AIChE

Energy Optimization of Bioethanol Production Via Hydrolysis of Switchgrass

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DOI 10.1002/aic.12735

The optimal flowsheet for the production of bioethanol from switchgrass via hydrolysis is proposed in this work. A superstructure embedding a number of alternatives is proposed. Two technologies are considered for switchgrass pretreatment, dilute acid and ammonia fiber explosion so that the structure of the grass is broken down. Next, enzymatic hydrolysis follows any of the pretreatments to obtain fermentable sugars, mainly xylose and glucose. Ethanol is obtained by fermentation of the sugars. To obtain fuel quality, ethanol and water must be removed from the water–ethanol mixture. A number of dehydration technologies is considered including rectification, adsorption in corn grits, molecular sieves, and pervaporation. The problem is formulated as a mixed-integer nonlinear programming (MINLP). The superstructure is optimized by decomposing the MINLP for each of the pretreatments. Then, multieffect columns and heat integration are used to reduce the energy consumption and cooling needs. Finally, an economic evaluation is performed. The optimal flowsheet consists of using dilute acid hydrolysis followed by molecular sieves as dehydration technology, which requires less energy and cooling and yielding a promising production price of 0.8 \$/gal. © 2011 American Institute of Chemical Engineers AIChE J, 58: 1538–1549, 2012

Keywords: energy, biofuels, bioethanol, mathematical optimization, hydrolysis, switchgrass

Introduction

The current trend toward environmentally friendly energy sources and the lack of security in fossil fuel supply has encouraged several such as the US and the European Union (EU) to propose policies that support the use and production of alternative fuels. Thus, ethanol has become the most promising short-term alternative fuel because of its compatibility with the current car engines and gasoline supply chain.[1] To increase the use of ethanol, the so-called 20-10 plan as well as the Alternative Fuels Standard proposes a large increase in the production of ethanol from corn and lignocellulosic raw materials.[2] The EU aims to replace diesel and gasoline with biofuels by 5.75% in 2010 and 10% by 2020.[3]

Together with the large increases in production capacity required by the different policies mentioned above and to reduce the pressure on food related raw materials, the resources allocated to increase the production of ethanol are in the direction of developing more efficient processes and the use of different raw materials. Therefore, the so-called second generation of biofuels, and in particular lignocellulosic ethanol, has gained support due to the high yield from the crop to ethanol, providing a higher net fossil fuel displacement, as well as in the production process in terms of energy balance and net greenhouse gas emissions with a price far lower than the best estimates using corn as raw material.[4,5] Among the different raw materials, energy crops such as switchgrass are gaining support due to the high yield from the ground to ethanol and, thus, in this article, we focus on this particular raw material. Currently, no production process from lignocellulosic raw materials is available due to existing technical, economic, and commercial barriers that need to be overcome.[6] However, Bioenegineering Resources Inc. (BRI) and Coskata[7] industries are already running pilot plants based on fermentation of syngas and planning the construction of commercial plants in the near future.

Two different production routes can be used to produce ethanol from lignocellulosic switchgrass, either biomass hydrolysis or biomass gasification. A previous paper by the authors[8] proposed an optimized conceptual production process for the production of bioethanol via gasification of switchgrass with very promising results in terms of energy consumption and production cost. However, gasification processes have faced some criticism due to the complexity of the production process and the high capital investment. The hydrolytic path is based on the hydrolysis of the raw material to break down the structure of the crops into sugars, which are fermented to ethanol. On the one hand, due to its similarity with the current ethanol production processes from corn or sugars, together with the expected lower investment cost of the plant, it has received increased attention over the last few years.[9–13] Most of the papers do not consider the pretreatment of the raw material in their analysis or in the model of the process, and its selection is based on literature review. Recently, Kazi et al.[14] presented a case study to evaluate different technologies including the pretreatment

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stage, revealing that dilute acid and ammonia fiber explosion (AFEX) pretreatments were the most economical ones. On the other hand, the main disadvantage of the hydrolytic-based production of ethanol is the fact that lignin cannot be processed, and, thus, a part of the carbon source of the raw material cannot be used to obtain ethanol.

In this article, we study the production process of ethanol from lignocellulosic raw materials comparing two hydrolytic pretreatments of the lignocellulosic biomass using mathematical optimization techniques.[15,16] We propose superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in ethanol production 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 optimize the structure minimizing the energy input in the ethanol production process. 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 for all the units in the system. This problem is solved decomposing the MINLP into two NLP subproblems to determine the structure of the process flowsheet. We then optimize the distillation columns by using multieffect columns, and finally we perform a heat integration analysis of the resulting process. The heat recovery network, together with a modified distillation column design, further reduces the energy consumption and the cooling requirements in the plant. Finally, an economic evaluation is also performed.

Overall Process Description

There are a number of pretreatment technologies for the hydrolytic production of ethanol from lignocellulosic biomass. Several papers present comprehensive reviews of the different technologies that are available.[12,17–22] We can classify the pretreatments into:

1. Physical pretreatment like grinding, milling, or chipping to reduce the size of the raw material. This stage is used to reduce the crystallinity of the cellulose fibers in the biomass and is highly dependent on the requirements of the process. Hydrolysis requires small size of the particles to avoid mass and heat transfer limitations, while gasification is not so demanding.
2. Physicochemical pretreatment such as steam explosion, CO_2 explosion, or AFEX. To date only AFEX has been applied.
3. Chemical pretreatment including the use of ozone, acids, alkali, organic solvents, and peroxides.
4. Biological pretreatment. Currently, no biological treatment is available as it is a very slow process that makes in unattractive at an industrial level.

The use of any one of the technologies or a combination of them depends on the raw material as their effectiveness toward breaking the structure of the biomass depends on the plant itself. Typical lignocellulosic crops include energy cane, sorghum, miscantus, switchgrass, water hyacinth, municipal solid waste, and agricultural residues.[23] Among them, switchgrass is particularly interesting because of its potential for reducing emissions and its high yield toward ethanol.[24–27]

Grinding is the first stage to reduce the size of the raw material and to increase the contact area for any other pretreatment. Next, to make the sugar-containing polymers accessible to the enzymes, two methods have been found to be competitive for industrial production of ethanol from hydrolysis of switchgrass due to the high yield toward the liberation of cellulose and hemicelluloses from the matrix of the crop: (1) dilute acid (H_2SO_4) pretreatment[3,11,13,28] and (2) AFEX.[18,29,30] This last method loses effectiveness in lignocellulosic materials like newspaper or aspen chips due to the lignin content and plant structure. Both pretreatments are considered in the model.

