

Optimal Simultaneous Production of Bio-i-butene and Bioethanol from Switchgrass

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Abstract.

In this work, we propose the optimal flowsheet for the production of i-butene from switchgrass. A superstructure embedding a number of alternatives is proposed. Two technologies are considered for switchgrass pretreatment, dilute acid and ammonia fibre explosion (AFEX) so that the structure of the grass is broken down. Surface response models are used to predict the yield. Next, enzymatic hydrolysis follows any of the pretreatments to obtain fermentable sugars, mainly xylose and glucose. I-butene is obtained by fermentation of the sugars. Next it is separated mainly from CO₂ for which PSA or membrane separation are considered. However, xylose cannot be easily converted, and thus we also evaluate the possibility of using it to produce bioethanol. The problem is formulated as an MINLP with simultaneous optimization and heat integration. Finally, an economic evaluation is performed. The most promising process involves the use of dilute acid pretreatment and membrane purification of the i-butene. However, the decision related to the production of i-butene alone or the simultaneous production of i-butene and ethanol depends on the prices for bioethanol and for switchgrass.

Keywords: Energy, Biofuels, Bioethanol, Mathematical optimization, Hydrolysis, Switchgrass

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Introduction

I-butene is an important intermediate that so far has been mainly obtained from the cracking of the C4 fraction of crude oil whether catalytic or thermal cracking [1]. This chemical is the basis for the production of a common additive to gasoline in search for a cleaner burning fuel, the methyl-tert-butyl ether (MTBE) as well as a monomer for the polymerization including butyl rubber as direct additive to gasoline. Its importance can be reflected in its price, around \$2/kg. However, the dependency on the crude oil, and the already limited availability due to the large number of applications, has increased the need for new sources of this chemical.

Recently, the company Global Bioenergies has patented their research on the fermentative production of isobutene, showing that bio-based isobutene production is possible [2-4]. Since isobutene is a gaseous compound at fermentative conditions, it might easily be recovered from the bioreactor. Moreover, if this compound is produced at a lower cost, its conversion into biofuel, or any other possible product, could become attractive. Also, i-butene has recently been used for the production of diesel substitutes from glycerol [5-7]. Although the main drawback of its use is its economics, from the energy and water consumption standpoint its use for the enhanced production of diesel substitutes is competitive with the process that directly sells the glycerol as byproduct. However, the expected decrease in the production cost of glycerol due to the saturation of the market, and the increased yield to fuels from oil, around 20%, when using the glycerol to obtain further diesel substitutes, have increased the interest of the production of i-butene from renewable sources.

In this paper, we study the production process of ethanol from lignocellulosic raw materials comparing two hydrolytic pretreatments of the lignocellulosic biomass and several purification methods for the i-butene produced using mathematical optimization techniques [8-9]. We propose a limited superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in i-butene production from switchgrass where we consider alternatives for some of the technologies. These units are interconnected to each other through network flows and other utility streams. The goal is to simultaneously optimize and heat integrate the production process of i-butene to assess its competitiveness with current crude based production. The optimization of the system is formulated as a mixed-integer nonlinear programming (MINLP) problem, where the model involves a set of constraints representing mass and energy balances, experimentally based models and rules of thumb for all the units in the system. Finally, an economic evaluation is also performed.

Overall Process Description.

Grinding is the first stage to reduce the size of the raw material, and to increase the contact area before pretreatment. There are a number of alternative pretreatments and a few comprehensive review papers have been published recently on the topic [10-13]. Among them the two most promising ones due to their scale up feasibility are the (1) dilute acid (H_2SO_4) pretreatment [14-17] and (2) ammonia fiber explosion (AFEX) [11,18,19]. So far both have been used to release the cellulose and hemicellulose for their hydrolysis.

Once the physical structure of the switchgrass is broken to allow the contact between the polymers and the enzymes, hydrolysis of the polymeric sugar takes place. This process is carried out in stirred tank reactors at 45-50 °C for 3 days where the accessible cellulose and hemicellulose are broken into fermentable sugars [14,15,20-22].

Next, the sugars, mainly glucose and xylose, are fermented. So far only glucose has been proved to generate i-butene using (*S. cerevisiae* bacterium). Therefore we evaluate three different options. The first one is the production of i-butene from the glucose that can be obtained from the biomass. Second, the possibility that xylose is also converted, which corresponds with the future expectations but is also feasible currently, see Figure 1. Finally, the simultaneous generation of ethanol and i-butene so that the xylose that is not converted into i-butene is fermented into ethanol using *Z mobilis* such as second generation of bioethanol production [15,23]. The gas phase consists of i-butene together with CO_2 and steam. First, we condense the water vapour accompanying the gas phase and then, two options are considered either PSA or membrane separation of the two cases. For the case where the unconverted xylose is further fermented to ethanol, we use a multieffect distillation column to separate the water – ethanol mixture and next a molecular sieves system to dehydrate the ethanol as in Martín & Grossmann [23], see Figure 1.

