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Process Alternatives for Bioethanol Production from Organosolv Pretreatment Using Lignocellulosic Biomass

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Organosolv pretreatment makes use of ethanol as a solvent to remove lignin and render the cellulose and hemicellulose present in the biomass available for conversion. However, solvent recovery is a crucial step to make organosolv pretreatment a competitive and reliable alternative for second generation bioethanol production. We used Aspen Plus v8.0 to simulate an initial organosolv pretreatment case based on published experimental works and proposed 4 different alternatives for the solvent ethanol recovery. Total energy consumption, ethanol productivity, ethanol concentration after fermentation, capital costs, variable costs and minimum ethanol selling price (MESP) were evaluated for the selection of the best design for the process. Furthermore, energy targets were calculated for the scenarios to investigate the saving potentials in the variable costs and were accounted for new MESP calculations. Ethanol productivity and recovery was similar for all the cases evaluated. The capital cost calculated for the base case was 20.8 million dollars and the total energy consumption was 732 MW, with a MESP of 1.117 $/kg of ethanol. The best process alternative with energy integration obtained savings of almost 30 % in the MESP, totalizing 0.782 $/kg of ethanol and the total energy consumption was 488 MW.

1. Introduction

Limited amount of oil reserves, price fluctuation due to geopolitical disputes and global warming push the development of a cleaner and renewable substitute for fossil fuels. Lignocellulosic ethanol emerges as a great alternative to replace the current fossil fuel based energy matrix. Considered as the second generation technology, lignocellulosic ethanol does not have the main drawbacks of the starchy based process, such as competing with food sources and incomplete use of the biomass (United Nations 2008). On the other hand, the recalcitrant structure of the lignocellulosic biomass requires large amount of energy and/or chemicals to surpass this barrier and access the desired cellulose and hemicellulose.

Cellulose is the most abundant organic polymer on Earth (Limayem & Ricke 2012) and it is found from softwood and hardwood trees to herbaceous plants and agricultural residues. Lignocellulosic biomass production is estimated in 1.4 billion of dry ton per year (Perlack et al. 2005). Bioethanol from wood is the more sustainable biofuel option available according to recent studies (Piemonte et al. 2014). However, with lignin protecting cellulose and hemicellulose from outside harm, a pretreatment step is of great importance for the final bioethanol yield and further economic competitiveness of the process. Crimes et al. (2015) evaluated several types of pretreatment and concluded that delignification of the biomass can reduce environmental impacts of the processes by 4 % to 68 % varying for the process evaluated.

One of the main features of organosolv pretreatment is the removal of lignin prior to the hydrolysis and fermentation reactors, allowing a reduced size in the equipment, savings on utilities consumption and less formation of inhibitory compounds. The second generation ethanol industry so far has overlooked the benefits of lignin production and commercialization. However, with the technological development of the lignocellulosic based bioethanol production large amounts of lignin are generated, contributing to the income and profitability of the process (Menezes et al. 2016). Environmental impacts, cost and ease of recovery are the main attributes to be evaluated when selecting the best solvent for the process (Zhang et al. 2016). Ethanol has been used in the pulping process to remove the lignin from the biomass since 1940s (Zhao et al. 2009) and it is a renewable, low cost and with low boiling point solvent. Furthermore, in a lignocellulosic bioethanol site it

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can be easily integrated for a makeup stream in the process. This paper describes a lignocellulosic based ethanol production process using the organosolv pretreatment method. In this paper, four different types of solvent recycle setups were investigated and their performances were compared using technical and economic indicators.

2. Organosolv Pretreatment

Softwood biomass has been proven a challenge for other types of pretreatment methods (Tengborg et al. 1998), however organosolv pretreatment thrives in this dense lignocellulosic source (Pan et al. 2005). Aspen plus v8.0 was used to set up a plant processing 88,500 kg/h of dry spruce. The biomass composition is 45 % of glucan, 22 % of xylan, 28 % of lignin, 3 % of acetate and 2 % of ashes in dry matter basis (Wingren et al. 2003). For a more accurate representation of biomass, it was considered that the biomass contains 20 % of moisture content, adding up to 106,200 kg/h as feedstock. Non-random two-liquid (NRTL) property method was selected and components in Aspen's databanks were used whenever possible, otherwise properties from the National Renewable Energy Laboratory (NREL) report were used instead (Humbird et al. 2011).