Once the physical structure of the switchgrass has been 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.[3,9,11,31,32]

Next, the sugars, mainly glucose and xylose, are fermented into ethanol. The reactions are different in terms of yield and kinetics. The optimal conditions are 28–38°C so that both are fermented at the same time for a day. A number of different products are obtained together with ethanol, such as different acid products of the metabolic paths of the microorganisms used (*Z. mobilis* bacterium) as well as cells are grown.[3,11,32]

The separation stages start with the removal of solids, lignin, and cells from the liquid slurry coming out of the fermentor using a mechanical separator. The lignin can be used to obtain energy for the process. Finally, to achieve fuel-grade ethanol, water from the ethanol–water mixture must be removed. A distillation column will remove most of the water. Next, we propose a superstructure similar to the one in a previous work by the authors.[8] Four possibilities are presented: rectification column, adsorption in corn grits, molecular sieves, and pervaporation. Rectification and corn adsorption cannot produce fuel-quality ethanol by themselves, thus, the exiting streams will feed either the molecular sieves or the pervaporation membranes. Figure 1 shows the flowsheet with the different alternatives.

Mathematical Modelling

All the operations in the bioethanol production process are modeled using short-cut models consisting of mass and energy balances and design correlations. The model is written in terms of the 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 from the optimization. The components in the system include those present in the switchgrass, plus those produced during the process of ethanol production, and belong to the set $J = \{$water, ethanol, H_2SO_4, CaO, ammonia, protein, cellulose, hemi-cellulose, glucose, xylose, lignin, ash, CO_2, O_2, cells, glycerol, succinic acid, acetic acid, lactic acid, gypsum$\}$. The different units in the superstructure are modeled as described below, but for the sake of reducing the length of the article we refer the reader to the Supporting Information for the actual equations.

Pretreatment

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

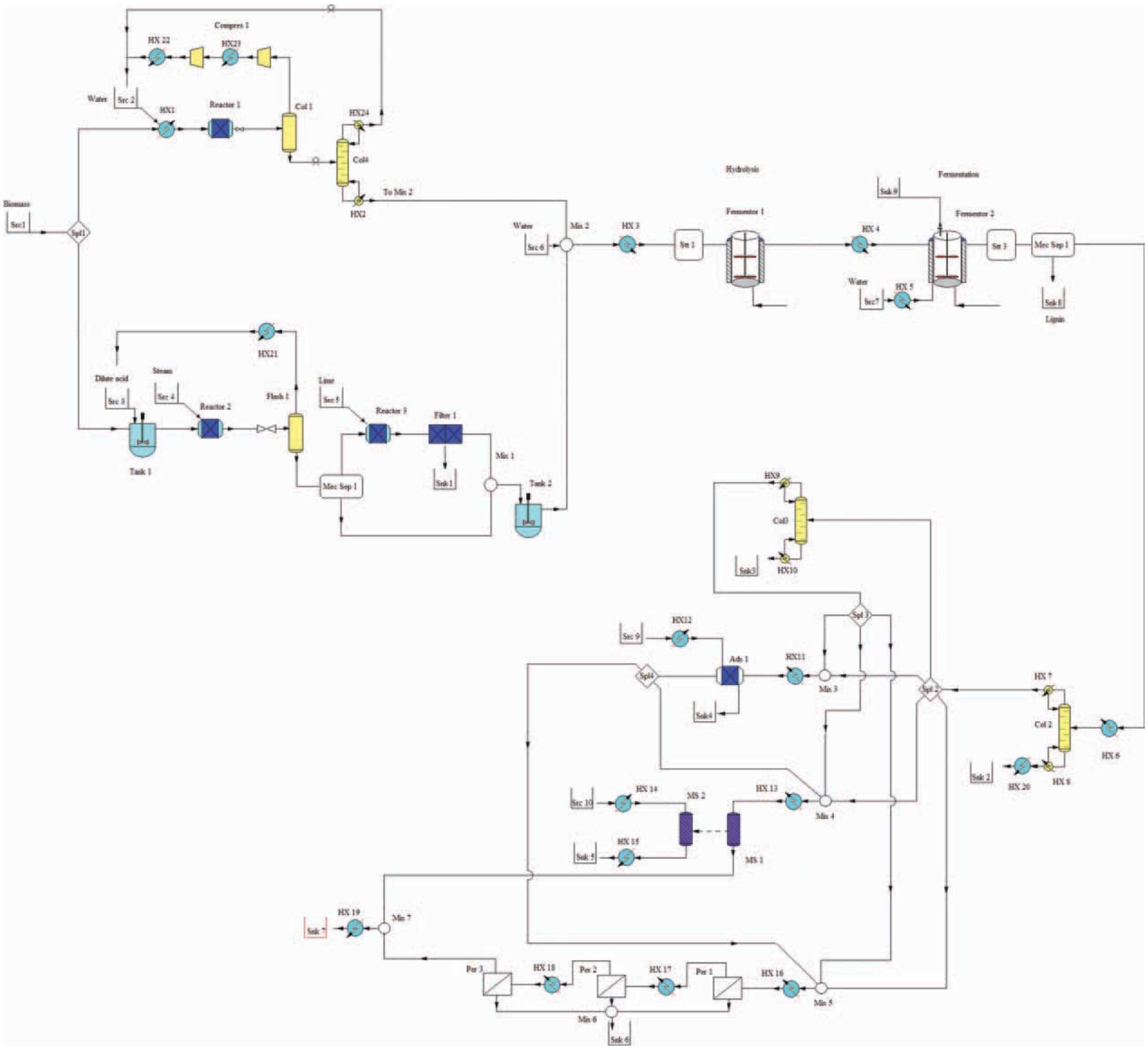

Figure 1. Superstructure of the ligno–ethanol production plant via hydrolysis.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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.[12,33] Both stages, washing and grinding, are considered only in terms of energy consumption (45 kW h/ton[33]) and cost analysis as 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.[18,23]

Amonia fiber explosion

Figure 3 shows a detail of the AFEX pretreatment. 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. 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.[18,29,30] The pretreatment is modeled using the following assumptions.

Ammonia is added in a ratio of 1 kg ammonia per kg of biomass based on the results by Sun and Cheng.[18] Water is also needed at a ratio of 0.6 kg water per kg biomass.[18,29,30] The mixture is heated up to the operating temperature of

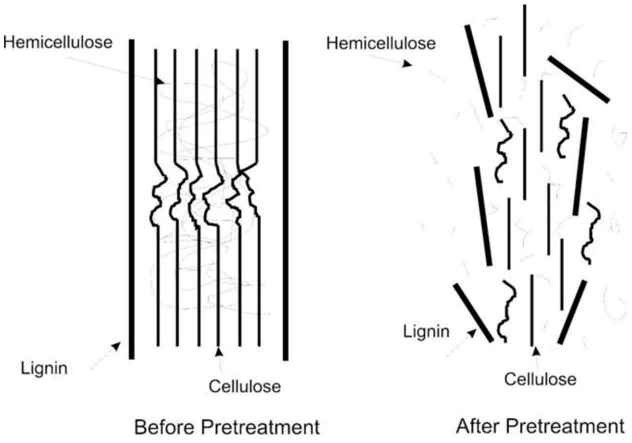

Figure 2. Lignocellulosic structure.