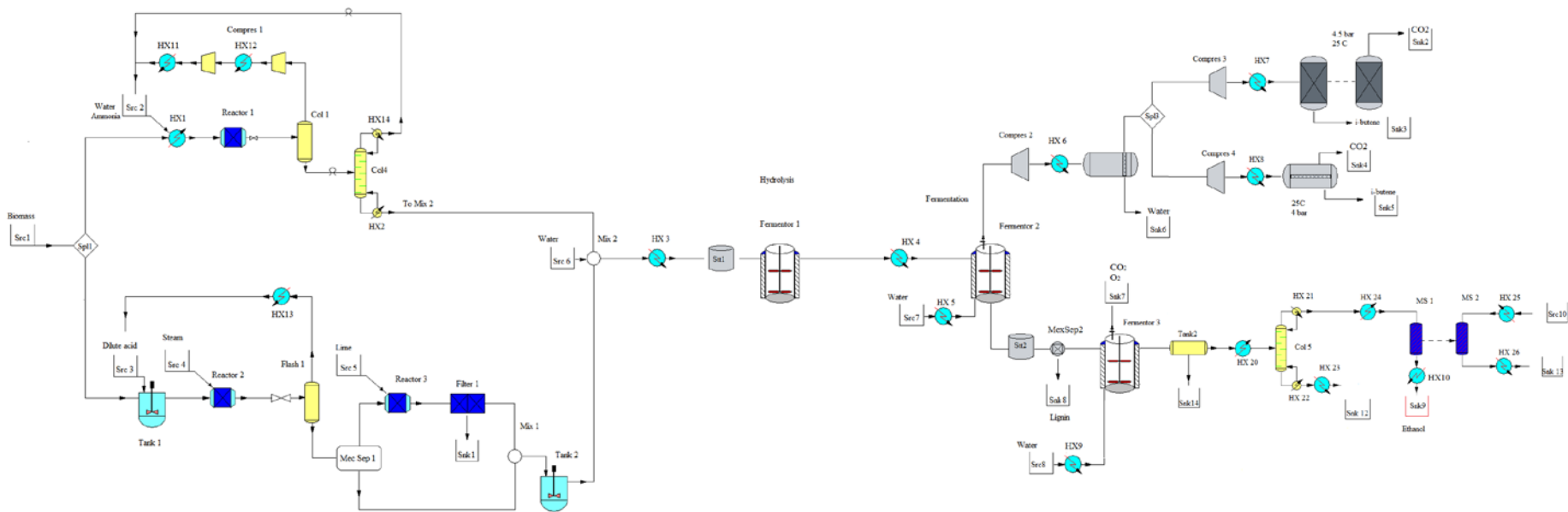


Figure 1.- Superstructure of for the simultaneous production of ligno – i-butene and lingo bioethanol.

Mathematical modelling.

All the operations in the bio-i-butene production process are modeled using short-cut models consisting of mass and energy balances, models based on the design of experiments methodology from experimental data in the literature, rules of thumb and design correlations. The model is written in terms of total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. These are the main variables whose values have to be determined in the optimization. The components in the system include those present in the switchgrass, plus those produced during the process of i-butene production, and belong to the set $J = \{ \text{Water, i-butene, ethanol, H}_2\text{SO}_4, \text{CaO, Ammonia, Protein, Cellulose, Hemi-Cellulose, Glucose, Xylose, Lignin, Ash, CO}_2, \text{O}_2, \text{Cells, Glycerol, Succinic acid, Acetic acid, Lactic acid, gypsum} \}$. The different units in the superstructure are modelled as described below, but for the sake of limiting the size of the paper we refer the reader to the supplementary material for the actual equations.

Pretreatment

In order for the fermentation to be effective, the bacteria must be able to reach the cellulose and hemicellulose. Any lignocellulosic raw material is created with a matrix of lignocellulose that protects the plant and maintains the structure. As it can be seen in Figure 2, inside the structure of the lignin, the hemicelluloses and the cellulose constitutes the structure of the plant. This structure must be broken so that the polymers of sugar (cellulose and hemicellulose) can be attacked. The feed is washed and the size of the switchgrass is reduced by grinding so that further pretreatments are more effective [10, 24]. Both stages, washing and grinding, are considered only in terms of energy consumption (45kWh/t [24]) and cost analysis since they do not change the properties of the feedstock. Next, the two alternatives indicated above, dilute acid pretreatment and AFEX, are analyzed due to their high capability to degrade this structure [11, 25-28].

Ammonia fiber explosion (AFEX): This method consists of treating the lignocellulosic material at a mild temperature and high pressure with ammonia to break the physical structure of the crop. In order to reduce the cost, the ammonia remaining in the slurry after the expansion should be recovered, and the slurry of biomass and water is sent to enzymatic treatment to break the polymers containing sugars [11,18,19,29]. The

pretreatment is modeled using the following assumptions. Garlock et al. [29] developed a design of experiments based model to evaluate the yield of the release of sugars from different switchgrass raw materials as function of the ammonia (kg / kg of biomass) and the water load, the operating temperature (C) and the contact time (min) at 20 atm.

Table 1.- Range of operating variables for dilute acid pretreatment

| | Lower bound | Upper bound |
|--------------------------|-------------|-------------|
| T (°C) | 90 | 180 |
| Ammonia (g/g dry matter) | 0.5 | 2 |
| Water (g/g dry matter) | 0.5 | 2 |
| Residence time (min) | 5 | 30 |

$$\text{Yield} = 0.01 * (-88.7919 + 26.5272 * \text{amonia_ratio} - 13.6733 * \text{water_pret} + 1.6561 * T_{\text{afex}} + 3.6793 * \text{time_pret} - 4.4631 * \text{amonia_ratio}^2 - 0.0057 * T_{\text{afex}}^2 - 0.0279 * \text{time_pret}^2 - 0.4064 * \text{amonia_ratio} * \text{time_pret} + 0.1239 * \text{water_pret} * T_{\text{afex}} - 0.0132 * T_{\text{afex}} * \text{time_pret}); \quad (1)$$

Next, the pressure is released and the content of the reactor discharged to a blowdown tank. Since the reactor operates in batch mode, at least two reactors in parallel are fed into an intermediate storage tank to ensure continuous operation [11,30]. Next, the ammonia remaining in the slurry, around 10% of the initial amount, is recovered by distillation at high pressure (15atm) [17, 31]. The distillate is at 40°C and the bottoms at 200°C [17, 41] and we assume a reflux ratio of 2. The evaporated ammonia is compressed, condensed and mixed with the ammonia recovered in the distillation column and reused again. This is the key point in the economics of this process. Following these stages, we assume that all of the ammonia is recovered. However, the traces that may be left, typically below 0.5% [30], are used as nutrients for the fermentation. Thus, we do not consider the traces in this model. We assume that after the pretreatment the monomer of glucose is generated. It will not be the molecule of glucose until the hydrolysis in which the monomer is hydrated, but for the sake of reducing the number of components, we assume that what is generated is glucose.

Dilute acid: The yield of the pretreatment depends on the operating conditions. We can identify two approaches to model it, surface response [32-34] and mechanistic kinetic based [35]. For optimizing superstructures the first approach is more convenient. Recently, Shi et al [32] studied the sugars released from lignocellulosic raw materials using dilute sulfuric acid solutions as a function of the operating temperature, the

concentration of the acid the residence time and the enzyme amount used in the hydrolysis stage. As in the previous case, we assume that after pretreatment we already have a form of glucose or xylose, which will be hydrated in the hydrolysis stage to get the sugars to be fermented. Using the experimental data provided in Shi's paper [32] we have developed DOE based models for the yield of the glucose and xylose released. In Figures 2 and 3 we can see the accuracy of the models.

