Accepted Manuscript

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PII: S2589-014X(18)30080-X
DOI: doi:10.1016/j.biteb.2018.08.015
Reference: BITEB 86
To appear in: Bioresource Technology Reports

Received date: 6 June 2018
Revised date: 11 August 2018
Accepted date: 17 August 2018

Please cite this article as: André Rodrigues Gurgel da Silva, Massimiliano Errico, Ben-Guang Rong, Systematic procedure and framework for synthesis and evaluation of bioethanol production processes from lignocellulosic biomass. Biteb (2018), doi:10.1016/j.biteb.2018.08.015

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Systematic procedure and framework for synthesis and evaluation of bioethanol production processes from lignocellulosic biomass

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Abstract

Bioethanol from lignocellulosic feedstock rises as a promising alternative to replace liquid fossil fuels in the energy market for the next years. However, the variety of available biomass combined with the necessity of possible pretreatments and their particular features make it difficult to clearly identify the favorable process routes. In this study a systematic approach consisting of seven steps was proposed to obtain possible and feasible alternatives for the conversion of lignocellulosic biomass into bioethanol. The method was exemplified with the aid of a general case study, from the biomass selection to possible by-products generation. The case study resulted in a corn stover based process to produce bioethanol through ammonia fiber explosion pretreatment. Following the systematic approach different alternatives were proposed to finally obtain the optimal flowsheet with a minimum ethanol selling price of 0.43$/kg of ethanol, 35.4% lower than the initial process.

Keywords: Bioethanol, Lignocellulosic Biomass, Process Synthesis, Process integration,

Systematic procedure

1. Introduction

The biomass produced each year could generate about 161 EJ (10^18 J) of energy considering a “food first” approach (Haberl et al., 2011). This value corresponds to 28.6% of our present energy intake and, currently, the renewable bioenergy share is merely 0.89% (Schiffer, 2016). This space for improvement can help reduce the greenhouse gas emissions and limit the global warming. Devoid
of competition from food crops, second generation bioethanol from lignocellulosic biomass emerges as an interesting option to replace gasoline in the transportation fuel sector. Lignocellulosic bioethanol can be produced from different types of feedstock, from forestry and agricultural residues, to energy crops and municipal solid wastes. However, the use of renewable feedstocks to produce fuels faces a difficult challenge: the sugars present in the lignocellulosic biomass are protected by a recalcitrant structure that needs to be surpassed for the process to be technically and economically feasible. In order for an effective conversion of the raw material into bioethanol, a pretreatment step is necessary to break the lignin-carbohydrate sheath that prevents the microorganisms from accessing the cellulose and hemicellulose molecules. An efficient pretreatment should provide high yields of the fermentable sugars while not generating process’ inhibitors, avoid the high usage of chemicals, prevent the usage of expensive materials in the reactors and keep the heat and power requirements low (Wyman et al., 2005a). Therefore, several pretreatments have been studied, and can be divided in four categories: physical, physico-chemical, chemical, and biological pretreatments according to their mechanism of action.

Physical pretreatment relies on sheer strength and energy to disrupt the lignin barrier and make the sugars available for conversion. Hideno et al. (2009) compared the effects of wet disk milling and ball milling on glucose and xylose yields. Wet disk milling resulted in 78.5% and 41.5% of glucose and xylose conversion, respectively, whereas ball milling yielded 89.4% of glucose and 54.3% of xylose. However, more interestingly, Hideno et al. (2009) observed that starting from around 50% of glucose yields, every increment of 10% in the yield doubled the amount of energy required in the system. To reduce the energy demand in the process, catalysts can be added, introducing a new layer of possible changes in the biomass due to ensuing chemical reactions. The main exponents of the physico-chemical pretreatments are ammonia fiber explosion (AFEX) and catalyzed steam explosion pretreatments. Teymouri et al. (2005) achieved more than 90% of fermentable sugars conversion when treating corn stover with AFEX at 90 °C, whereas Tucker et al. (2003) obtained
similar results employing sulfuric acid catalyzed steam explosion at 190 °C. So far, the promising leading pretreatment technologies require the addition of one or more chemicals, such as dilute acid pretreatment and alkali pretreatment (Wyman, 1996; Barakat et al., 2014). Ballesteros et al. (2008) investigated the effect of temperature, sulfuric acid concentration and solid-liquid ratio on sugar yield for *Cyanara cardunculus*, and concluded that only the temperature and acid concentration influenced the final yield of the process. Chang et al. (1998) showed in his experiments that lime pretreatment increased by tenfold the enzymatic digestibility of herbaceous feedstocks, however the same was not observed on woody biomass due to the high lignin content. To remove part of the lignin from the biomass, organic solvents, such as ethanol and glycerol, can be employed. For instance, Romaní et al. (2013) achieved 64.3% of *Eucalyptus* wood delignification after 70 minutes of pretreatment at 200 °C using glycerol as the solvent in the process, whereas Brosse et al. (2009) recovered 71% of the ethanol organosolv lignin (EOL) from *Miscanthus x giganteous* using ethanol at 170 °C. Biological pretreatment can also be applied to remove the lignin from the biomass without further addition of chemicals. Wan and Li (2010) obtained 31.6% of corn stover delignification and 94% of cellulose conversion, however, the pretreatment required a total of 18 days to complete. The long time necessary for the process, the large space requirement and the constant monitoring of microorganisms growth are obstacles for this type of pretreatment to fully develop (Wyman et al., 2005b).

As shown above, the multitude of possible pretreatments to examine and combine with each type of biomass can be overwhelming, since the efficacy of the pretreatment and its optimal conditions are subject to the lignocellulosic raw material, which in turn has different availability depending on geographical location and weather. Mathematical programming and superstructure optimization can be a tool to help assess the great number of alternatives, however, the large number of equations to describe the possible systems combined with the discrete characterization of the problem arising from the structural decisions can hinder the efficacy of those methods.
In this study, we propose a systematic approach for decision making regarding the process synthesis of a bioethanol facility using lignocellulosic feedstock. In order to reduce the amount of possible alternatives to be evaluated and to generate a viable and competitive setup, the guidelines and principles of process synthesis and integration in process system engineering (PSE) are applied.

2. Methodology

The envisioned systematic procedure herein portrayed contains seven sequential steps as shown in Figure 1 and described in the following paragraphs.

![Figure 1: Systematic procedure for bioethanol production process synthesis and integration.](image_url)

2.1. Step 1: Raw material selection and characterization

Lignocellulosic biomass is obtained from different sources, such as forestry residues, agricultural waste or dedicated energy crops, such as switchgrass. It is important to have a reliable estimate of the biomass, biowaste and agro-residue generated to define policies for their valorization as well as
identifying technologies which could be used for such purpose (Cardoen et al., 2015). Although the plant morphology varies widely among the groups, the basic structure and components are nearly identical. Glucose (6C) and xylose (5C) are the main sugar molecules present in the biomass, and they are the monomers that together form the cellulose and hemicellulose organic polymers present in the primary cell wall structure of green plants. Lignin is the final major component in the lignocellulosic biomass and provides stiffness to the cell wall and allows water transportation in the vascular tissues of plants.