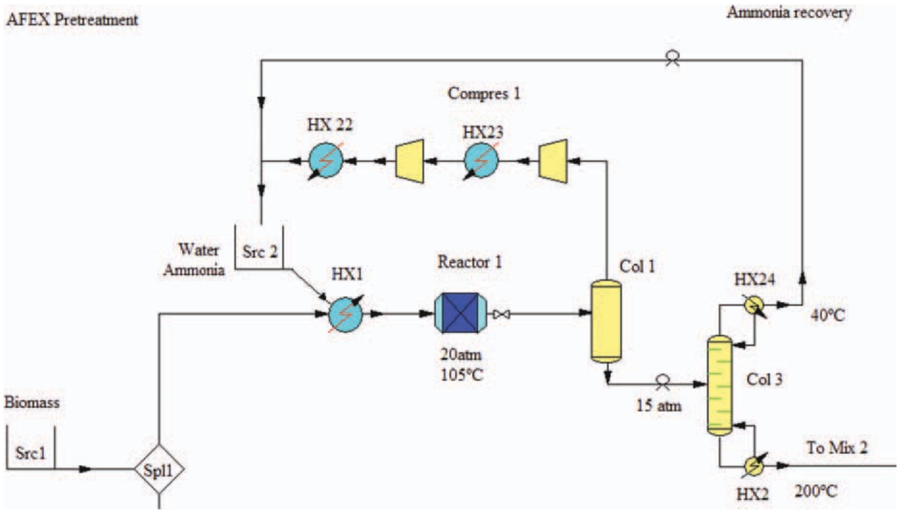

Figure 3. Flowsheet for AFEX pretreatment.

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105°C in heat exchanger (HX) 1 and fed to the reactor. The residence time in the reactor is 5 min at 20 atm, and next the pressure is released and the content of the reactor discharged to a blowdown tank. As the reactor operates in batch mode, at least two reactors in parallel are fed into an intermediate storage tank to ensure continuous operation.[18,34] Next, the ammonia remaining in the slurry, around 10% of the initial amount, is recovered by distillation at high pressure (15 atm).[14] The distillate is at 40°C and the bottoms stream at 200°C[14] 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%,[34] and they are used as nutrients for the fermentation. Thus, we do not consider the traces in this model.

According to the literature,[9,18,29] AFEX pretreatment liberates 92% of the glucose and 70% of the xylose from switchgrass making it effective for the hydrolysis step. However, AFEX performance loses its efficiency for lignin content above 10%[18] making it unattractive for other raw materials. 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

Figure 4 shows part of the flowsheet for dilute acid pretreatment. Dilute acid treatment consists of putting into contact the lignocellulosic material with a dilute solution of sulfuric acid. A solution of sulfuric acid is mixed with the biomass and later heated up with steam up to 180°C and 12 bar. The final concentration of acid in the water is fixed to be 1.2% w/w, which is obtained considering the condensed water from the steam together with the water coming from the previous stage, Tank 1. The source of fresh water from Src3 as well as in the form of steam, Src4, are calculated to verify the energy balances and water requirements in the process. In Reactor 2, the residence time is 30 min.[28] 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).[3,11,13,28] It is

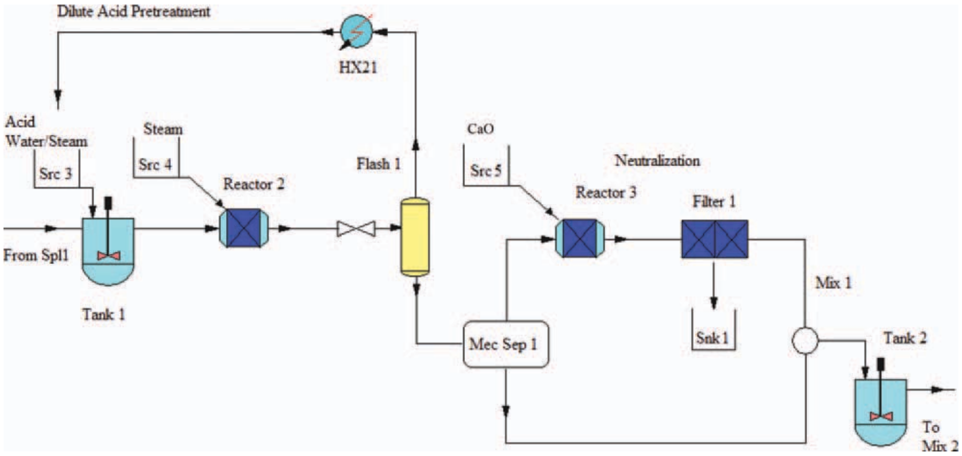

Figure 4. Dilute acid pretreatment.

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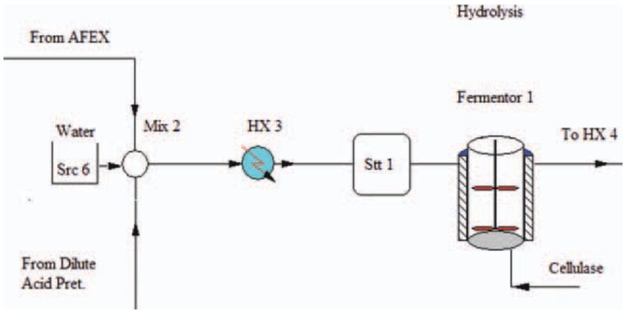

Figure 5. Flowsheet for hydrolysis.

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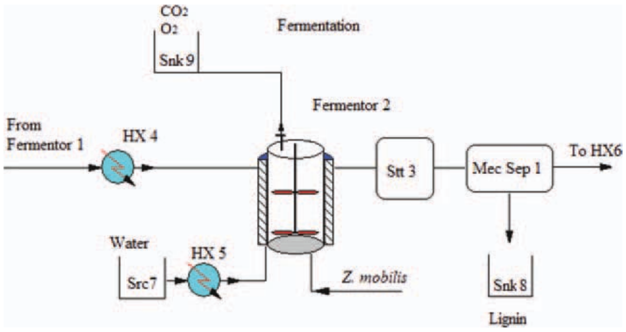

Figure 6. Detail of flowsheet for fementor.

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reported that lime is the cheapest chemical for this reaction due to the low cost of CaO and also because the precipitation of gypsum ($CaSO_4$), which allows its easy separation from the liquid.[35] The residence time in Reactor 3 is 10 min. Neutralization reactions are exothermic, heating up the exiting stream from Reactor 3. $CaSO_4$ (gypsum) precipitates and it 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 was sent to hydrolysis.

According to the literature, it is assumed that 90% of glucose as well as 90% of xylose are liberated from the crop.[12] As in the previous case, we assume that the monomers generated are the sugars themselves, even though actually they will not become sugars until the hydrolysis.