Table 2.- Range of operating variables for dilute acid pretreatment

| | Lower bound | Upper bound |
|------------------------------|-------------|-------------|
| T (°C) | 140 | 180 |
| Acid concentration (%w/w) | 0.5 | 2 |
| Residence time (min) | 1 | 80 |
| Enzyme load (mg/g of glucan) | 4.8 | 96.6 |

The yield of glucose is given by:

$$\begin{aligned}
 \text{yield_cellu} = & -0.00055171 + 0.00355819 * T_acid + 0.00067402 * \text{conc_acid_mix} + \text{time_pret} * 0.00100531 - \\
 & \text{enzyme_add} * 0.0394809 - 0.0186704 * T_acid * \text{conc_acid_mix} + 0.00043556 * T_acid * \text{time_pret} \\
 & + 0.0002265 * T_acid * \text{enzyme_add} - 0.0013224 * \text{conc_acid_mix} * \text{time_pret} \\
 & - 0.00083728 * \text{time_pret} * \text{enzyme_add} + 0.044353 * \text{conc_acid_mix} * \text{enzyme_add} + 0.000014412 * T_acid^2;
 \end{aligned}
 \tag{2}$$

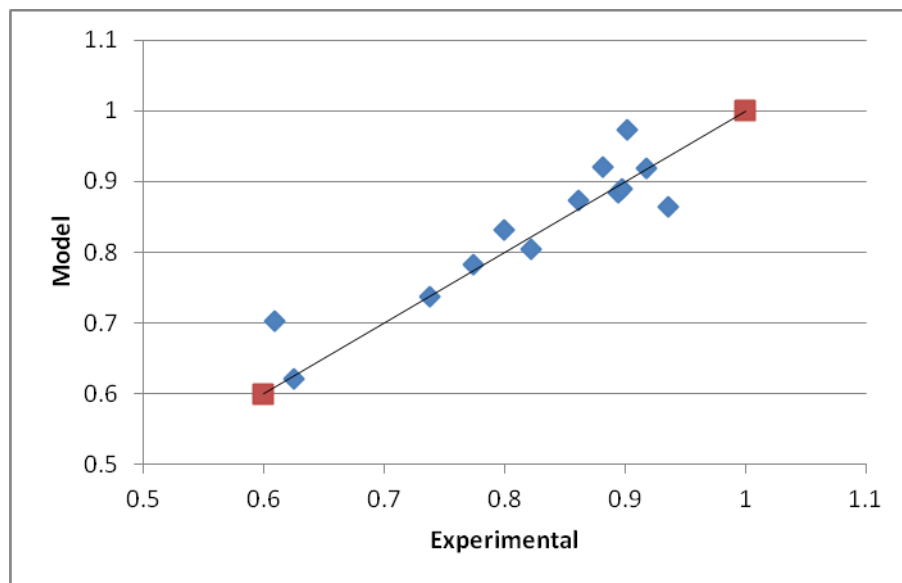


Figure 2. Model fit for glucose release

The yield of xylose is given by:

$$\begin{aligned}
 \text{yield_hemi} = & -0.00015791 - 0.00056353 * T_acid + 0.000694361 * \text{conc_acid_mix} - 0.00014507 * \text{time_pret} - \\
 & \text{enzyme_add} * 0.01059248 - 0.02142606 * T_acid * \text{conc_acid_mix} + 0.000694055 * T_acid * \text{time_pret}
 \end{aligned}$$

$$+0.00013559 \cdot T_{\text{acid}} \cdot \text{enzyme_add} - 0.00145712 \cdot \text{conc_acid_mix} \cdot \text{time_pret} \\ + 0.04769633 \cdot \text{conc_acid_mix} \cdot \text{enzyme_add} - 0.00138362 \cdot \text{time_pret} \cdot \text{enzyme_add} + 0.0000059419 \cdot T_{\text{acid}}^2; (3)$$

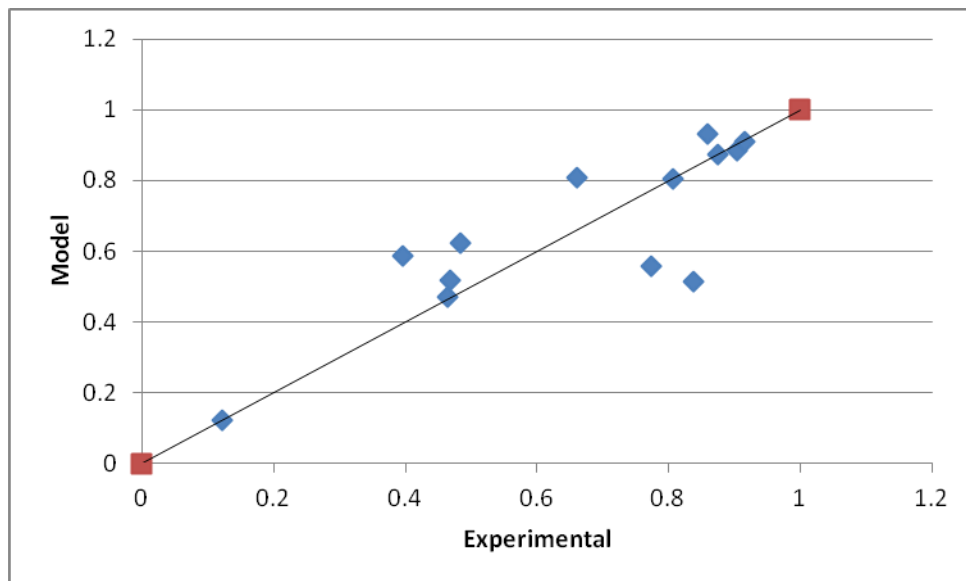


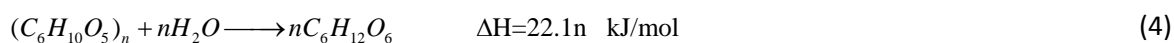
Figure 3. Model fit for xylose release

Next a flash evaporation of water (Flash 1) reduces the amount of water in the slurry and provides energy for the process. The slurry is separated in a mechanical centrifuge (Mec Sep 1). The liquid stream is treated with lime, CaO, to adjust the pH to the one needed in the hydrolysis (Reactor 3) [14-16, 36]. Lime is the cheapest chemical for this reaction due to the low cost of CaO, and also because the precipitation of gypsum (CaSO₄) that allows its easy separation from the liquid [37]. The residence time in Reactor 3 is 10 min. Neutralization reactions are exothermic, heating up the exiting stream from reactor 3. CaSO₄ (gypsum) precipitates, and can be easily recovered from the liquid stream by filtration (Filter 1). Gypsum can be sold to improve the economics of the process. The neutralized liquid stream is mixed adiabatically in tank 2 with the biomass, and the resulting slurry sent to hydrolysis.