The ratio of those three components depends mainly on the species of the plant which the feedstock is originated, but geographic conditions, such as average temperature, sun exposure and precipitation levels also play an important role in the composition distribution. Furthermore, harvesting time and techniques as well as storage conditions have an influence in the final composition of the plant as the biomass’ molecules may degrade.

From literature data, the average composition of the most used biomass for bioethanol production was calculated to determine the theoretical ethanol yield (TEY) from those crops. Although it is extremely difficult to establish the precise amount of monomers in the cellulose and hemicellulose molecules, an upper limit of the chain length is known and used to calculate the hydrolysis yield. The hydrolysis reactions employ water to break the cellulose and hemicellulose polysaccharides into glucose and xylose. The maximum theoretical yield of hexoses and pentoses are 1.136 kg and 1.11 kg per kilogram of cellulose and hemicellulose, respectively (Kang et al., 2014). The fermentation reactions convert the hexoses and pentoses to ethanol by a variety of microorganisms, such as bacteria, yeast or fungi. The conversion rates differ depending on the vector used, the inhibitors present in the medium and the conditions where the fermentation occurs, such as pH, temperature and pressure (Mood et al., 2013). Following the stoichiometry, presented in Equations 1 and 2, the maximum amount of ethanol obtained is 0.639 kg of ethanol per kg of glucose and 0.511 kg of ethanol per kg of xylose.
\begin{align*}
C_6H_{12}O_6 & \rightarrow 2C_2H_5OH + 2CO_2 \\
3C_5H_{10}O_5 & \rightarrow 5C_2H_5OH + 5CO_2
\end{align*}

With the value of the conversion from reaction stoichiometry, it is possible to calculate the theoretical ethanol yield that helps the selection of biomass as feedstock for the process. It is important to keep in mind that feedstock supply limitation is a reality, thus adjustments should be made in this step to better represent the biomass availability of one’s region. However, even though most of the lignocellulosic materials are considered agricultural or forestry residues, competition for its use may arise. The market strife for lignocellulosic employment combined with the harvest and transportation costs, especially of the biomasses with a higher silica, extractives and ash content, puts the feedstock cost as around one third of the bioethanol production cost (Balat and Balat, 2008). Therefore, an economic indicator can be of good use for the decision maker when selecting the most interesting alternatives of biomass.

2.2. Step 2: Pretreatment screening and selection

The values for the theoretical ethanol yield are goals extremely difficult to achieve, since not all the cellulose and hemicellulose are available for conversion. An efficient pretreatment is essential for the product competitiveness and should comprise characteristics such as increase in the cellulose and hemicellulose digestibility, high recovery of carbohydrates, limited formation of inhibitors for hydrolysis and fermentation, low energy demand and should be on overall economic attractive, displayed by a small number of equipment and limited or recoverable chemicals inputs (Sun and Cheng, 2002). Therefore, the main goal of the second step is to recognize how the pretreatment acts on the biomass and to identify the main process features in connection to the total process structure, such as separation agents and solvents, and recycle characteristics, to finally list a suitable set of alternatives for the desired system.
Based on literature, the most employed pretreatment methods were selected and classified regarding their effect on lignin and hemicellulose removal, and how they affect the crystallinity and porosity of the biomass. Furthermore, technological aspects such as if the process is indicated for biomasses with high lignin content, the formation of inhibitors, utilities requirement and so on were evaluated. However, the knowledge of how the pretreatment affect the biomass and the main process features are not enough to pinpoint a small set of pretreatments. Instead, the understanding of the pretreatment methods should be used to answer conceptual process synthesis questions, such as: should 5C fermentation be considered or should economic efficiency over process development be prioritized. Some design questions do not necessarily reduce the number of alternatives at hand. To further narrow down the options one possibility is to use Equation 3 and calculate the pretreatment score (PTS) as a way of combining the process parameters explored:

\[
PTS = a \times EPT + b \times CR + c \times DT - (d \times IF + e \times SPC + f \times HUR + g \times EC)
\] (3)

Where, EPT is the effect of pretreatment on the biomass, combining the effects of lignin removal, hemicellulose removal, porosity and crystallinity. CR, DT, IF, SPC, HUR and EC are obtained from the main features of the pretreatment processes, and stand respectively for chemicals recovery (CR), developed technology (DT), inhibitor formation (IF), severe process conditions (SPC), high utilities requirement (HUR) and equipment corrosion (EC). The indexes a, b, c, d, e, f, and g can be changed to suit the designer needs. For instance, if one wants to prioritize the effect of pretreatment in the biomass over economic and environmental aspects, “a” should be the higher index, whereas if the engineer wants to focus on a higher scale production, and therefore a more established technology, index c should be one of the highest. By screening through the pretreatments literature reported data and process engineering knowledge, it is possible to have an initial insight on the fruitful matches in order to achieve the desired designer objective.

2.3. Step 3: Base case Process synthesis and simulation
By the end of step 3, it is possible to define a realistic base case flowsheet (BC) with the main unit operations of the process and stream data necessary for the next steps of the systematic procedure.

As opposed to classical chemical reactions, lignocellulosic pretreatment and conversion deal with a series of complex and sometimes unclear molecular structures reacting in a biological pathway and prone to a broad array of variables. Therefore, a series of assumptions must be taken into consideration when devising a bio based process. To start with, ideally, the pretreatment reactor function is to alter the biomass structure making it more susceptible to microorganism attack for the upcoming series of conversion reactors, without generating hydrolysis products and process’ inhibitors. However, it is known that part of the reactions in the pretreatment reactor involves the hydrolysis of a small fraction of the biomass and thus some conversion should be assigned to the pretreatment reactor to represent the process as close as possible to reality. Furthermore, rarely kinetic data will be available for novel reactions, especially when dealing with such uncertainty in the composition as in lignocellulosic processes, thus we rely on stoichiometry and conversion data from experiments for reliable simulations.

Currently, three technologies for the conversion of biomass into bioethanol are mostly used with their own set of advantages and drawbacks. Separate hydrolysis and fermentation method (SHF) employs two different set of reactors for the biomass conversion. The first reactor is responsible for the hydrolysis of the biomass, whereas in the second one the fermentation reactions take place. The main advantage of the SHF process is that each reactor can be carried at their optimal conditions. In the simultaneous saccharification and fermentation (SSF) setup, the hydrolysis reactions occur in the same vessel as the fermentation. That way, inhibitor activity caused by glucose in excess can be reduced, and as the reactions happen simultaneously, fewer reactors are required. The last of the three is called simultaneous saccharification and cofermentation (SSCF), where 5C sugars are also converted to bioethanol in the same reactor as the SSF platform. There is not, currently, a consensus in the academia regarding the best biomass conversion route. However, it is highly recommended
the use of experimental data when simulating the processes. Being subjected to less process variables when compared to pretreatment and separation areas, it is suggested that one chooses one method and keep it to set a benchmark for comparison when analyzing other process variables and pathways.