Hydrolysis

The slurry at 50% water is hydrolyzed at atmospheric pressure to generate glucose and xylose from the polymers.[3,9,11,31,32] The batch process lasts for 72 h. 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 place[3] using HX 3. Figure 5 shows a part of the flowsheet for the hydrolysis. The basic reactions taking place are given by Eqs. (1) and (2)

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_12O_6 \quad \Delta H = 22.1n\ \text{kJ/mol} \tag{1}$$

$$(C_5H_8O_4)_m + mH_2O \rightarrow mC_5H_{10}O_5 \quad \Delta H = 79.0m\ \text{kJ/mol} \tag{2}$$

Both reactions are endothermic and require energy. 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 when 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.

Fermentation and solid separation

The liberated sugars are fermented using a bacterium (*Z. Mobilis*). The reaction time is about 24 h at atmospheric pressure. Furthermore, a number of secondary reactions also take place where glycerol and different acids are generated. Once the sugars are liberated, they are fermented. Figure 6 shows a scheme of the fermentation process. Table 1 summarizes the reactions and conversions where a number of compounds such as gycerol as well as different acids are generated together with CO_2 and O_2. The maximum concentration of ethanol in the water is 6–8%[3,11,32] even tough higher values are expected in the near future.[36]

The model for the fermentor is as follows. The stream coming from the hydrolysis is cooled down to the fermentation temperature of 38°C.[3] Water must be added to the fermentor after being heated up in HX 5 so that the final concentration of ethanol in the water is below toxic levels. At this point, the chemical reactions presented in Table 1 are considered. Using the National Renewable Energy Lab (NREL) database,[37] the main reactions are given by Eqs. (3) and (4)

$$3C_5H_{10}O_5 \xrightarrow{\text{yeast}} 5C_2H_5OH + 5CO_2 \quad \Delta H = -74.986\ \text{kJ/mol}_{\text{xylose}} \tag{3}$$

$$C_6H_{12}O_6 \xrightarrow{yeast} 2C_2H_5OH + 2CO_2 \Delta H = -84.394\text{kJ/mol} \tag{4}$$

The balance for the different species in the reactor is given by the reactions and conversions in Table 1. The gases generated in the reactions, CO_2 and O_2 are discharged from the reactor. The energy balance for the fermentor is calculated based only on the two main reactions, Eqs. (1) and (2) 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. Based on the studies by Karuppiah et al.,[38]

Table 1. Chemical Reactions in Fermentor 2

Reaction	Conversion
Glucose → 2ethanol + $2CO_2$	Glucose 0.92
Glucose + $1.2NH_3$ → 6*Z. mobilis* + $2.4H_2O$ + $0.3O_2$	Glucose 0.035
Glucose + $2H_2O$ → Glycerol + O_2	Glucose 0.002
Glucose + $2CO_2$ → 2succinic acid + O_2	Glucose 0.008
Glucose → 3acetic acid	Glucose 0.022
Glucose → 2lactic acid	Glucose 0.013
3Xylose → 5ethanol + $5CO_2$	Xylose 0.8
Xylose + NH_3 → 5*Z. mobilis* + $2H_2O$ + $0.25O_2$	Xylose 0.03
3Xylose + $5H_2O$ → 5glycerol + $2.5O_2$	Xylose 0.02
3Xylose + $5CO_2$ → 5succinic acid + $2.5O_2$	Xylose 0.03
2Xylose → 5acetic acid	Xylose 0.01
3Xylose → 5lactic acid	Xylose 0.01

the best option for the separation of solids is before the beer column because the flow rate through HX6 and HX8 are smaller. 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.

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, four different alternatives are considered: (1) rectification column, (2) adsorption in corn grits, (3) molecular sieves, and (4) pervaporation.

Beer column

Figure 7 shows the scheme of the distillation column. The relative volatility of ethanol with respect to water is taken to be 2.24 and is assumed to be constant over the temperature range of the column. Calculating the relative volatilities of the glycerol and the acids leads to negligible small relative volatilities. Therefore, water is chosen to be the heavy key and ethanol the light key for the calculations in both the beer column as well as in the rectification column. As all components except ethanol are heavier than water, they are all assumed to go into the bottom outlet. Hence, the effect of all components except water and ethanol on the condenser temperature is neglected. Further, only ethanol and water are assumed to be present in the vapor distillate stream coming out from the condenser of the beer column. Therefore, only these components are considered to be present in the ethanol purification section. A partial condenser is used in the beer column to obtain a vapor distillate as the molecular sieves and the corn grit adsorption bed present in the ethanol purification section handle vapor mixtures of ethanol and water. In the feed to the beer column and in the reboiler, the effect of the components other than water on the bubble point is negligible as their relative volatilities are extremely small and their mole fractions are also very small. The beer column operates at atmospheric pressure. A pressure drop of 0.1 atm across the beer column is assumed. Therefore, the temperature of the inlet stream is calculated at 1 atm, the temperature of the reboiler is computed at 1.05 atm, and the temperature in the condenser is calculated at 0.95 atm.

The temperature as well as the optimal removal of water are calculated while the recovery of ethanol is fixed to be 0.996. With this and the relative volatility, we calculate the number of trays of the column. The actual number of trays is calculated assuming an efficiency of 0.8. The temperatures of the inlet and outlet streams are calculated based on bubble and dew point calculations, Biegler et al.[39] We consider a partial condenser and the reflux ratio is taken to be (R_{BC1}) of 1.5 according to the results by Karuppiah et al.[38]

As a partial condenser is used in the beer column, the composition of the condensed liquid is not the same as the top product, which is removed as saturated vapor. It is assumed that the extracted vapor is in equilibrium with the condensed phase. The composition of the refluxed stream can be calculated by using the vapor–liquid equilibrium relationship for water and ethanol at the temperature of the condenser. The heat loads in the reboiler and the condenser depend on the reflux ratio also, as the recovery of ethanol at the top is fixed at 99.6%, the bottom stream contains almost no ethanol. As discussed above, the contribution of the other species to the heat of vaporization in the reboiler may be neglected.

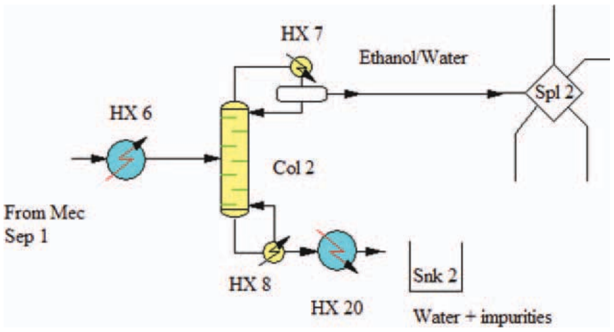

Figure 7. Detail for the beer column.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ethanol dehydration

Four different alternatives have been considered for the dehydration of ethanol, which can be used in parallel or sequentially. Figure 8 shows the superstructure for the final dehydration of the ethanol. Only the rectification and the adsorption in corn grits do not yield the final product because they cannot provide fuel quality but can be alternatives for reducing the energy consumption. Apart from these two options, molecular sieves and pervaporation are also considered. Splitter 2 divides the stream into the four alternatives.