Hydrolysis

The slurry at 50% water is hydrolyzed at atmospheric pressure to generate glucose and xylose from the polymers [14-16,21,38]. The batch process lasts for 72 h. In order to satisfy this water content, water may be

needed from Src 6. The temperature must be adjusted to 50 °C for the reaction to take place³ using heat exchanger 3. The basic reactions taking place are given by eqs. (4)-(5):



Both reactions are endothermic. It is after the hydration of the liberated monomers when glucose and xylose sugars are available in the liquid stream. Water from a reservoir (Src 6) may be fed in case the water remaining in the slurry is not enough for the operation at fermentor 1. The resulting stream has to be adjusted to a temperature of 50°C. We assume that buffer/storage tanks are used to ensure the continuous operation of the process. We neglect those tanks for simplicity in the analysis.

i-butene production

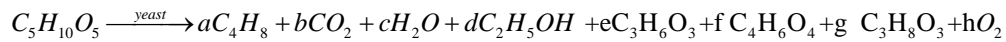
To achieve an economically and ecologically sustainable process, future isobutene processes might be focused on using lignocellulosic hydrolysate as a substrate. This might be obtained by processes that are still in the development stage [39]. Analogous to ethanol-producing microorganisms, isobutene-producing microorganisms could be engineered for conversion of all C5- and C6- sugars in lignocellulose hydrolysate into product, and for tolerance towards potential inhibitors such as furanics, phenolics, and acetic acid. The liberated sugars are fermented using a bacterium (*S. cerevisiae*). The reaction time is about 24h at atmospheric pressure. The model for the fermentor is as follows. The stream coming from the hydrolysis is cooled down to the fermentation temperature of 38 °C[14]. Water must be added to the fermentor after being heated up in heat exchanger 5 so that the final concentration of ethanol in the water is below toxic levels. To be on the safe side, we assume that the fermentation process is performed with 100 gL⁻¹ fermentable carbohydrate[40]. This value affects the water consumption of the plant, although for the production of i-butene it is not crucial. If we aim to simultaneously produce ethanol, the energy consumption in the separation stages is highly correlated with this, and therefore it will have an effect on the final production cost of the i-butene and bioethanol. Given the low aqueous solubility of i-butene, lower than 0.5% of the produced isobutene, we assume that all of it will go with the off gas.

The main reaction is given by equation (6), based on van Leeuwen et al [40].



Formation of ATP from ADP and P requires 30.5 kJ/mol and thus this is the energy involved in these reactions. A conversion of 85% based on van Leeuwen et al [40] (25 g/g vs the theoretical 31g/g) is assumed.

For the future expectations, we add the production of i-butene from xylose. This reaction is not experimentally validated yet, although some recent work [40] and patents [41] claim the possibility of generating i-butene using different carbon sources, C5 and C6. Furthermore, it is possible to reach glucose metabolism paths from xylose [42]. In order to determine the stoichiometry, and based on the pathways presented by van Leeuwen [40] we consider as products the typical ones of sugars fermentation, ethanol, lactic acid, succinic acid, glycerol, oxygen, water and CO₂.



And we maximize a, the production of i-butene, subject to

-Mass balances to the C, O and H

-b > 0

-c ≥ 0 .

-h=0 since the optimum glucose production requires anaerobic conditions [40].

- $\Delta H_{f,25C} < 0$, exothermic reaction

-Similar to the use of glucose as substrate, some ATP is generated to support cell growth and cellular maintenance. We assume the formation of 2 ATP per mol of xylose consumed.

Thus, we obtain a reaction similar to (6). To be on the conservative side, we assume a conversion for (4) of 80% for the reaction in (7)



Isobutene purification.

The off-gas from the fermentor is saturated by water. The allowable concentrations of contaminants in purified isobutene depends on its use. For simplicity, we concentrate here on the removal of CO₂, and H₂O from

isobutene only. There are several possible ways to achieve such a gas separation [43] such as stage-wise condensation to liquid, pressure swing adsorption (PSA), membrane permeation and absorption. We avoid the use of refrigerants and we use condensation only to remove part of the water vapor accompanying the gases as we compress them for further separation. Next, we consider two alternatives:

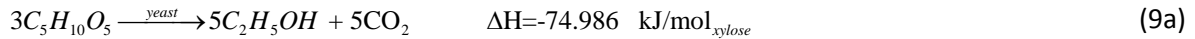
PSA: Pressure swing adsorption should be able to achieve the required purity because in an adsorption column, poorly adsorbed species will be pushed forward by stronger adsorbed species. Such an adsorption processes may use relatively expensive adsorbent material and will operate at high pressure with which the capital investment may be high. The operating conditions are 25° C and 4.5 bar.

Membranes: Separation of isobutene from CO₂ by either adsorption or permeation might be achieved using DD3R-zeolite, for example. Isobutene molecules do not penetrate in the zeolite, while carbon dioxide molecules can (van den Bergh, 2010). The operating conditions are usually 25 °C and 4 bar, and the flux of CO₂ is around $3.5 \cdot 10^{-2}$ mol/m²s [44, 45].

Final product: i-butene

Fermentation to bioethanol and solid separation.

For the case when xylose cannot be converted into i-butene, the remaining sugars are fermented using a bacterium (*Z. Mobilis*). In this way we evaluate the feasibility of producing bioethanol and i-butene simultaneously. We base our model on the one presented in Martin & Grossmann [23]. The sugars are fermented mainly to ethanol at 38 °C, but a number of secondary reactions also occur, see Table 3. The reaction time is about 24h at 1.2 bar to avoid entrance of air. The maximum concentration of ethanol in the water is 6- 8%, [14-16] even though higher values are expected in the near future [46], and water may need to be fed to the fermentor. Using the NREL data base [22, 47], the main reactions are given by equations (8) –(9) . Even though there is agreement in the literature for the conversion of glucose to ethanol, eq (8) with respect to the reaction that converts xylose to ethanol, we can find two different reactions in the literature (eqs. 9a & 9b) [15, 22]. To be on the safe side we consider (9a) for our modelling since the yield is somewhat lower. We produce 5 moles of ethanol from 3 moles of xylose, versus a ratio of 2 that can be obtained from eq. (6b) even though it would be better to obtain the yield given by this last one.