In the separation section two distillation columns are commonly used to concentrate the ethanol up to around 90% to 92% in a mass basis. Compositions above 95.6% are impossible to achieve by regular distillation due to thermodynamic limits in the azeotropic point of the mixture. However, in order to meet the fuel purity requirements, ethanol is further dehydrated. Several technologies exist, such as pressure swing distillation, azeotropic distillation, extractive distillation, adsorption, pervaporation, and so on. Cardona et al. (2010) showed the viability of commercial process simulators to predict the behavior of a process given an adequate thermodynamic model of the studied system, aiding on the decision making for the ethanol dehydration process.

After defining the process flowsheet and unit operations required to run the process, a simulation software is used to perform in the calculations of the mass and energy balances required for the next steps.

2.4. Step 4: Process evaluation and new flowsheets generation

The process alternatives generated were evaluated in regard to technical operational indexes, i.e. ethanol productivity, hot and cold utilities demand, water consumption and chemicals usage, and economical performance, i.e. total capital investment (TCI), total annual costs (TAC) and minimum ethanol selling price (MESP). By analyzing the indexes per process area, improvements opportunities can be spotted leading to changes in the original flowsheet or in the initial process parameters, such as reactor temperatures and separation operations. The new flowsheet is then evaluated again in a self-sustaining feedback loop generating novel setups in an evolutionary system. Designs deemed as unfit based on the indexes results and engineering expertise are discarded, whereas the promising alternatives are further developed and compared.
2.5. Step 5: Process integration

As a natural continuation from the previous step, process integration makes use of the devised flowsheet information, such as streams temperatures and mass balance, to search for energy and mass integration opportunities. Systematic procedures are now well established, mostly following the frames of pinch point analysis. Following the pinch methodology guidelines, hot streams that require cooling are matched with cold streams that need to be heated to minimize additional external utilities consumption. In this framework, the selection of the minimum approach temperature, $\Delta T_{\text{min}}$, is the key design variable for the synthesis of the heat exchanger network due to its effect on both heat exchanger area and the effect on lost work associated with the heat transfer phenomena.

Similarly to the pinch point analysis, El-Halwagi & Manousiouthakis (1989) introduced the concept of mass exchange networks, allowing for a mass integration of the process by identifying possible sources and targets of a given material. Such principle can be applied for water and chemicals recycling in a biorefinery concept for further process integration, since various source and demand streams at different concentrations are available.

The process integration is a step inherently connected to the flowsheet generation, working in a feedback loop, where each iteration can generate several different setups that can be further explored. Therefore, as shown in Figure 1, the steps 3, 4, 5 and 6 are interconnected and they work together for the generation of new alternatives as improvement opportunities are sought and explored, rather than a linear approach. By the end of step 5, an integrated and energy efficient flowsheet is expected.

2.6. Step 6: Environmental impact analysis

As part of an alternative solution for fossil fuels consumption, the bioethanol production plant must have at least a zero sum balance on its greenhouse gas emissions (Cardona et al., 2010). Some of the alternatives generated may have similar technical and economic performances, a proper
evaluation of their environmental impacts can show the discrepancies intrinsic to each process. Following the combined economic value and environmental impact analysis (EVEI) methodology described by Sadhukhan et al. (2014), it is possible to evaluate the environmental performance of new process quantitatively. The approach starts by setting the system boundaries. In a bioethanol production system, the limit is drawn including the biomass feedstock production, to take into account procedures required on the management of the different possible raw materials and the carbon dioxide credit absorbed during the plant growth. Transportation emissions were not taken in account for our analysis, under the assumption that the distances of the feedstock production to the processing facility, and from that to the end use are the same for all evaluated processes.

The simulated processes provide stream data required for the EVEI calculations in terms of equivalent carbon dioxide emissions and considering all products from the system. The products afford an environmental credit related to the products they displace, such as gasoline in the case of bioethanol. The required hot and cold utilities as well as additional power contribute to the emissions following the guidelines of the European Reference Life Cycle Database (ILCD). The final result of this step is the total carbon dioxide equivalent emissions from the processes, enabling a direct comparison of the evaluated processes. Furthermore, an environmental impact profile can be drawn to help assess the main contribution areas of the devised setups and aid by changing certain process routes as mitigation measures and generating new and more efficient flowsheets.

2.7. Step 7: Waste minimization and by-products value generation

Bioethanol production from lignocellulosic biomass generates gaseous, liquid and solid waste streams. Waste treatment is expensive and acts as a restraining measure to avoid excessive contamination of the environment. Production and economic advantages increase with a higher level of integration of the biorefinery. Devising a way to reduce the amount of waste and transforming it into valuable and salable products is a win-win situation as on one hand it decreases the expenses on effluent treatment and, on the other hand, it increases the biorefinery revenue.
Each pretreatment method generates waste and product streams with its own characteristics, making it a challenge to assert a one-way-fits-all solution. In step 7 different possibilities for minimizing the waste generated are discussed in the light of possible new bioproducts to be commercialized with the popularization of biorefineries. By knowing the flowsheet and mass balance from previous steps, possible solutions for a more complete use of the raw material aiming on adding value to the waste streams and integrating its products to the biorefinery portfolio are suggested and discussed.

3. Results

The methodology described above was applied to a case study to exemplify how the systematic approach can be used and adapted to suit different needs according to the designer specifications. Different possible sets of process pathways were generated and analyzed.

3.1. Step 1: Raw material selection and characterization

The first step involves literature research to obtain the biomass composition for initializing the estimation of the theoretical ethanol yield. Experiments can also be useful to determine the biomass composition, especially when data is scarce in the literature or when a specific biomass is targeted.

As no geographical limitation was comprised for the base case, the most promising feedstock for bioethanol production and their respective average composition was reported in Table 1.