Distillation. The rectifier column is modeled in a similar fashion as the beer column. A partial condenser and reboiler are used in this unit. The pressure drop in the column and the tray efficiencies are assumed to be the same as those for the beer column. Again, the ethanol recovery is fixed at 99.6% and the recovery of water at the top of the column is selected to be a variable. The composition of the condensate in the condenser of this column is calculated assuming equilibrium between the vapor outlet and the liquid reflux stream. The condenser temperature is determined from the dew point equation for the top outlet composition. Furthermore, it is assumed that only water is vaporized in the reboiler and the temperature of the reboiler is calculated using the bubble point equation for the bottom outlet composition. A reflux ratio of 5 is selected so that the column design is feasible. The equations for determining the temperatures of the bottom and distillate are basically the same as the ones presented for the beer column. As the azeotropic composition of an ethanol–water mixture at atmospheric pressure is about 95 wt % of ethanol, this is the maximum achievable purity of ethanol in an atmospheric rectification column. The required purity for fuel grade ethanol is higher, so the mixture must be purified further. Splitter 3 divides the stream so that it can be fed to the adsorption system, the molecular sieves, or the pervaporation system. The split fraction is a continuous variable that takes values from 0 to 1.

Adsoprtion Corn Grits. Some researchers have investigated the use of biomaterials such as corn grits as absorbents[40,41] to reduce the energy consumption in the ethanol purification part of the plant. We propose the use of a bed made of corn grits to selectively adsorb water from an ethanol–water vapor mixture coming from the mixer Mix3. The corn grits for this bed come from a source unit (Src9). HX 12 heats the corn grits to the adsorption temperature, 91°C.

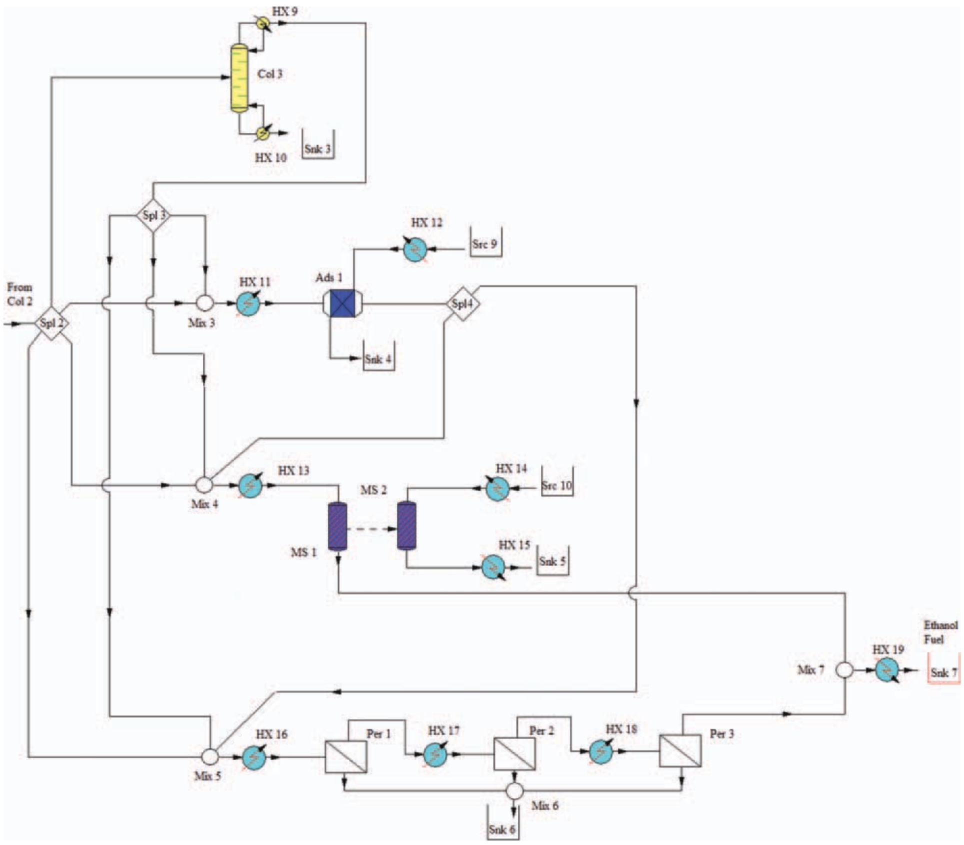

Figure 8. Ethanol dehydration superstructure.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The bed adsorbs water from the ethanol–water vapor mixture and the ethanol is sent to the splitter Spl4. The inlet stream is required to have at least 77% w/w[40] of ethanol. The ethanol–water mixture increases the bed temperature as the water adsorbs into the bed. The maximum concentration of ethanol obtainable at the outlet of the bed is assumed to be 97.7% w/w.[40] We consider a scheme using two corn grit beds working in parallel, one being saturated with water while the other is dehydrated (or regenerated). For the cost analysis of the overall plant, we consider a dual-bed corn grit adsorber as well as the energy cost for the regeneration of the bed (Table 2).

Molecular Sieves. There is a lower bound on the fraction of ethanol entering the molecular sieve (0.8). Adsorption takes place at 95°C. HX 13 heats the inlet stream from the mixer Mix4 up to 95°C. The molecular sieve is a bed of zeolite that operates in semicontinuous mode similar to the cycle described for the corn grit absorbers. The bed is saturated with water after a period of time and is then regenerated. Hence, there are usually two sieves being operated in parallel—one being saturated with water (MS1) while the other (MS1) is being regenerated (or dehydrated) using air under vacuum. HX 14 heats air with an assumed relative humidity of 70% at 20–95°C. The air at the outlet of the dehydrating molecular sieve is cooled down to 25°C in HX 15, and this stream leaves this exchanger saturated with water at 25°C. The data used in the model for the molecular sieves is taken from Jacques et al.[42] and is summarized in Table 3.

Pervaporation. Membranes can also discriminate between components because of an interaction between one of the separating components and the membrane taking place during diffusion, such as seen with ion-exchange and hydrophilic membranes. Pervaporation separates a component from a liquid mixture based on the permeability of the membranes to one of the components. A three pervaporation system is considered to achieve fuel quality. It can receive flows from the rectification column, the corn grit adsorption unit, or the molecular sieves. The mixing of these streams (Mix5) is assumed to be adiabatic. Each effect operates at 90°C. Thus, HX 16 is used to adjust the inlet temperature. The maximum water composition at the inlet is 15%. The water recoveries are 0.95, 0.97, and 1 in each of the effects, respectively.[43] In each of the stages, the energy to evaporate the water is obtained from cooling the liquid stream. Thus, reheating is needed between effects to heat up the stream again up to 90°C by means of HX 17 and HX 18 for the second and third effect, respectively.