The initial organosolv pretreatment setup was based on previously published theoretical and experimental works (Pan et al. 2005; Hallac et al. 2010). The complete organosolv process is shown in Figure 1. The biomass is initially heated with steam to 130 °C and subsequently combined with ethanol (50/50 w%) in a ratio of 5:1 to dry weight biomass. Sulfuric acid, 1.75 % (w/w) to dry biomass weight, is added as catalyst to the process, allowing the use of milder temperature in the pretreatment reactor (R1) and shorter residence times (Zhang et al. 2016). The pretreatment reactions are carried out at 180 °C and 27.2 atm for 40. Following the pretreatment reactor, the pressure is released and the biomass is filtered (F1) to obtain two streams, a pulp stream rich in solids and one liquid stream. The pulp stream, with high content of cellulose, is washed in a two-step process. The first washing step (W1) is done with ethanol solvent, in a ratio of 2:1 to the pulp weight to recover part of the ethanol soluble lignin (EOL) and the solvent drenched in the biomass. The second washing stage (W2) is done with water in a ratio of 2:1 in order to recover the remaining solvent present in the pulp stream. The solid stream is then sent to a mixing tank (T1) before hydrolysis and fermentation take place. The liquid stream from the pretreatment reactor is rich in lignin, hemicellulose, water and ethanol. To start the solvent recovering process, the liquid stream is flashed (FL1). The top stream has a high amount of solvent ethanol and water. The bottom stream is mixed with the washing liquids and more water is added to precipitate the lignin in the precipitation tank (P1). The material is filtered (F2) to remove the lignin and the remaining liquids are sent to a distillation column (C1) to recover the remaining ethanol as distillate. The bottom stream of the distillation column needs to have its pH corrected with ammonia to neutralize the sulfuric acid and acetic acid produced in the process. After the neutralization (R2), part of the water is recovered in a flash operation (FL2) and the remaining stream is mixed with the pulp stream in the mixing tank (T1). The flashed streams are cooled down into liquids, and afterwards the streams are mixed with the distillate from the distillation column to recycle the solvent into the process. The solids contents are kept at 20 % (wt.) before the hydrolysis and fermentation and the stream is sent to the conversion reactors. The separate hydrolysis and fermentation (SHF) process was used for the ethanol production. 10 % of the biomass is deviated to in-site production of enzymes and bacteria. The hydrolysis reactions are held at 48 °C for 84 h. Cellulase enzyme 20 mg/g of cellulose is added in the reactor and converts 90 % of cellulose to glucose (Humbird et al. 2011). Before the fermentation reactions, the slurry is cooled to 32 °C and Zymomonas mobilis is added. The inoculum level is 10 % volume and the fermentation runs for 36 h (Humbird et al. 2011). After the fermentation reaction is completed the fermentation broth is sent to the downstream recovery and purification process.

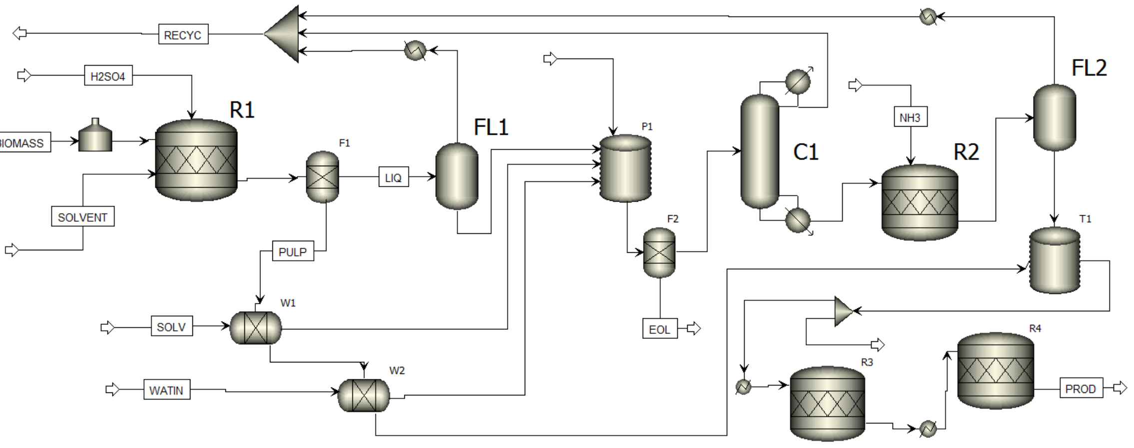

Figure 1: Flowsheet setup for organosolv pretreatment.