Table 1: Feedstock’s composition according to literature data.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Lignin</th>
<th>Others</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood (Spruce)</td>
<td>43.2%</td>
<td>21.1%</td>
<td>26.3%</td>
<td>9.5%</td>
<td>Arshadi &amp; Grundberg (2011)</td>
</tr>
<tr>
<td>Hardwood (Hybrid Poplar)</td>
<td>44.2%</td>
<td>19.1%</td>
<td>26.8%</td>
<td>9.9%</td>
<td>Hamelinck et al. (2005)</td>
</tr>
<tr>
<td>hardwood (Poplar)</td>
<td>33.12%</td>
<td>44.63%</td>
<td>21.46%</td>
<td>0.77%</td>
<td>Gnansounou et al. (2009)</td>
</tr>
<tr>
<td>Hardwood (Eucalyptus)</td>
<td>45.1%</td>
<td>24.0%</td>
<td>25.7%</td>
<td>5.2%</td>
<td>Gnansounou et al. (2009)</td>
</tr>
<tr>
<td>Hardwood (Aspen wood)</td>
<td>48.1%</td>
<td>22.8%</td>
<td>17.6%</td>
<td>11.6%</td>
<td>Arshadi &amp; Grundberg (2011)</td>
</tr>
<tr>
<td>Corn Stover</td>
<td>37.6%</td>
<td>25.7%</td>
<td>15.5%</td>
<td>21.2%</td>
<td>Garrote et al. (1999), Aden et al. (2002), Arshadi &amp; Grundberg</td>
</tr>
</tbody>
</table>
Switchgrass 37.7% 28.3% 19.2% 14.8% Sun & Cheng (2002), Gnansounou et al. (2009)
Wheat Straw 34.2% 36.0% 14.7% 15.0% Garrote et al. (1999), Sun & Cheng (2002), Gnansounou et al. (2009)
Rice Straw 41.0% 21.5% 19.6% 15.8% Garrote et al. (1999), Lee et al. (2015)

Based on the yield reported in the paragraph 2.1, the TEY was evaluated for the selected biomasses. An economic indicator obtained by combining the TEY with the feedstock price was used as an aid to narrow down the alternatives for the process. In Table 2 the price per thousand liters of ethanol as well as the theoretical ethanol yield was reported.

Table 2 shows that, cost wise, spruce biomass is more advantageous than the alternatives, having the lowest price either per dry ton and when considering just the cellulose value. When all the convertible sugars are taken into account, cellulose and hemicellulose, eucalyptus takes the lead as it has a higher hemicellulose content. Just by analyzing the theoretical ethanol yield for all the biomasses, one can notice that poplar, due to its high amount hemicellulose, has the best performance compared to the options listed, but its price puts a barrier on a further selection of it for the next steps. Spruce, eucalyptus and corn stover on the other hand are attractive judging by the price per liter.

Table 2: Feedstock average price and ethanol price considering only the biomass contributions.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Price ($/dry ton)</th>
<th>Price ($/dry ton C)</th>
<th>Price ($/dry ton C+HC)</th>
<th>TEY (liter EtOH/kg BM)</th>
<th>Price EtOH ($/1000 Liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood (Spruce)</td>
<td>$ 65.10\textsuperscript{a}</td>
<td>$ 150.69</td>
<td>$ 101.32</td>
<td>0.469</td>
<td>$ 138.78</td>
</tr>
<tr>
<td>Hardwood (Hybrid Poplar)</td>
<td>$ 90.33\textsuperscript{b}</td>
<td>$ 204.44</td>
<td>$ 142.85</td>
<td>0.462</td>
<td>$ 195.55</td>
</tr>
<tr>
<td>Hardwood (Poplar)</td>
<td>$ 156.17\textsuperscript{c}</td>
<td>$ 471.53</td>
<td>$ 200.86</td>
<td>0.565</td>
<td>$ 276.52</td>
</tr>
<tr>
<td>Hardwood (Eucalyptus)</td>
<td>$ 69.39\textsuperscript{c}</td>
<td>$ 153.86</td>
<td>$ 100.42</td>
<td>0.504</td>
<td>$ 137.60</td>
</tr>
<tr>
<td>Hardwood (Aspen wood)</td>
<td>$ 102.09\textsuperscript{c}</td>
<td>$ 212.25</td>
<td>$ 143.99</td>
<td>0.518</td>
<td>$ 197.20</td>
</tr>
</tbody>
</table>
Corn Stover $ 66.26^{d,e} \quad $ 176.13 \quad $ 104.57 \quad 0.462 \quad $ 143.46 \\
Switch grass $ 105.79^{c,f} \quad $ 280.75 \quad $ 160.38 \quad 0.481 \quad $ 220.14 \\
Wheat straw $ 121.20^c \quad $ 353.97 \quad $ 172.49 \quad 0.511 \quad $ 237.17 \\
Rice straw $ 194.08^g \quad $ 473.94 \quad $ 310.78 \quad 0.456 \quad $ 425.82 \\


C: cellulose, HC: hemicellulose, BM: biomass, EtOH: ethanol

However, particular attention should be payed considering eucalyptus since, due to the lack of data available in the literature for the biomass composition and price, the results presented can be somewhat biased due to regional effects on those parameters. As spruce feedstock is mostly available on temperate areas of the northern hemisphere, and the objective of this case study is to be as generalist as possible, corn stover was chosen as the feedstock for the next steps of the process.

3.2. Step 2: Pretreatment screening and selection

Extensive literature data exist on the effect of different pretreatments on the lignocellulosic biomass. Data from review papers of Sun & Cheng (2002), Alvira et al. (2010), Brodeur et al. (2011) and Mood et al. (2013) were gathered and combined to form a general consensus on how the different types of available pretreatments act on the lignocellulosic biomass. It is important to mention that new techniques as well as established technologies are under continuous improvement, thus one should be aware of the state-of-the-art when building the evaluation benchmark. Table 3 lists the pretreatments evaluated and the effect they have on physical and chemical properties critical for bioethanol conversion, whereas Table 4 evaluates the main process features for each pretreatment.

Table 3: Effect of pretreatment technologies on lignin removal, hemicellulose removal, biomass porosity and biomass crystallinity.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Lignin</th>
<th>Hemicellulose</th>
<th>Porosity</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Extrusion</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Pretreatment</td>
<td>Effect</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>--------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microwave</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulsed Electric Field</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultrasound</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO2 Explosion</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia Fiber Explosion</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia Recycle Percolation</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid Hot Water</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet Oxidation</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lime</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diluted Acid</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozonolysis</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organosolv</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionic Liquid</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fungi</td>
<td>++</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Limited Effect; + Medium Effect; ++ High Effect.

Lignin removal of the biomass is intrinsically related to the porosity of the biomass and can lead to less inhibitors formation in acidic reactions conditions (Moiser et al., 2005). Chemical and physico-chemical pretreatments have advantage on this matter when compared to physical treatments due to a stronger interaction with the stiff lignin molecule. Hemicellulose removal, on the other hand, is desirable to increase cellulose accessible area as it is deeply intertwined with the cellulose molecules. Furthermore, if no 5C sugars fermenting microorganisms are employed, the removal of hemicellulose in a liquid stream can reduce the amount of material to be processed, decreasing the capital cost for the process' equipment.