Table 2. Data for Adsorption on Corn Grits

Parameter	Value
$x_{\text{in,ads}}^{\text{ethanol,min}}$	0.77
$x_{\text{out,ads}}^{\text{ethanol,max}}$	0.977
$\text{ads\_potential}_{\text{Ads1}}$ ($\text{kg}_{\text{water adsorbed}}/\text{kg}_{\text{adsorbent}}$)	0.075

Table 3. Data for Molecular Sieves

Parameter	Value
$x_{\text{in,MS}}^{\text{ethanol,min}}$	0.8
$\text{ads\_potential}_{\text{MS}}$ ($\text{kg}_{\text{water}}/\text{kg}_{\text{adsorbent}}$)	0.08
$\text{t\_MS}_{\text{saturation}}$ (s)	360
$\text{rh}_{\text{in,MS}}$ (%)	70
$\text{rh}_{\text{out,MS}}$ (%)	70

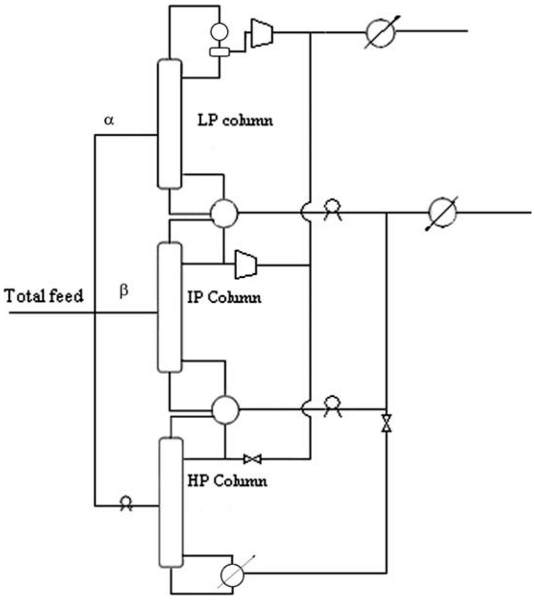

Figure 9. Superstructure for the multieffect columns.

(α) Fraction of total feed to low pressure (LP) column. (β) Fraction of total feed to intermediate pressure (IP) column.

Final Product The ethanol with fuel quality is condensed and/or just cooled down to 25°C.

Solution procedure

To solve the superstructure, the MINLP is decomposed into two NLPs of about 2000 equations and 3000 variables each, one for diluted acid pretreatment and another one for AFEX. The superstructure for separation is modeled with split fractions. The problem is optimized in terms of energy consumption in the flowsheet.

Once this optimization is completed, multieffect columns[44,45] are used to replace the distillation column by two or more columns. By operating the columns at different pressures, the condenser of a higher pressure column serves as the reboiler of a lower pressure column. The inlet feed is split between all the columns, and their top and bottoms products are mixed together to obtain the final products with the desired flow rates and compositions. A schematic of a three effect distillation column, like the ones used in this work, is shown in Figure 9.

In this study, we considered multieffect columns with up to three columns. For determining the fraction of feed to be sent to each column and the operating pressures of the columns, we set up an optimization model to minimize the total annualized cost for the multieffect columns

$$\text{cost} = \text{annualized equipment cost} + \text{annual steam cost} + \text{annual cooling water cost} \quad (5)$$

subject to the constraint that product composition at the top and bottom of each column must match the ones obtained for a single distillation column from the results of the previous optimization. Hence, additional HXs as well as compressors may be required to meet the initial conditions, whose investment cost and utility cost would be included in the total cost objective. Also, isenthalpic expansion valves may be needed for some streams so as to match the pressure of the low pressure columns.

Finally, heat integration[39,46] is performed to further reduce the energy consumption. Because of the fact that the flowsheet has no recycle and the conversions of the reactors as well as the operating conditions are fixed, the need to perform simultaneous structural optimization and heat integration is not as critical. Heat integration among the hot and cold streams across the whole plant yields considerable savings in the utilities (steam, cooling water) and consequently in the operating costs.[39,46] To carry out the heat integration, the software SYNHEAT (http://newton.cheme.cmu.edu/interfaces) is used. The software is based on the work by Yee and Grossmann (1990),[47] and uses an MINLP model to determine a minimum cost network, where the heat exchanger areas and the stream matches are optimized simultaneously given the heat loads in different streams and the inlet and outlet temperatures of these streams.

In the case of the dilute acid pretreatment, the vapor recovered from the process is used in HX21, see Figures 1 and 4, to provide energy for the process in the heat exchanger network (HEN). Once no more energy can be recovered, the water is fed to Tank 1, which reduces the vapor needed in the pretreatment as well as the water. To determine the temperature of Tank 1, several iterations are carried out as follows:

1. Energy optimization of the flowsheet.
2. Developement of HEN using SYNHEAT and implementation of multieffect column.
3. Readjust the conditions in Tank 1 and reoptimize. Go to 1.

Repeat until the flows do not change.

Results

The production capacity of bioethanol plants from lignocellulosic biomass is limited by the availability of biomass in the region. Current trends as well as NREL reports suggest values in the range of 40–60 Mgal/year. Thus, to compare with results in the literature,[8,38,48] the production capacity of the plant is fixed at 60 Mgal/year.

Based on the energy optimization of the process flowsheet, the energy consumption for the dilute acid pretreatment is 87 MW vs. 105 MW for the AFEX. The optimal flowsheet is shown in Figure 10. It uses the dilute acid as pretreatment and to dehydrate the ethanol, a combination of beer column and molecular sieves is suggested by the optimization. Even though we could stop the analysis of the AFEX pretreatment at this point, it is useful to show the results for energy integration and the production cost of both pretreatments so as to obtain more detailed information of both alternatives.

We first substitute the beer column by multieffect columns to reduce the energy and cooling water use. A three effect multieffect column is the best option. Next, we perform heat integration using SYNHEAT to obtain the optimal HEN. As an example, Figure 11 shows the *T–Q* curve for the dilute acid pretreatment. In the *T–Q* curve, the multieffect columns are included but neither the energy demand of the reactors nor the steam injected for the pretreatment are included. As it can be seen if Figure 11, a fair amount of energy can be integrated, which helps in the economy of the process.