The energy balance for the fermentor is calculated based only on the two main reactions, eqs (8) – (9a). We neglect the energy in the other reactions due to their low conversions. The solids are separated from the liquid stream in a mechanical press before the stream is sent to the distillation column [48]. Thus, the cells, the lignin and other solids are recovered in a two stage process from the liquid phase so that the lignin can be used to obtain energy and improve the profitability of the process.

Table 3.- Chemical reactions in fermentor 3

| Reaction | Conversion |
|---|---------------|
| Glucose \rightarrow 2 Ethanol + 2 CO ₂ | Glucose 0.92 |
| Glucose + 1.2NH ₃ \rightarrow 6 Z. mobilis + 2.4 H ₂ O + 0.3 O ₂ | Glucose 0.035 |
| Glucose + 2 H ₂ O \rightarrow 2 Glycerol + O ₂ | Glucose 0.002 |
| Glucose + 2 CO ₂ \rightarrow 2 Succinic Acid + O ₂ | Glucose 0.008 |
| Glucose \rightarrow 3 Acetic Acid | Glucose 0.022 |
| Glucose \rightarrow 2 Lactic Acid | Glucose 0.013 |
| | |
| 3 Xylose \rightarrow 5 Ethanol + 5 CO ₂ | Xylose 0.8 |
| Xylose + NH ₃ \rightarrow 5 Z. mobilis + 2 H ₂ O + 0.25 O ₂ | Xylose 0.03 |
| 3Xylose + 5 H ₂ O \rightarrow 5Glycerol + 2.5 O ₂ | Xylose 0.02 |
| 3 Xylose + 5 CO ₂ \rightarrow 5 Succinic Acid + 2.5 O ₂ | Xylose 0.03 |
| 2 Xylose \rightarrow 5 Acetic Acid | Xylose 0.01 |
| 3 Xylose \rightarrow 5 Lactic Acid | Xylose 0.01 |

Ethanol purification.

Once the liquid stream is separated from the one with solids, the ethanol must be dehydrated to fuel grade. The first stage is a beer column to remove a large amount of water. Next molecular sieves are employed

Beer column: Multieffect distillation system

Karrupiah et al [48] and later Ahmetovic et al.[49] proved that the use of multieffect columns in the dehydration of bioethanol reduces energy consumption by one third, while cooling water consumption is reduced by a half. Thus, we implement a system of three distillation columns, modeled using shot-cut methods [50, 51]. The results, however, have been validated with process simulation. We fix the recovery of ethanol to be 0.996

and the reflux ratio for each of the columns to be 1.5. The pressure drop across the column is assumed to be 10% of the operating pressure. The distillate is a vapor since the final dehydration step requires this phase while the bottoms involves basically all the byproducts generated in the number of different reactions presented in table 3.

Final ethanol dehydration: We feed the zeolite bed with a stream that has at least a fraction of ethanol of 0.8 by weight. We heat the stream up to 95°C. For costing purposes, we consider two beds in parallel so that the second one is being regenerated to maintain continuous operation. Atmospheric air, with an assumed relative humidity of 70% at 20 °C, is heated up to 95°C, it removes the water that saturates the bed, and is cooled down to 25°C. We assume that the flow of air required is that which allows a final humidity of 70%.

Solution procedure

We consider several options to evaluate the scenarios that can be realized depending on the development of the production of i-butene for different sugars as we have presented in the process description. The first case involves the production of i-butene alone for which first we assume that only glucose fermentation generates i-butene as has been validated in the literature, and a second case where xylose is also capable of generating i-butene, based on the assumptions presented before. Taking into account that this second reaction is uncertain, we consider that the sugars that have not been used for the production of i-butene can be further fermented to generate bioethanol. For each of the cases we have several alternatives regarding the pretreatment technology, either dilute acid pretreatment or AFEX, and for the purification of i-butene using either PSA or membrane separation. We perform simultaneous optimization and heat integration for the optimal production of i-butene, or for the simultaneous production of bioethanol and i-butene. As objective function we consider a simplified production cost involving the income from i-butene (\$2/kg) and the cost for the energy, electric power for the compressors and thermal energy as steam, and for the injected steam to the acid pretreatment and the energy for the heat exchangers. Each pretreatment involves of 2600 equations and 3000 variables.

Next, we develop the heat exchanger network and perform an economic evaluation. Water consumption for each of the cases is also calculated. We follow the same procedure as in Ahmetovic et al.[49] where further details on the operation of typical units and operating parameters can be found. We identify as process units the

biomass washing step, the cooling tower and the boiler. As demand units we have the cooling tower, the boiler, the pretreatment and the fermentors and as source units either the distillation column or the solid liquid separation after the i-butene production.

Results

The production cost involves, annualized equipment, chemicals (enzymes, sulfuric acid, CaO, ammonia, and the profit from gypsum), labor, utilities, raw material and the credit that can be obtained from ethanol. The cost for the equipment such as heat exchangers, fermentors, tanks, distillation columns, mechanical separation, filters, molecular sieves is updated from the values calculated using the correlations developed by the authors, see supplementary material of Martin & Grossmann [52]. The cost for the membrane is \$1500/m² and depends on the CO₂ flux which has been determined experimentally to be 0.035 mol/m² [53]. The costs for utilities are updated from the literature (0.019 \$/kg Steam, 0.057 \$/ton cooling water [54], Electricity: 0.06 \$/kWh [55])

1.-Production of bio-i-butene

a) From glucose alone

The flowsheet is given by the upper part of Figure 1, while the bottoms of the reactor will contain lignin and secondary products. We optimize a simplified production cost given by eq (10). We do not include the cost of sulfuric acid for the dilute acid pretreatment due to the low amount required, and the fact that we can get profit for the gypsum generated. In the case of the AFEX most of the ammonia can be recovered, and thus we also neglect its effect on the simplified production cost since the ammonia that is lost is due to the nutrients required in the fermentors, and those will be accounted for in the detailed production cost. Table 4 presents the main operating parameters of the plant. The optimal flowsheet involves the use of dilute acid pretreatment and PSA for the production of i-butene. However, this is the least interesting alternative since we produce xylose that is further processed, and thus a large part of the raw material is underused. Table 7 shows the summary of the processes including energy generation and water consumption. Due to the fact that xylose is produced but not used along the process, the waste stream contains a certain amount of xylose that is not rejected. Therefore, it makes no sense to calculate the water consumption of this alternative since xylose is an organic contaminant in that stream, but in

fact it should be raw material for another product. Even though this process is not an acceptable option, it represents a lower bound to the profitability of the process.