It is easy to spot that most pretreatments focus on the increase of porosity to improve the hydrolysis reactions conversion, especially in the “explosion” and chemical categories. Whereas for crystallinity, while it is agreed that the enzymes readily convert the amorphous part of cellulose, an increase in the crystallinity has been reported for higher pH pretreatment simultaneously with an increase of hydrolysis yield of the pretreated biomass (Kim and Holtzapple, 2006). This does not mean that an increase in the crystallinity index is desired, but rather that one should evaluate the pretreatment effects as a whole due to the heterogeneous nature of lignocellulosic biomass.
All pretreatments herein portrayed have positive effects on the increase of biomass’ sugars conversion to ethanol. However, some of them require harsher conditions than others and different residence times. Furthermore, additional steps such as slurry detoxification and neutralization may be required, changing the final economic outcome of the processes. Table 4 shows some of the most important characteristics of the pretreatment processes that influence in the final pathway decision. As expected from pretreatment section, the utility requirements for the process is considered almost always high, with the exception for Ozonolysis pretreatment, carried at room temperature and regular pressure (Alvira et al., 2010).
Table 4: Process features for pretreatment technologies.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>High Lignin Recovery</th>
<th>Hemicellulose Recovery</th>
<th>Chemicals Recovery</th>
<th>Inhibitor Formation</th>
<th>Severe Process Conditions</th>
<th>High Utilities Requirement</th>
<th>Equipment Corrosion</th>
<th>Developed Technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Milling</td>
<td>Y</td>
<td>N.a.</td>
<td>N.a.</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Extrusion</td>
<td>N</td>
<td>N.a.</td>
<td>N.a.</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>Microwave</td>
<td>N</td>
<td>N</td>
<td>N.a.</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pulsed Electric</td>
<td>Y</td>
<td>N.a.</td>
<td>N.a.</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ultrasound</td>
<td>Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Steam Explosion</td>
<td>Y</td>
<td>Y</td>
<td>N.a.</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>CO2 Explosion</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>AFEX</td>
<td>N</td>
<td>N.a.</td>
<td>Y</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>ARP</td>
<td>N</td>
<td>N</td>
<td>Y</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Liquid Hot Water</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>+</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Wet Oxidation</td>
<td>N</td>
<td>Y</td>
<td>N</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Alkali</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Lime</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Diluted Acid</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Ozonolysis</td>
<td>Y</td>
<td>N</td>
<td>N</td>
<td>+</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Organosolv</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>-</td>
</tr>
<tr>
<td>Ionic Liquid</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fungi</td>
<td>Y</td>
<td>N.a.</td>
<td>N.a.</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Y: Yes; N: No; N.a: Not applicable; -: Faintly valid; +: Partially valid; ++: Highly valid
Moreover, severe process conditions are seen especially on chemical or physico-chemical pretreatments, whereas new alternatives (low development stage technologies) tend to focus on milder settings.

Having a low lignin content biomass (corn stover), as decided on step 1, 5C sugars fermentation is desired to improve the final ethanol yields of the process. For equation 3, the same importance for all process parameters was given, keeping the indexes values of 1. EPT values were obtained by adding the “plus” signs from Table 3 and assigning the value of 1 for each plus. Table 4 was used for the CR, DT, IF, SPC, HUR and EC calculations, where every Y and “plus” have the value of 1, and every N or N.a. have the value of zero. The result indicated ammonia fiber explosion as the first option, followed by organosolv pretreatment as the second choice of pretreatment.

3.3. Step 3: Base case Process synthesis and simulation

For the base case generation in our study case, technical literature was combined with the hierarchical approach which relies on the RSR (Reactor/Separation/Recycle) structure as the main feature of the flowsheet architecture. Aspen Plus v8.8 was used to simulate the initial devised process. According to Humbird et al., 2011, the processed biomass input was set at 97,100 kg/h. Non-random two liquid (NRTL) property method was selected for the simulations and Aspen’s databank components were used whenever possible, otherwise components properties from the National Renewable Energy Laboratory report were used instead.

The ammonia fiber explosion pretreatment requires a rapid expansion of the gas to disrupt the biomass structure and enhance the digestibility of the carbohydrates. Therefore, as shown in Figure 2, after the pretreatment reactor (PTRCT) the slurry was flashed (F1) to both promote an explosion of the ammonia impregnated in the biomass and a partial recovery of the ammonia used. Data from Tao et al. (2011) was used to describe the pretreatment conditions. The pretreatment reactor (PTRCT) operates at 150 °C and 15 bar, with a residence time of 30 minutes. The ratio of water to
dry weight biomass was set to 0.81, whereas ammonia to dry weight biomass ratio was set as 1.52. As stated by Mood et al., 2013, ammonia recycle is a prerequisite for the economic feasibility of the AFEX process due to expensive cost of anhydrous ammonia. For a further recovery of the ammonia in the process, Tao et al. (2011) proposed the use of an absorber column followed by a series of multi-stage compressors interleaved with coolers to maintain the temperature below 150 °C and avoid a thermal break-down of the compressor oils. The recovered ammonia was kept in a storage tank (NH3TANK) to be used on the next batch. A washing step was used to adjust the process pH prior to (HYDRCT) and fermentation (FERMRCT) reactions. Cellulase was used for the hydrolysis conversion with a residence time of 84h at 48 °C. The slurry was then cooled to 35 °C and Zymomonas mobilis was responsible for fermenting the sugars during 36h of residence time. The gases from the fermentation were vented and the broth was sent to the beer well tank (BEERTANK). Two sets of distillation columns were used to concentrate the ethanol to the azeotropic point. The first distillation column, named beer column (BEERCOL), removed the remaining carbon dioxide and the solids from the broth. The carbon dioxide was sent to a vent scrubber (SCRUB) where water in a counter current was used to recover a recycle the carried ethanol from the gas stream. A side stream containing a mixture of ethanol and water from the beer column was directed to the second distillation column, named rectifying column (RECTFCOL), responsible for concentrating the ethanol near to the azeotropic point, around 93% w/w.

Of the available alternatives for ethanol dehydration, azeotropic distillation is arguably the most studied one (Cardona et al., 2010). However, due to the high energy consumption of separations by distillation, alternative extractive configurations were proposed for the bioethanol dehydration (Errico et al., 2014). Moreover, integrated and intensified configurations for simultaneous recovery and dehydration of the real fermentation broth were developed (Torres-Ortega and Rong, 2016).
While Singh and Rangaiah (2017) reviewed and compared different technologies available for ethanol dehydration.