Discussion

Heat integration is performed using SYNHEAT to design the optimal HEN. Figure 12 shows the energy consumption (orange) and cooling requirements (blue) after heat

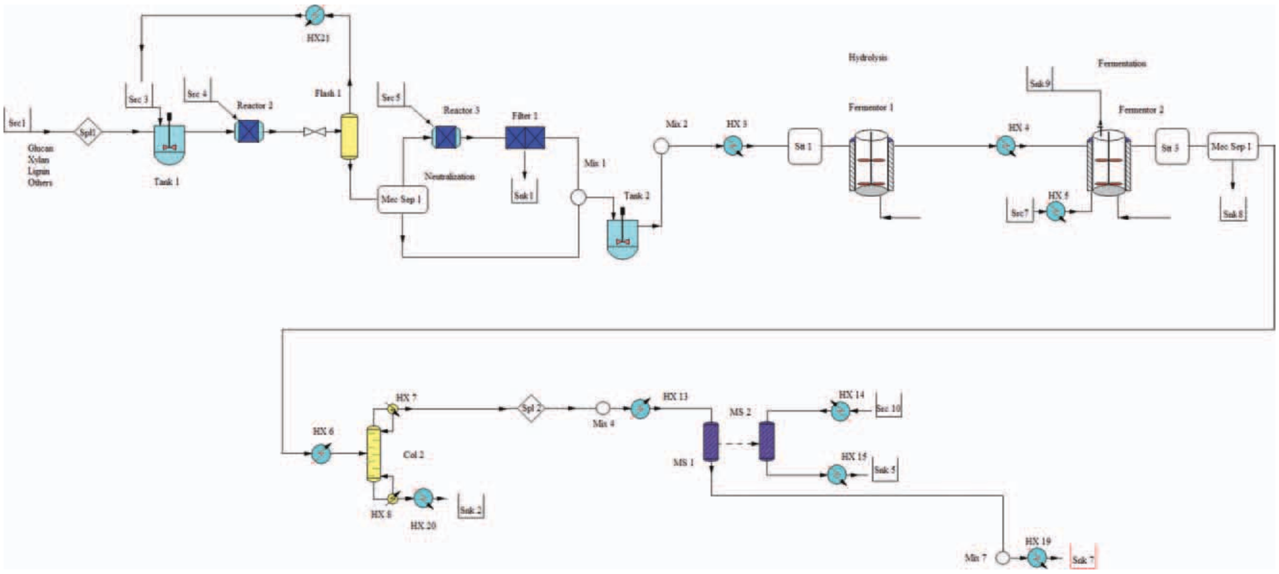

Figure 10. Optimized flowsheet.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

integration. The production of ethanol from lignocellulose using dilute acid pretreatment requires more energy but only half the cooling of AFEX.

In Figure 12, we see that the thermal energy consumption for the production of ethanol from switchgrass via hydrolysis is almost twice the one requried for the corn-based process as well as the cooling needs. On these grounds, the process is not attractive compared to the corn-based ethanol, since the only advantage is that the raw material does not interfere with the food chain. However, there is another source of energy in the process. The energy obtained from the lignin is not included in the orange columns of Figure 12. Lignin is a very interesting coproduct to produce energy. It is reported that lignin can produce 26,100 kJ/kg, a value close to the enegy obtained by burning coal.[49] In typical power plants, its maximum efficiency is about 75–80%.[50] Thus, a boiler is considered to generate the steam from lignin and its cost is included in the equipment cost. In red, we show the contribution of the energy generated by burning the ligning to the energy consumed/produced in the process. In this case, both processes are energetically more favorable than using corn as raw material (the electrical energy in the grinding is not included so as to compare with the results presented in the corn based process[38]). In Figure 12, the cooling water requirements are also shown. Both cases require higher consumptions of cooling water than the case of the corn ethanol. In the case of the dilute acid, this difference is smaller.

Economic evaluation

The energy analysis of the process reveals a trade-off between both processes as AFEX not only generates more energy but also requires more cooling than dilute acid. Furthermore, according to the literature[18] the yield of AFEX is lower due to the high fraction of lignin in the switchgrass. Figure 13 shows the comparison of the raw material consumption for the two alternatives compared with corn-based ethanol. The consumption of lignocellulosic biomass is higher than that of corn grains for the same production of ethanol. Thus, the solution to the tradeoffs relies on a detailed economic evaluation of both alternatives.

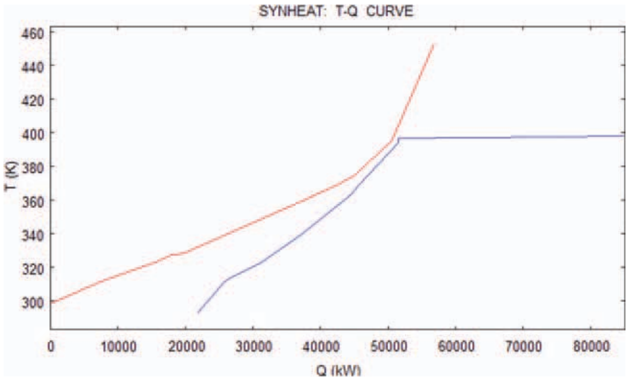

Figure 11. *T–Q* curve for the production of ethanol using dilute acid pretreatment.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

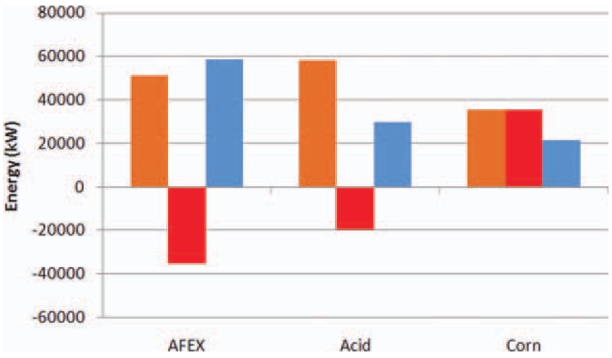

Figure 12. Energy balance for the production of ethanol from switchgrass and corn.

Orange: Energy consumed after superstrucure optimization with heat integration. Red: Energy consumed after the contribution of lignin. Blue: Cooling water requirements after heat integration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

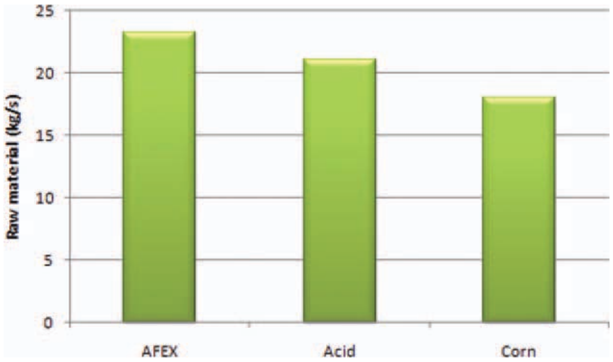

Figure 13. Consumption of raw material for the production of 60 Mgal/year.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