2.1 Solvent Ethanol Recovery

The solvent ethanol recovery process starts with a flash operation after the pretreatment reactor where 45% of the total ethanol used as solvent is recovered. However, for the process to be economically feasible a larger fraction must be recycled. The remaining solvent is not easily recovered and it is mixed with other chemicals produced in the pretreatment reactor. Those other chemicals compounds, such as sulfuric acid, acetic acid, furfural and hydroxymethylfurfural (HMF), have inhibitory effects in the biomass conversion reactions and need to be neutralized or separated from the reagents stream prior to the hydrolysis and fermentation steps (Dussán et al. 2014).The base case scenario (BC) presents a method for recuperating the remaining solvent ethanol first with a distillation column followed by a neutralization tank and finishing with a flash operation to recover the water needed to obtain the solvent composition of 50/50 w%. This route is defined as SNE: separation, neutralization, evaporation; corresponding to the order of the separation operations performed. The process allows the recovery of 99.6 % of the total solvent ethanol used, however it is responsible for 87 % and 32 % of the total hot utilities and cold utilities consumption in the whole process respectively.

Water and the chemicals that need to be neutralized, namely sulfuric acid and acetic acid, play important roles in the total energy performance of the process. Together with ethanol, water is the most abundant component in the process and its high specific heat capacity requires a lot of energy for it to change temperature. Acetic acid and sulfuric acid on the other hand, are not present in high quantities, but just a small amount of these components can cause inhibitory effects on the fermentation process, reducing the ethanol concentration for the downstream processing. Furthermore, the high boiling point of both compounds and its interactions with water and ethanol makes the distillation process more difficult (Taherzadeh & Karimi 2007). Therefore, four new scenarios for the solvent ethanol recovery process were investigated. Process Alternative 1 (A1) consists of an initial neutralization of the acids in the process, followed by the distillation column and flash operation for water recovery. Alternative 2 (A2) also starts with the neutralization process, but it is followed by a further flash operation, in this case recovering water and ethanol, and finishes with a distillation column to recover the remaining ethanol. Process Alternative 3 (A3) begins with the flash operation and has in sequence a separation by a distillation column and ends with the neutralization of the acids. And finally, Alternative 4 (A4) commences with a flash operation and is followed by the neutralization and finally the distillation process. For a direct comparison of the alternatives, all process parameters were kept constant whenever possible, e.g. same amount of biomass processed, pretreatment temperature and pressure, 20 % of solids loading prior to the hydrolysis reaction and temperature at the neutralization reactor. Operating specifications for the distillation columns were changed to minimize the energy consumption while recovering as much ethanol as possible for the processes. Total energy consumption, ethanol productivity, ethanol concentration after fermentation, capital costs, variable costs and minimum ethanol selling price (MESP) were calculated to compare the scenarios. Furthermore, pinch method was used to calculate energy targets for all the alternatives investigated and MESP was reevaluated to assess the possible savings.

3. Results and Discussion

Solvent ethanol recovery for all the cases was above 99.5 %. Alternative A1 recovered 99.5 % of solvent ethanol, whereas alternatives A2, A3 and A4 obtained values of 99.9 % of recovery. The base case recovered 99.6 % of the solvent ethanol with a total energy consumption of 732 MW. Alternative cases total energy consumption varied from 614 MW (A3) to 774 MW (A1).

For the base case, ethanol productivity from the conversion of biomass was 24,658.8 kg/h. Similar value was obtained for process alternative 1 (A1), whereas A2, A3 and A4 were slightly higher around 24,765 kg/h with little difference. Ethanol concentration in the product stream, on the other hand, showed the reverse trend, it was higher for the base case, at 11.55 % (w/w), decreasing for A1, 11.14 % (w/w), and reaching a minimum of 10.8 % (w/w) for A2, A3 and A4 as shown in Figure 2. The difference in the ethanol concentration is mostly due to the difference of solids loading in the hydrolysis and fermentation reactors. Although the ideal value was 20 %, small fluctuations were observed in the simulations, resulting in the variation observed in the ethanol concentration.