Cardona et al. (2010) reported an energy consumption of 3.43 kW/kg of ethanol for azeotropic distillation, 4.25 kW/kg of ethanol for pressure swing absorption and 2.70 kW/kg of ethanol for molecular sieves. Therefore, for the initial base case, molecular sieves (MSIEVE) were used to adsorb the water and obtain the fuel grade ethanol as the setup require fewer equipment and is easier to control. Further discussion on alternatives for the separation process will be presented on the next steps of the systematic procedure. In the initial setup for the AFEX process, reported in Figure 2, the pretreatment section was highlighted in blue, while the conversion steps, and the separation and purification area in green and red respectively.

Figure 2: AFEX setup for bioethanol production; in blue, pretreatment area; in green, the biomass conversion area; in red, the product separation and purification area.

3.4. Step 4: Process evaluation and new flowsheets generation

Results from the base case simulation showed a total ethanol productivity of 18,509 kg/h. The theoretical ethanol yield of corn stover as in Table 2 shows that the maximum productivity achieved is 0.462 liter of ethanol/kg of dry biomass. Converting to a mass basis and taking into account the
biomass entering the process, the theoretical ethanol yield for the process is 35,344.4 kg of ethanol per hour, meaning that AFEX set up reached the 52.37% of the upper limit for the biomass. Energy wise, the pretreatment area was responsible for nearly 72% of the hot utilities, 73.9% of cold utilities and almost all electricity necessary for the process. It is important to state that at this stage of the process, no energy integration or co-generation were performed. However, this figure gives an important hint on how the pretreatment area can be costly and essential for the bioethanol production.

For an initial estimation of the capital costs, the Bridgewater method, or stepping count method, shown in Equation 3, was used (Towler and Sinnott, 2008):

\[ C = 3200 \times N \left( \frac{Q}{s} \right)^{0.675} \]  

Where C is the capital cost obtained in U.S. dollars (referred the year 2000), Q is the plant capacity in metric tons per year, s is the reactor conversion and N is the number of functional units excluding pumps and heat exchangers. For this equation, the reactor conversion is defined as the amount of desired product achieved per mass fed to the reactor, therefore the 52.37% earlier discussed.

Assuming the plant running 330 days per year the corresponding plant capacity, Q, is of 769,032 metric tons per year. Calculating the capital cost and updating its value by the CEPCI index of 2015, 562.2, results in a total capital cost of 1,515 million dollars. Where two thirds of this value corresponding to the pretreatment area due to the large number of compressors required to recycle the ammonia back to the process.

3.4.1 Generation of process alternatives and comparison

Arising from the discussion above, two lines of investigation for process improvements could be identified with process systems engineering methods: process design by optimizing the pretreatment reaction parameters to increase biomass conversion, and process integration by revamping the ammonia recycling process to reduce the number of equipment and energy consumption.
According to the first approach the conversion of the AFEX process can be increased changing the reaction parameters (Teymouri et al., 2005; Zhao et al., 2014). Da Silva et al. (2016) by changing the process parameters, the optimized process has achieved a MESP reduction of 28% for the AFEX pretreatment due to a productivity increase.

Following the process integration approach an improved ammonia recycle process was defined according to the work of Laser et al. (2009). As reported in Figure 3, a steam stripping column (STRC) was used to recover the ammonia after the initial flash (F1), the recovered stream is then condensed first by water quenching and later by indirect cooling. In this case, instead of recycling back to the process anhydrous ammonia, the solution is already mixed with water. Although usually the biomass is presoaked in water, most experimental studies use pure liquid ammonia during the AFEX pretreatment. Therefore, the efficacy of the AFEX pretreatment using a mixture of ammonia and water is still to be further confirmed.

![Figure 3](image_url)

Figure 3. Alternative ammonia recycling path (A2) for the AFEX pretreatment process

For the new process alternatives, initially the parameters change for the AFEX pretreatment (A1) (Da Silva et al., 2016) was considered and in a second round of evaluation the new ammonia recycling path (A2) was added (Laser et al., 2009). Simulation results are shown in Table 5 and are compared to the initial base case. Pressure swing adsorption is discussed qualitatively in
comparison with other cases and with literature data quantitatively comparing its energy consumption. As seen from Table 5, the new process parameters for the pretreatment reactor were responsible for increasing the ethanol productivity by 41.92% and, thus, reducing the capital cost by 21.05% for A1. However, the total energy consumption almost doubled, as well as the required ammonia in the make-up stream due to a more difficult separation of the low concentration ammonia.

Table 5: Process parameters evaluated.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>AFEX – Base Case</th>
<th>AFEX – A1</th>
<th>AFEX – A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol productivity (kg/h)</td>
<td>18,509</td>
<td>26,268</td>
<td>26,284</td>
</tr>
<tr>
<td>Ethanol broth concentration (wt%)</td>
<td>5.91</td>
<td>7.56</td>
<td>6.67</td>
</tr>
<tr>
<td>Number of equipment</td>
<td>23</td>
<td>23</td>
<td>19</td>
</tr>
<tr>
<td>Pretreatment reactor operation conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>150</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>5</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Water content (wt%)</td>
<td>30%</td>
<td>60%</td>
<td>60%</td>
</tr>
<tr>
<td>Ammonia make-up stream (kg/h)</td>
<td>190</td>
<td>250</td>
<td>20</td>
</tr>
<tr>
<td>Water (kg/h)</td>
<td>239.8</td>
<td>280.7</td>
<td>328.7</td>
</tr>
<tr>
<td>Total energy (MW)</td>
<td>382.02</td>
<td>612.39</td>
<td>331.54</td>
</tr>
<tr>
<td>Heating demand (MW)</td>
<td>173.58</td>
<td>297.82</td>
<td>173.06</td>
</tr>
<tr>
<td>Cooling demand (MW)</td>
<td>185.23</td>
<td>299.56</td>
<td>158.28</td>
</tr>
<tr>
<td>Electricity (MW)</td>
<td>23.21</td>
<td>15.01</td>
<td>0.20</td>
</tr>
<tr>
<td>Capital Cost - Bridgewater method (million US$)</td>
<td>1515</td>
<td>1196</td>
<td>988</td>
</tr>
</tbody>
</table>

When ammonia stripping is employed in alternative A2, the number of equipment is greatly reduced as no more multi-stage compressors are required. The removal of compressors was also responsible for the decrease in the electricity demand for the process. Although steam had to be generated for the stripping column, the overall energy balance of the process was improved when compared to alternative A1. The increase of biomass conversion combined with the reduced number of equipment cut by one third the total capital cost for this alternative. Not listed in the table, the total energy consumption for the separation and dehydration of ethanol was 4.76 kW/kg of ethanol, 4.17 kW/kg of ethanol and 4.52 kW/kg of ethanol for the base case, alternative A1 and alternative A2, respectively.
The possibility of improving the efficiency of the separation system which will be addressed on the next steps of the systematic approach with energy and mass integration of the process.

