the same evaluation weight is given to all the technical, economic, energy and environmental parameters, then the best pretreatment would be DAP and there was no distinction between the AMS and EDS separation processes.

Table 1: Criteria for technical, economic and environmental assessment.

Parameter	Case 1: DAP – AMS	Case 2: SEP – AMS	Case 3: DAP - EDS	Case 4: SEP - EDS
Ethanol production (t/y)	73.68	78.35	73.50	78.26
Y (L ethanol /kg wheat straw)	0.22	0.24	0.22	0.24
NUPC ($/L ethanol)	1.33	1.05	1.34	1.01
TEC (kW-h/L ethanol)	6.46	10.34	7.39	5.24
FWC (L H_2O/L ethanol)	10.15	25.15	10.07	25.09
E_{CO2} (kg CO_2/L ethanol)	3.66	3.36	3.67	3.36

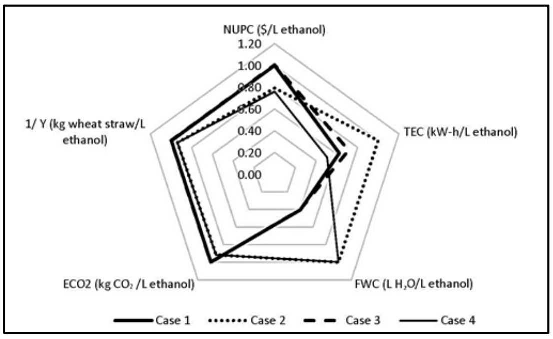

Figure 7: Comparison of standardized evaluation criteria for the case studies.

4. Conclusions

The intensification of the 2G ethanol production process was studied by evaluating alternatives for the synthesis of the process, taking into account different pretreatment and purification technologies, the net energy consumption, the operating costs, the heat integration and the waste reduction using wastewater treatment and electricity cogeneration. To sum up, several aspects were identified: (i) the heat integration is a decisive step for the profitability of the biorefinery, (ii) the extractive distillation and the adsorption with molecular sieves were equally competitive and sustainable, (iii) the steam explosion pretreatment was better than dilute acid pretreatment if only technical-economic criteria are taken into account, but (iv) dilute acid pretreatment is better than steam explosion pretreatment when all technical-economic-energy-environmental criteria are considered. Of course, there are still other issues that could be studied to increase the sustainability of the biorefinery, such as simultaneous saccharification and fermentation, the lignin recovery from the solid residue, the use of xylose for other secondary products (such as xylitol), the possible capture, purification and reuse of CO_2, among others.

Acknowledgments

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References

Da Silva R.G.A., Errico M., Rong B.G., 2017, Process alternatives for bioethanol production from organosolv pretreatment using lignocellulosic biomass, Chemical Engineering Transactions, 57, 1-6.
Errico M., Rong B.G., 2012, Synthesis of new separation processes for bioethanol production by extractive distillation, Separation and Purification Technology, 96, 58-67.
Gil I. D., Uyazán A. M., Aguilar J. L., Rodríguez G., Caicedo L. A., 2008, Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: process simulation, Brazilian Journal of Chemical Engineering, 25(1), 207-215.
Gonzalez-Contreras M., Sanchez A., Lopez-Arenas T., 2017, Heat integration for the production process of 2G bioethanol from wheat straw, Computer Aided Chemical Engineering, 40, 2917-2922.
Kumar R., Tabatabaei M., Karimi K., Sárvári Horváth I., 2016, Recent updates on lignocellulosic biomass derived ethanol - A review, Biofuel Research Journal, 9, 347-356.
Lakatos G.E., Ranglová K., Manoel J.C., Grivalský T., Kopecký J., Masojídek J., 2019, Bioethanol production from microalgae polysaccharides, Folia Microbiologica, 64, 627–644.
Lara-Montano O.D., Melendez-Hernandez P.A., Bautista-Ortega R.Y., Hernandez S., Amaya-Delgado L., Hernandez-Escoto H., 2019, Experimental Study on the Extractive Distillation Based Purification of second Generation Bioethanol, Chemical Engineering Transactions, 74, 67-72.
Sanchez A., Magaña G., Partida M. I., Sanchez S., 2016, Bi-dimensional sustainability analysis of a muti-feed biorefinery design for biofuels co-production from lignocellulosic residues, Chemical Engineering Research and Design, 107, 195-217.
Vaghari H., Eskandari M., Sobhani V., Berenjian A., Song Y., Jafarizadeh-Malmiri H., 2015, Process Intensification for Production and Recovery of Biological Products, American Journal of Biochemistry and Biotechnology, 11, 37-43.