$$Z = C_{ibut} m(\text{Ibut}) + C_{Steam} \left(\sum_i Q / \lambda + m(\text{Wa}) \right) + C_{elect} \sum_i W_{Compres} \quad (10)$$

Table 4.-Main operating parameters production of i-butene using glucose alone

| | ACID | AFEX |
|--------------------------------|----------|----------|
| Acid concentration/ammonia w/w | 0.005 | 1.318 |
| T(°C) | 151 | 138 |
| Enzyme added mg/g of glucan | 44 | |
| Time (min) | 11 | 23 |
| Water ratio w/w | 1.5 | 2 |
| Sep technology | Membrane | Membrane |

b) From glucose and xylose

In this option we consider the flowsheet given by Figure 1, but the advantage is that all the sugars, C5 and C6, are fermented towards the production of i-butene, while the waste stream coming from fermentor 2 contains the residue and lignin that is recovered to provide energy for the plant. We maximize eq. (11) involving the use of utilities, heat, electricity or steam for the optimal production of i-butene. Again the best process involves the use of dilute acid pretreatment, but in this case membrane purification of the i-butene is selected. Table 5 summarizes the main operating parameters of both pretreatment alternatives. In Table 7 we display the main economic parameters of this option. We see that the production cost is promising (based on \$30/t of switchgrass). Due to the volatility of the biomass price, a sensitivity study is performed in order to evaluate the actual profitability. This study is presented in the next section of the paper.

$$Z = C_{ibut} m(\text{Ibut}) + C_{Steam} \left(\sum_i Q / \lambda + m(\text{Wa}) \right) + C_{elect} \sum_i W_{Compres} \quad (11)$$

Table 5.-Main operating parameters production of i-butene using glucose and xylose

| | ACID | AFEX |
|--------------------------------|----------|-------|
| Acid concentration/ammonia w/w | 0.02 | 1.776 |
| T(°C) | 159 | 144 |
| Enzyme added (mg/g of glucan) | 79.4 | |
| Time (min) | 80 | 19 |
| Water_ratio (g/g dry) | 1.5 | 2 |
| Sep technol | Membrane | PSA |

2.-Simultaneous production of bioethanol and bio-butene.

For this case we fully use the plant, but we evaluate the possibility of generating two products of interest, bioethanol and i-butene. The advantage is the flexibility of the plant. We use glucose to generate the i-butene, following the results reported in the literature [40], while use make use of the xylose to produce ethanol similar to second generation bioethanol production plants [23]. We optimize the objective function given by eq. (12) where we assume a price for i-butene of \$2/kg, typical of this product, and for ethanol we assume \$1/kg. Table 6 summarizes the main operating data. The optimal process involves the use of dilute acid pretreatment followed by i-butene recovery using membranes. We see that the operating parameters vary by a small amount to the ones presented in previous processes. There is lower used of the enzymes in the hydrolysis of the polymers, and the acid concentration is lower. The profitability of this option, compared to the previous one where we can only produce i-butene, depends largely on the price of the ethanol and that of the biomass. The credit due to the ethanol indicates what the simultaneous production of ethanol and i-butene is preferred. Thus, in the next section we evaluate the effect of the biomass and ethanol prices on the selection between simultaneous production of ethanol and i-butene or i-butene alone. In any case, both are more promising that the first case where only glucose could be used:

$$Z = C_{ibut} m(\text{Ibut}) + C_{EtOH} m(\text{EtOH}) + C_{Steam} \left(\sum_i Q / \lambda + m(\text{Wa}) \right) + C_{elect} \sum_i W_{Compres} \quad (12)$$

Table 6.-Main operating parameters production of i-butene using glucose and ethanol

| | ACID | AFEX |
|----------------------------------|-------|-------|
| Acid concentration/ammonia (g/g) | 0.005 | 1.79 |
| T(°C) | 151 | 144 |
| Enzyme added (mg/g of glucan) | 44 | |
| Time (min) | 11 | 19 |
| Water ratio (g/g) | 1.5 | 2 |
| Sep. Tecnol | Membr | Membr |
| Beer α 1 | 0.084 | 0.082 |
| Beer α 2 | 0.237 | 0.234 |
| PLO(bar) | 180 | 275 |
| PLO/PI | 2.15 | 2.36 |
| PI/PH | 2.05 | 2.79 |

Table 7.- Summary of production cost, energy and water consumption

| | Acid pretreatment | | | AFEX | | |
|---|-------------------|----------|--------------------------|------------|----------|----------------------|
| | lbut gluc. | lbut g+x | lbut+etoh | lbut gluc. | lbut g+x | lbut+etoh |
| η (kg/kg biomass) | 0.086 | 0.15 | 0.22 | 0.072 | 0.13 | 0.19 |
| Prod cost \$/kg | 0.75 | 0.45 | 0.92 | 1.05 | 0.60 | 1.08 |
| Prod cost \$/kg after cred (etOH \$1/gal) | - | - | 0.39 | - | | 0.55 |
| Energy generated/kg ibut | 33MW | 19MW | 22MW | 46MW | 24MW | 36.6MW |
| Water consump (gal/kg i-butene) | Na | 0.52 | 1.91 | Na | 1.91 | 4.58 |
| Prod capacity (ibut/etOH) | 48.5Mt/yr | 85Mt/yr | 48.5Mt/yr 25.6Mgal/yr | 40Mt/yr | 73Mt/yr | 41Mt/yr 22Mgal/yr |
| Investment (MM\$) | 122 | 143 | 188 | 189 | 202 | 204 |

Therefore, we can identify the dilute acid pretreatment to be the preferred one and the membrane separation. For the two alternatives, either the production of i-butene, or the simultaneous production of bioethanol and i-butene, Figure 4 shows the detailed production cost distribution and Table 8 the corresponding values. We base the cost of chemical, labor and maintenance on the operation of that second generation bioethanol plant which involves the same feed of raw material [23, 48]