3.5. Step 5: Process integration

To initialize the pinch methodology, the $\Delta T_{\text{min}}$ was set to 10 °C, in order to identify the pinch point of the process. From the mass and energy balance obtained for the flowsheets it is possible to draw the composite curves and calculate the pinch point temperature. The base case, alternative A1 and alternative A2 are all single pinch system and the pinch point temperature are respectively at 103.5 °C, 93.6 °C and 86 °C. After identifying the pinch point it is possible to calculate the energy targets of the system and establish the minimum demand for hot and cold utilities.

From the grand composite curves of the processes, shown in Figure 4, it is possible to identify the noses close to the pinch point, where a heat pump could be beneficial since there is a large amount of enthalpy for a small increase in temperature. For the cases studied, the plateaus in the grand composite curves are composed by the rectifier column condenser, for the bottom one, and by the beer column reboiler, for the top one. The vapor from the rectifying column is compressed to have its temperature increased and it is used as hot utility in the beer column reboiler (ETOHAZT), providing savings of 19 MW at the cost of 4.4 MW of electricity. As electricity is usually 4 to 5 times more expensive than hot utilities, the economical savings generated are borderline advantageous, however the process is more environmentally friendly if we consider the emissions associated. The same has been done to alternatives A1 and A2 generating savings of 27 MW and 25.9 MW, respectively at the cost of 6.1 MW of electricity for A1 and 6.2 MW of electricity for A2. The processes as they require 239.8, 280.7 and 328.7 tons of water per hour, respectively for base case (BC), A1 and A2.
However, fresh water is a limited resource and should be used sparsely. Instead, the processes offer options to recycle the water in a closed cycle reducing the environmental and economic impacts of the biorefinery. The bottom product from the rectifying column (W2) contains mostly water and can be easily recycled back to the pretreatment area without further purification. The recycled water is obtained at a higher temperature and pressure, meaning that hot utilities can be spared in the pretreatment preheating stage, but it only represents 10.6%, 11.8% and 10.7% of the total water required in the BC, A1 and A2 processes, respectively. The bulk of the water input in the process leaves in the stillage of the beer column together with the unconverted insoluble and dissolved solids (W1). The stillage water can not be recycled without a proper treatment due to its high level of soluble inorganic material from the biomass and fermentation nutrients. Therefore, the stillage
stream is cooled down to 47 °C and the solids are separated in a pressure filter. The water is then sent to wastewater treatment whereas the solids are directed to a combustor to produce the steam and power required in the process.

The wastewater treatment was based on the work of Humbird et al. (2011) and employs an anaerobic digestion tank, an aerobic digestion pool and a clarifier. From the literature data, 86% of the biomass is converted to biogas in the anaerobic digester, being 51% CH₄ and 49% CO₂ in a dry molar basis. In aerobic digestion pools, 74% of the remaining biomass is converted to water and carbon dioxide, which is later released in the atmosphere. The unconverted biomass is removed in the clarifier, dried and sent to the combustion area according to Sofia et al. (2014). In the combustion area the unconverted solids are burned in the combustor and the heat is used to upgrade the water to high pressure steam (500 °C and 40 bar). The high pressure steam generates power in a turbine and the low pressure steam (172 °C, 5 bar) discharged is used as hot utilities for the process together with the flue gas from the combustor. From the grand composite curves in Figure 4 it is possible to see that only low pressure steam is required in the processes, therefore no intermediate stage turbines are required. Table 6 summarizes the amount of water recovered in the processes, the amount of biogas generated, the power and hot utilities generated and consumed in the combustion area and the final energy balance for the processes. For the evaluated cases we added the suffix 2 to highlight that the processes are now different and more integrated from the ones evaluated in Table 5. Base case-2 (BC-2) showed the highest water recovery among the alternatives and due to energy integration and cogeneration is independent of external hot utilities. AFEX alternative 1-2 (A1-2) on the other hand still needs a considerable amount of external utilities due to streams temperature difference leading to a not so effective heat integration. Compared to the initial cases, without heat integration, BC-2 obtained savings of 46.1% in cold utilities and 61.1% in electricity consumed, while generating a surplus of hot utilities.
Table 6: Setups evaluation after process integration.

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>AFEX – Base Case-2</th>
<th>AFEX – A1-2</th>
<th>AFEX – A2-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Recovered (%)</td>
<td>99.65%</td>
<td>98.21%</td>
<td>97.87%</td>
</tr>
<tr>
<td>Rectifying column bottom (kg/h)</td>
<td>25,500</td>
<td>33,200</td>
<td>35,200</td>
</tr>
<tr>
<td>Beer column stillage treatment (kg/h)</td>
<td>213,500</td>
<td>242,500</td>
<td>286,500</td>
</tr>
<tr>
<td>Biogas produced (kg/h)</td>
<td>2370</td>
<td>4070</td>
<td>4030</td>
</tr>
<tr>
<td>CH₄ produced (kg/h)</td>
<td>660</td>
<td>1120</td>
<td>1120</td>
</tr>
<tr>
<td>Combustion power generated (MW)</td>
<td>18.79</td>
<td>18.91</td>
<td>18.91</td>
</tr>
<tr>
<td>Combustion power consumed (MW)</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>Combustion net power generated (MW)</td>
<td>18.58</td>
<td>18.70</td>
<td>18.70</td>
</tr>
<tr>
<td>Combustion hot utility net production (MW)</td>
<td>88.85</td>
<td>89.63</td>
<td>89.63</td>
</tr>
<tr>
<td>Energy balance</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating demand (MW)</td>
<td>-52.53</td>
<td>130.69</td>
<td>-26.44</td>
</tr>
<tr>
<td>Cooling demand (MW)</td>
<td>99.83</td>
<td>221.77</td>
<td>48.88</td>
</tr>
<tr>
<td>Electricity (MW)</td>
<td>9.03</td>
<td>2.41</td>
<td>-12.30</td>
</tr>
</tbody>
</table>

A1-2, on the other hand reduced the demand of hot utilities in 56.1%, cold utilities in 26.0% and electricity in 83.9%. Finally, alternative 2-2 (A2-2) showed a good balance energy wise, as it became self-sufficient in hot utilities and produces extra electricity that can be sold to the grid. A2-2 has the lowest cooling demand of the evaluated processes, with savings of 69.1%, and produces the highest amount of methane, that can be either burned or further processed for commercialization.

3.6. Step 6: Environmental impact analysis

After the process integration step, the process was evaluated regarding its environmental impact using the equivalent carbon dioxide emissions as a proxy agent according to the methodology described by Sadhukhan et al. (2014). According to this methodology, the equivalent carbon dioxide emissions should be calculated for the inputs and outputs of the process in order to allow a benchmark for comparison and aid at identifying the process’ hotspots that should be addressed.