Figure 3 depicts the share of energy consumption between process alternatives. Electricity consumption was the same for all the cases, 476.5 kW. Hot utilities and cold utilities consumption showed similar values for alternatives A2, A3, and A4 which were lower than the base case and process alternative 1 (A1), the highest among them all. The difference in hot utilities and cold utilities used can be explained by better equipment placing, avoiding big temperature fluctuation difference and specially the removal of water prior to neutralization and distillation operations, preventing the unnecessary usage of heating and cooling utilities.

For water consumption, the base case was responsible for the lowest rate of water used in the process, 143,500 kg/h, whereas A3 consumed the highest amount of approximately 153,500 kg/h. The ammonia required to neutralize the acids from the pretreatment was fewer for cases A3 and A4, at 950 kg/h and highest for the base case and process alternatives A1 and A2, with a value of 1,200 kg/h. Water and ammonia consumption is showed in Figure 4.

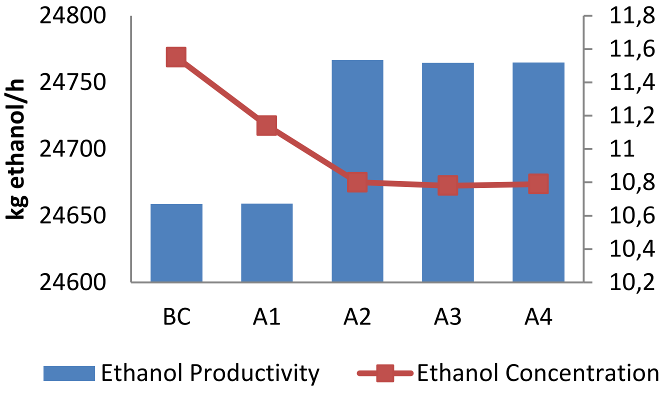

Figure 2: Ethanol productivity (kg/h) and ethanol concentration (% w/w) for organosolv pretreatment base case and process alternatives.

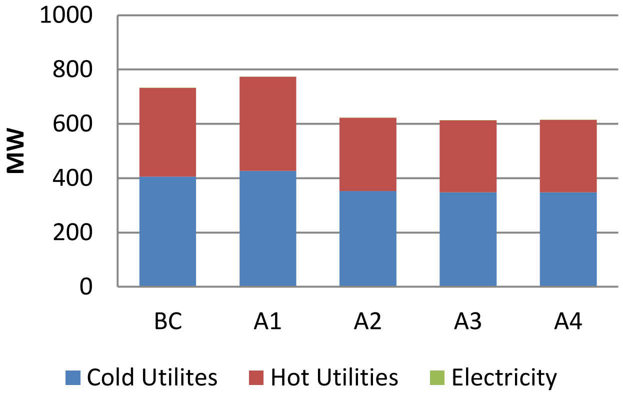

Figure 3: Energy consumption for organosolv pretreatment base case and process alternatives.

Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) was used to calculate the total capital cost for the base case and all the process alternatives. The variable cost was calculated based on the utilities and chemicals consumption obtained from the simulations. Utilities and chemicals prices as well as the feedstock price are listed in Table 1. In Figure 5a shows the comparison between the process alternatives for capital cost and variable cost, with and without energy integration. Energy integration was performed using Pinch methodology for a temperature difference of 10 °C (ΔT_{min} = 10 °C) (Kemp et al. 2007). The results showed that the base case was the most capital intensive process, with a value of almost 20.9 million dollars, whereas process alternative A3 was almost 26% cheaper, costing approximately 15.5 million dollars. For the variable costs, alternative A1 presented the highest value, as it required more hot and cold utilities. On the other hand, process alternative A3 had the lowest costs, due to a combination of fewer utilities consumed and less ammonia used. However, after energy integration, process alternative A2 presented the lowest value for the variable costs, at approximately 98.2 million dollars per year.