Table 8.- Summary of production cost break down

| | <i>I-butene</i> | | <i>Bioethanol + I-butene</i> |
|------------------------|----------------------------|--|-------------------------------------|
| <i>Cost type</i> | <i>Annual Costs (MM\$)</i> | | |
| Equipment (annualized) | 10.9 | | 14.6 |
| Electricity | 2.9 | | 2.9 |
| Salaries | 1.9 | | 1.9 |
| General + Admn. | 1.7 | | 1.7 |
| Chemicals | 6.5 | | 6.5 |
| Maintenance | 1.3 | | 1.3 |
| Switchgrass | 1.7 | | 1.7 |
| Other expenses | 1.2 | | 1.2 |
| Steam | -5.4 | | -3.6 |
| Cooling water | 0.4 | | 1.1 |
| Total | 38.3 | | 44.5 |
| Kg ibut | 85.2 | | 48.5 |
| \$ / kg i-butene | 0,45 | | 0,92 |
| Credit (MM\$) | 0 | | 25.7 |
| \$ / kg i-butene | | | 0,39 |
| Energy Lignin (MW) | 51 | | 34 |

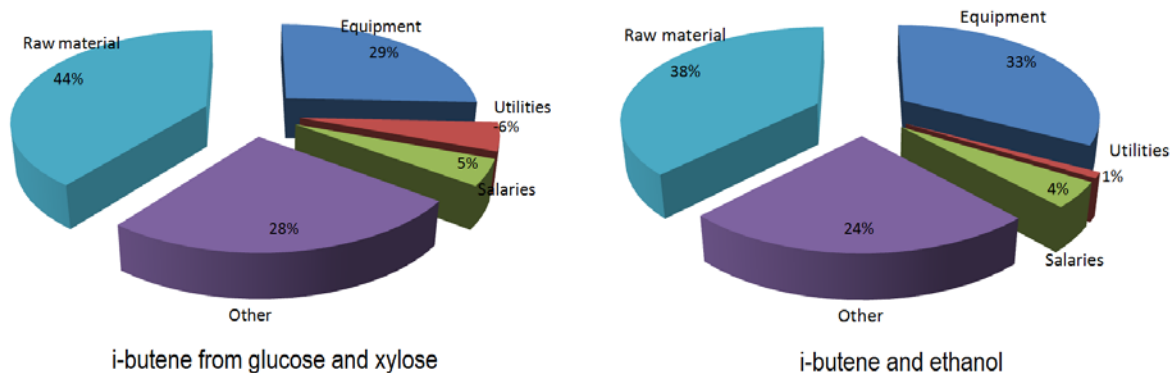


Figure 4.- Detail for the production cost break down.

3.-Sensitivity analysis.

-The cost of biomass

The biomass price is volatile, and together with the high dependency of the production cost of any biorelated product to its cost a sensitivity study is in order in terms of the price of the biomass, and in case of producing ethanol, with the price of ethanol. In Figure 5 we present the competitiveness of the process by which we can produce i-butene from xylose and glucose compared to the one that produces i-butene and ethanol simultaneously. We can see that as the price of ethanol increases, the second process is preferred until a higher price of biomass is reached. However, we can always find a trade off price for biomass from which the production of i-butene alone is the best option. Finally, for the target price of \$0.9/kg [40] we need biomass prices below \$100/t .

The AFEX pretreatment has lower yield due to the energy related to the recovery of ammonia. Figure 6 shows the results for the sensitivity analysis. As it can be seen, lower prices of biomass are required to keep the i-butene production cost below the target of \$0.9/kg. Again there is always a breakeven point for the pair biomass price/bioethanol cost for which we should select either the i-butene production mode or the production of ethanol and i-butene simultaneously.