However, corn stover is accounted negatively for the carbon dioxide emissions as it is responsible for binding the carbon dioxide from the atmosphere through photosynthesis at a rate of 1.494 kg of
$\text{CO}_2/\text{kg of corn stover}$, based on Spatari et al. (2005). Emissions related to fresh water attainment, ammonia production, natural gas for hot utilities generation and electricity were obtained from Sadhukhan et al. (2014) and the European Reference Life Cycle Database (ILCD) and are respectively: 6.52 kg of $\text{CO}_2$/ton of water, 2390 kg of $\text{CO}_2$/ton of ammonia, 220.32 kg of $\text{CO}_2$/MW of natural gas and 668.52 kg of $\text{CO}_2$/MW of electricity. Data from Tables 5 and 6 regarding water and chemicals usage as well as hot utilities requirement and the emissions from the combustion area were used to obtain the carbon dioxide equivalent for the studied processes as shown in Figure 5.

Figure 5: Main contributions to $\text{CO}_2$ emissions in the studied alternative cases.

All evaluated processes had negative $\text{CO}_2$ emissions when weighing the feedstock contributions and the product displacement. Although the base case had lower productivity of ethanol, directly correlated to the product displacement, its production, on the other hand, was the most environmental friendly among the alternatives, contributing with 702.9 thousand tons of $\text{CO}_2$ per year, compared to 876.4 thousand tons of $\text{CO}_2$ per year of A1-2 and 723.5 thousand tons of $\text{CO}_2$ per year for A2-2. The increased ethanol conversion for cases A1-2 and A2-2 reflected on the increased emissions of the scrubber vent and in more waste to be treated in the waste water treatment increasing the emissions of biogas and the aerobic lagoon. Biogas can be sent to the combustor and at the same time increase the energy output from the turbines and convert the methane to $\text{CO}_2$, 21
times less harmful to the atmosphere (IPCC, 1990). However, the main contribution to the emissions is the flue gas, responsible for 53.2%, 41.3% and 50.2% of the emissions for the BC-2, A1-2 and A2-2, respectively. The flue gas is the main product of the lignin and unreacted biomass combustion, add to that the surplus of hot utilities for BC-2 and A2-2 and there is an opportunity for a side process to convert the lignin into useful product to increase the economic appeal for the process and reduce even more the environmental impacts related to it.

3.7. Step 7: Waste minimization and by-products value generation

We used the factorial method described by Towler & Sinnott (2008) to calculate the capital cost for the processes, and in addition, the costs in the Lang factors were accounted to obtain the fixed capital investment (FCI). The FCI values were corrected through 2015 CEPCI value of 562.2. Taking the productivity into account together with the variable and fixed operating costs was possible to calculate the minimum ethanol selling price of the setups. Data for process water (0.4$/ton), ammonia (300$/ton), cooling water (0.35$/GJ), hot utility (16.50$/GJ) and electricity (16.80$/GJ) were obtained from literature (Turton et al., 2009). The base case BC-2 resulted in a MESP of 0.670$/kg of ethanol, whereas A1-2 and A2-2 achieved 0.539$/kg of ethanol and 0.435$/kg of ethanol, respectively. When analyzing the savings obtained from the pressure swing adsorption for case A2-2, as discussed in section 3.4 the MESP obtained was 0.431$/kg of ethanol, shown as case A3 in Figure 6. The main contributions to the MESP for all evaluated cases are the feedstock price and capital cost followed by the enzymes costs, as shown in Figure 6. Hot utilities represent 15.2% for alternative A1 as the process does not produce enough heat and is dependent on external sources. The next major cost area is labor cost, contributing to 8.8% of the final ethanol selling price, on average, and included in the “Others” tab. Besides improving the bioethanol conversion, there is nothing much to be done in those expenses. However, several waste streams can be enriched to increase the value generation for the biorefinery. Carbon dioxide from the
fermentation can be pressurized and sold to the food and drink industry or a separate processing unit can be added to make use of excess hot utilities available and further process the CO₂ to methanol, formic acid or urea (Cheng, 2010).

Figure 6: MESP breakdown for the evaluated cases.

Biogas produced from the anaerobic digestion in the waste water treatment contains 27.5% in a mass basis of methane, with the remaining being carbon dioxide. One solution could be to burn the produced biogas, however the carbon dioxide, although not interfering with the combustion, dilutes the energy density of the biogas and heat generated in the combustion is used to warm up the CO₂ present in the stream. Pressurized water can be used to scrub CO₂ from the biogas in a physical absorption process or activated carbon or zeolites can be employed to purify the biogas (Cheng, 2010). The upgraded natural gas (biogas with methane content over 99%), can then be sold for household utilization or used as fuel for automobiles.

Unconverted biomass and lignin are dried and burned to produce electricity. Lignin is, however, the most abundant renewable material that contains aromatics, and can theoretically be used as a source to substitute petro-chemical feedstocks. The pulping industry can already produce vanillin from lignin, although at a low reaction conversion (Tuck et al., 2012). Lignin gasification offers the
opportunity to generate syngas (carbon monoxide/hydrogen), and the inclusion of a water-gas-shift technology can separate the hydrogen into a pure product. Furthermore, lignin can be converted into carbon fibers, BTX chemicals, resins, phenol and others, subjected to the type of process used in the system (Holladay et al., 2007). Further considerations on the profitability of such processes from lignocellulosic biomass need to be addressed as there is a trade-off between electricity and by-products manufacturing, and could be the focus of future studies on biorefineries challenges.

4. Conclusions

A seven-step systematic procedure for process synthesis and integration of bioethanol production facilities from lignocellulosic biomass was proposed. A case study was considered for the application of the methodology, corn stover was selected as the feedstock and ammonia fiber explosion was applied as the pretreatment method. The systematic procedure can generate and improve the process alternatives along the steps coupling process integration targets, which can approach the final optimal process with its technical, economic and environmental performance accounted and evaluated. From the base case, 3 alternatives were generated and evaluated. By changing reactor conditions and using water quenching to recover the ammonia from the pretreatment process, the best alternative achieved savings of 35.4% in the minimum ethanol selling price. Conceivable products were suggested for improving the biorefinery profitability, but further studies are required to a proper integration in the devised production facility.

E-supplementary data of this work can be found in online version of the paper.

Acknowledgments

We thank the National Council for Scientific and Technological Development – Brazil (CNPq) for the financial support for this study, under the grant number 247077/2013-5.

References


Pacific Northwest Natl Lab, PNNL-16983.


Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. Bioresour. Technol. 96, 2026–2032.


Highlights

- A seven-step systematic procedure for lignocellulosic bioethanol process synthesis
- The systematic approach was applied in a study case with corn stover as feedstock
- New alternatives were evaluated for technique, economy and environment
- Production process with AFEX pretreatment was obtained and optimized
- Process improvements following the guidelines achieved savings of 35.4% in the MESP