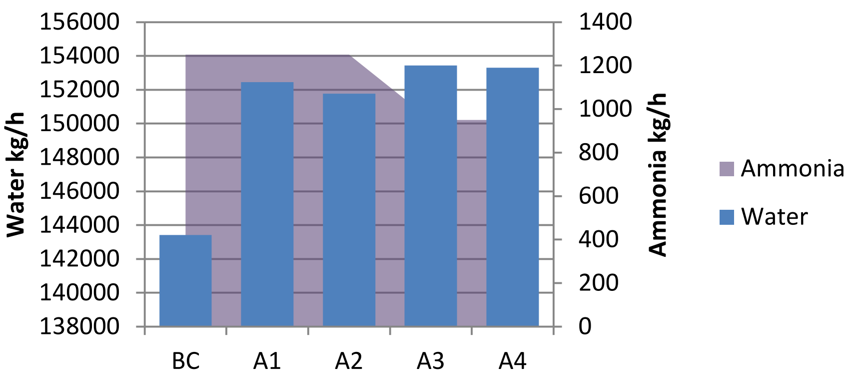

Figure 4: Water consumption (bar) and ammonia consumption (background area) in kg/h for organosolv pretreatment base case and process alternatives.

Combining the data for capital cost, variable cost and the feedstock price with plant operational information, such as plant life (30 years), total running hours per year (7,920 h), internal rate of return (10 %), taxes (35 %) and depreciation method (Internal Revenue Service Modified Accelerated Cost Recovery System – IRS-MACRS) we calculated the minimum ethanol selling price (MESP) for all the process by iterating the net present value (NPV) until its value equals zero. Figure 5b compares all the processes regarding its MESP values with and without energy integration. For the processes without energy integration, A3 and A4 have the best values, 0.957 $/kg of ethanol, 14% lower than the initial value for the base case. With energy integration, process alternative A2 is the best option to be considered, with a value of 0.782 $/kg of ethanol, slightly lower than the energy integrated processes A3 and A4, 0.786 $/kg of ethanol and 0.787 $/kg of ethanol respectively and 30% lower than the base case value.

Table 1: Feedstock, chemicals and utilities price

Input	Price
Spruce	67.13 $/t
Sulfuric Acid	0.085 $/kg
Ammonia	0.30 $/kg
Water	0.40 $/t
Vapour – Hot utility	16.50 $/GJ
Cool water – Cold utility	0.35 $/GJ
Electricity	16.8 $/GJ

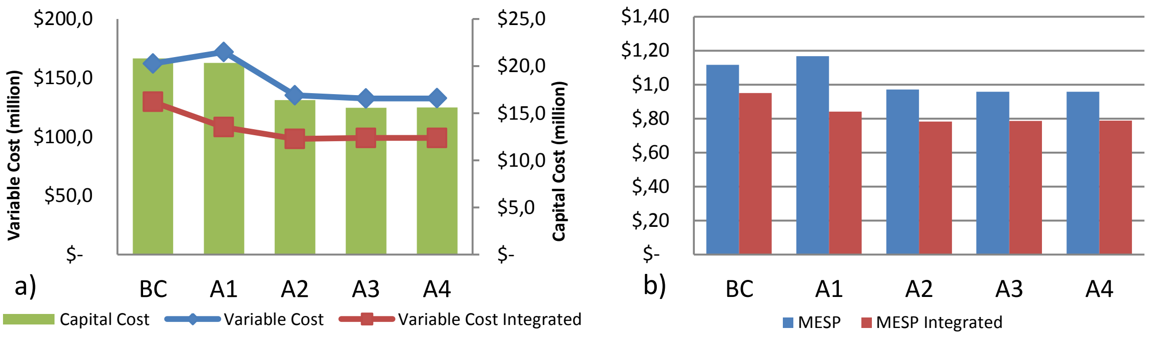

Figure 5a and 5b: (a)Capital cost (bar) and variable cost with and without energy integration (diamond and square, respectively) in millions of dollars for organosolv pretreatment base case and process alternatives; (b) Calculated MESP ($/kg of ethanol) with and without energy integration for organosolv pretreatment base case and process alternatives.

4. Conclusions

Delignification of the biomass can reduce equipment size and avoid the presence of inhibitory compounds in the biomass fermentation reactions. Organosolv pretreatment emerges as an interesting option for a high lignin biomass such as spruce. This work has highlighted the importance of the solvent recovery in the process, which was responsible for 56.5 % of the total energy consumed and 87 % of the total hot utilities required. A better understanding of the process provided an improved setup resulting on savings of approximately 15 % in the MESP for alternatives 2, 3 and 4. In addition, if energy integration was performed in the processes the savings reached 30 % in the MESP as seen for Alternative 2, due to a better management of available energy in the streams providing reductions in the utilities consumption.

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