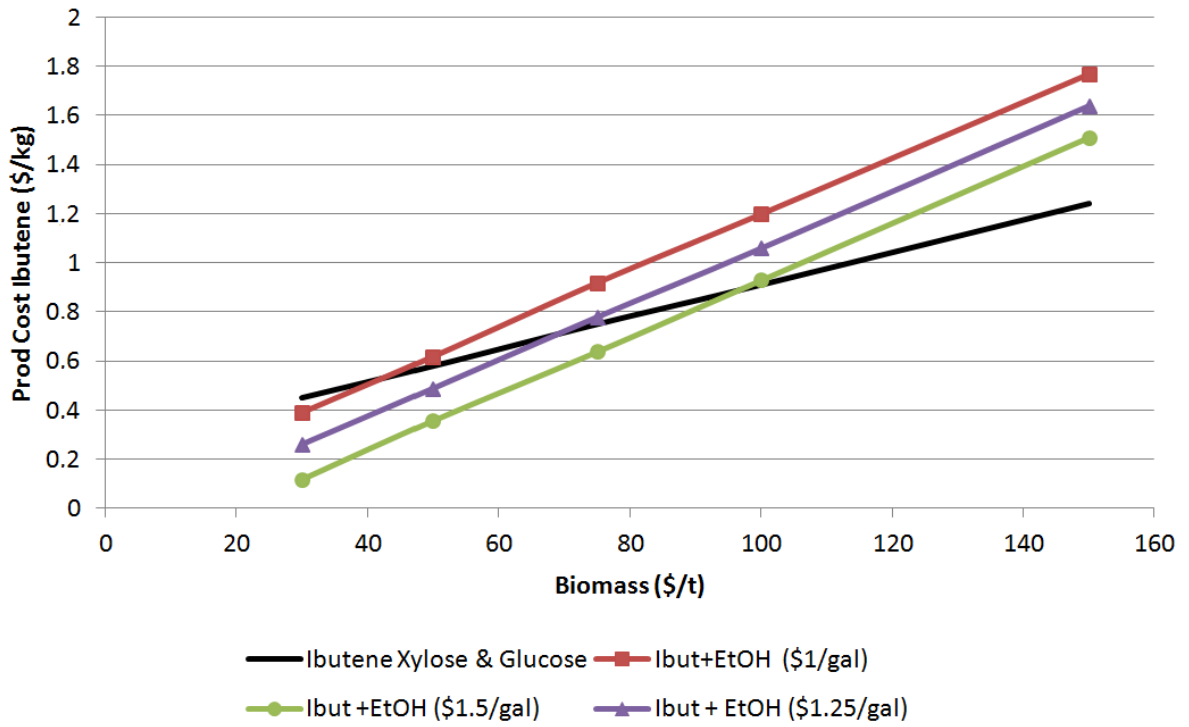


Figure 5.- Sensitivity study for the dilute ACID pretreatment

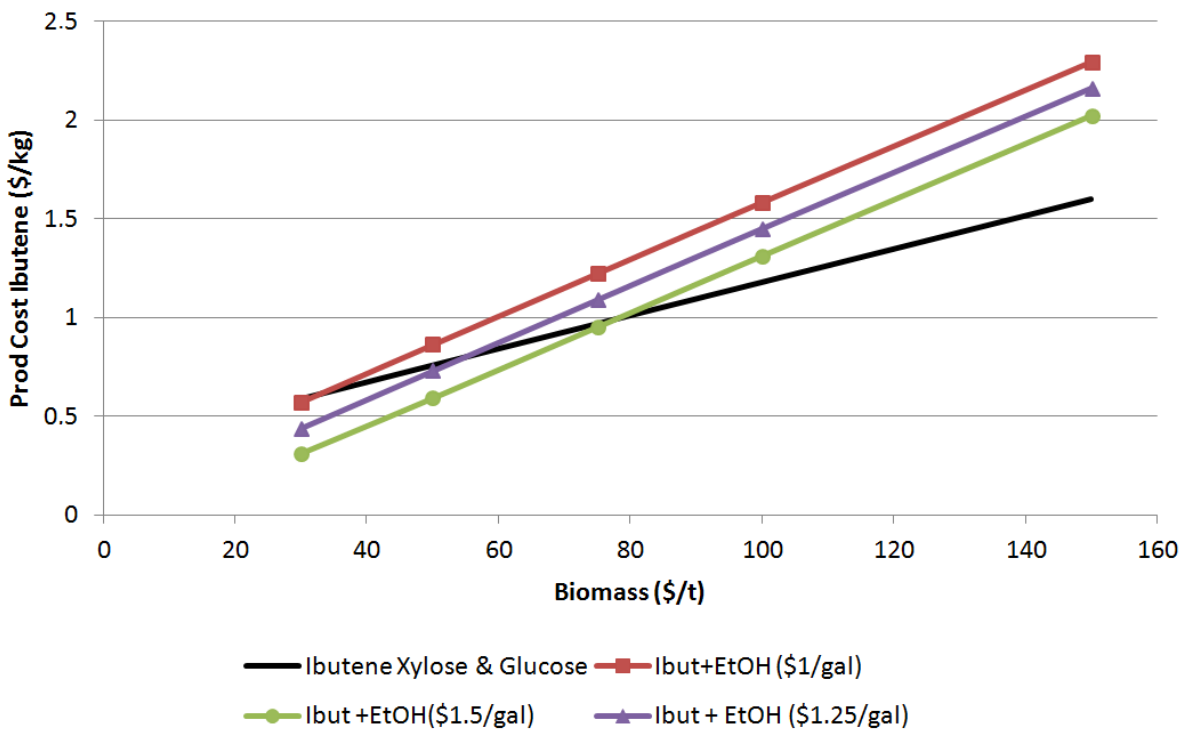


Figure 6.- Sensitivity study for the dilute AFEX pretreatment

-Integration capability

In a previous paper by the authors, the production of diesel substitutes from glycerol was evaluated (Martín & Grossmann, 2013). In that paper the main drawback was the high cost of i-butene and its non renewable origin. Therefore, there was scope for the evaluation of the production of i-butene from renewable sources to evaluate its profitability. If we revisit Figure 7 of Martín & Grossmann [7] we can see that for i-butene production prices below \$1/kg, the simultaneous production of biodiesel, diesel substitutes and bioethanol is promising. Comparing the results presented in the sensitivity study above, it can be seen that there is possibility of integrating that production facility of biodiesel and glycerol ethers from algae with the one presented in this paper. In particular, the integration is interesting for production levels of biodiesel and diesel substitutes of 92 Mgal/yr and bioethanol of 37Mgal/yr so that there is no need for non renewable energy source. In this case the energy generated from the lignocellulosic biomass can cope with the one in that facility, with no need for intermediates such as methanol or i-butene, from non renewable sources, with production prices that are very promising.

Conclusions.

The production of i-butene from lignocellulosic switchgrass has been evaluated considering different scenarios related to the possibility of obtaining it from glucose, or from glucose and xylose simultaneously, and incorporating the use of the non fermented sugars to the production of bioethanol simultaneously.

We use a superstructure optimization approach to simultaneously optimize and heat integrate the production of i-butene and ethanol. We developed reduced order models for the pretreatments, using experimental data, short cut and "black box" based models for the units involved. We also propose a stoichiometry for the use of xylose as carbon source for bioi-butene.

The most promising process involves the use of dilute acid pretreatment and membrane purification of the i-butene. However, the decision related to the production of i-butene alone or the simultaneous production of i-butene and ethanol depends on the prices for bioethanol and for switchgrass. As the price of ethanol increases, the simultaneous production of both products is favored up to higher costs for the switchgrass. In both cases, the

production of i-butene using renewable sources is feasible and may be competitive for its use to generate diesel substitutes, see Martín & Grossmann [7].

Nomenclature

| | |
|----------------------------|--|
| amonia_ratio | Ratio of ammonia added vs. dry biomass to afex pretreatment (g/g dry matter) |
| conc_acid_mix | Acid concentration at pretreatment (%w/w) |
| C_i | Material cost (\$/Kg or kW) |
| enzyme_add | Ratio of enzyme added to hydrolysis for acid pretreatment (mg/g of glucan) |
| Fcp(unit) | Flow heat capacity (kg/s· kJ(kg K)) |
| m (J) | mass flow of component J (kg/s) |
| Q(unit) | thermal energy involved in unit (kW) |
| QS_max | Integrated hot utility (kW) |
| Tpinch(pinches) | Temperature pinch (°C) |
| T(Unit, Unit1) | Temperature of the stream from unit to unit 1 (°C) |
| time_pret (min) | Time for acid pretreatment |
| T_acid (°C) | Operating temperature acid pretreatment |
| T_afex (°C) | Operating temperature afex pretreatment |
| Time_pret (min) | Time for afex pretreatment |
| water_pret(g/g dry matter) | Ratio of water added to afex pretreatment |
| W(unit) | electrical energy involved in unit (kW) |
| yield | yield of the pretreatment |
| λ | Latent heat steam (kJ/kg) |

Appendix

Wa: Water
 Ibut: I-butene
 EtOH: Ethanol
 CaO: Lime
 CaSO₄ : gypsum
 H₂SO₄ : Sulfuric acid
 CO₂: Carbon dioxide
 O₂ : Oxygen.

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