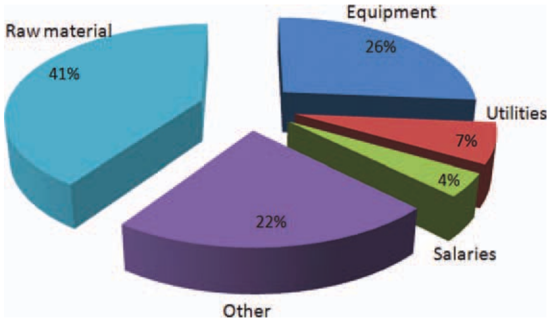

Figure 14. Cost distribution for the diluted acid pretreatment.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The costs for utilities and raw material are updated from the literature (0.019 \$/kg steam, 0.057 \$/ton cooling water,[51] electricity: 0.06 \$/kWh,[52] switchgrass price: 30 \$/TM; Ref. 53, and Dow Chemical, Personal Communication). The generation of an excess of steam is considered as a revenue of 0.0077\$/kg$_{\text{steam}}$ (updated from Smith and Varbanov[54]) and the equipment pricing which is obtained from www.matche.com.[8] Table 4 summarizes the results of the economic evaluation. Dilute acid and AFEX pretreatment show similar results, but the lower yield of the AFEX pretreatment together with its higher demand of cooling water shown in Figure 12, makes this pretreatment alternative less attractive.

Figure 14 shows the distribution of manufacturing cost for the optimal process that is based on dilute acid pretreatment (Figure 10). The contribution of the raw material is in the range reported by the literature, around 40%,[13] followed by the annualized equipment cost and miscellaneous, including chemicals, maintenance and administration, for a total of \$48.5 MM/year (Table 5).

If we compare the final production costs for second-generation ethanol in Table 4 with different values available in the literature, the results are promising. We acknowledge that the comparison is not totally consistent because of different assumptions of the various sources. However, the results should still provide a useful indicator. In terms of production cost for biochemical production of ethanol from lignocellulosic raw materials, for the acid/enzymatic hydrolysis process the target by NREL is 1.33 \$/gal from corn stover,[13] while others are more optimistic aiming at values lower that 1.10 \$/gallon ethanol.[55] However, a recent study by Kazi et al.[14] reports a production cost much higher than the ones in the literature based on the different price for the feedstock or the assumptions in the model (e.g., conversions, yield). The estimate of the current commercial scale for lignocellulosic materials is at 2.43 \$/gal.[13] This work reports values in the range of 0.8 \$/gal for ethanol produced from switchgrass.

Table 4. Production Cost of Ethanol Via Hydrolysis of Lignocellulosic Raw Material

Pretreatment	Dilute Acid	AFEX
Raw material contribution (%)	40.5	43.0
Net utilities contribution (%)	7.0	3.0
Ethanol yield (%)	27.6	25.0
Production cost (\$/gal)	0.80	0.83

We can also compare with production costs of thermochemical path. It turns out that Phillips et al.[48] reported a price for ethanol of 1.22 \$/gallon (with a reduction of 20.7/100 \$/gallon of byproduct credits) via indirect gasification and high alcohols synthetic path, while Dutta and Phillips (2009)[56] reported a price of 1.95 \$/gal for direct gasification and high alcohols synthesis. For the production of ethanol via gasification–fermentation Huhnke (2008)[57] reported a target price of 1.2 \$/gal. In both cases, these values can be improved. In fact the Coskata process, based also on the fermentation of syngas, is claiming production costs under 1 \$/gallon.[7,58] Martín and Grossmann[8] showed that for the gasification-based process the optimal flowsheet involves a thermochemical path, with a yield to ethanol is 20% (kg$_{\text{ethanol}}$/kg$_{\text{biomass}}$) generating 18 MW of energy and requiring 68 MW of cooling. When selling the surplus of hydrogen, the manufacturing cost turns out to be 0.41 \$/gal (\$63.9 millions/year) and the investement cost is \$335 millions.

Even though the manufacturing costs via hydrolysis are larger compared to the gasification-based process, the main advantage of the biochemical processes vs. the thermochemical or thermobiochemical ones is the simpler process. As a result, the total investment cost[59] of the optimal design is \$169 MM (the equipment cost is \$38.4 MM calculated using the supporting Information in previous papers[8]), around half the one reported by Martín and Grossmann[8] for the gasification-based production of ethanol from switchgrass.

Finally, we mention some of the uncertainties in the process and its impact in the energy consumption and its economics:

Table 5. Summary of Economic Data of the Optimal Design

Costs	\$MM
Total investment cost[58]	169
Manufacturing cost (\$MM/year)	
Equipment (ROI + depreciation; Cargill, Personal communication)	12.79
Utilities	3.40
Salaries	1.93
General + Admin.	1.71
Chemicals (Cargill, Personal communication)	6.47
Maintenance	1.33
Swichgrass	19.65
Other expenses	1.22
Total	48.50

1. To keep the production cost below 1 \$/gal for the optimal process flowsheet based on dilute acid pretreatment, the cost of the switchgrass must lie below 50 \$/MT (wet). For a price of 100 \$/MT (wet), the cost of ethanol increases up to 1.57 \$/gal.

2. It is expected that further development in fermentation technology will allow ethanol concentrations in the reactor of 12%.[36] If the concentration of ethanol in the reactor increases from 8% (the value used in the study) to 12%, a decrease in the consumption of energy up to 10% could be reached based on the lower needs in the dehydration step.

3. The uncertainty in the operating conditions and the yield of the pretreatments[11–13,18,60,61] may change the decision on the best process. It is expected that further experimental results will allow higher yields for the pretreatments consuming less energy, ammonia, and freshwater. For instance, if the conversion of the AFEX reaches 90% for both hemicellulose and cellulose (similar to the values considered for the dilute acid pretreatment), the production cost drops to 0.81 \$/gal generating 40 MW of energy and requiring 60 MW of cooling with a yield of 0.276 $kg_{ethanol}/kg_{biomass}$ reaching the same efficiency of the dilute acid-based process.

4. There is uncertainty in the use of a boiler for generating energy from the lignin. On the one hand, this was proposed as alternative to make use of the lignin and, thus, obtain energy that will change the net energy balance. On the other hand, we need to invest on a boiler. If we decide not to burn the lignin, then we save investment cost but we need to pay for the steam required in the plant, as a result the manufacturing cost increases to 1.04 \$/gal, 25% increase, while the investment decreases to \$141 MM, 16%.

Conclusions

The ethanol production from lignocellulosic swichgrass via hydrolysis has been modeled and optimized. Two different pretreatments, dilute acid and AFEX, and four different dehydration processes (rectification, adsorption, molecular sieves and pervaporation) were considered.

The optimal process involves the use of dilute acid pretreatment and for the dehydration a beer column followed by molecular sieves to obtain fuel-grade ethanol. The use of lignin is key for the profitability of the process in terms of energy consumption. By burning the lignin, the optimized process produces energy even though the requirements for cooling water are a somewhat higher than in the case of ethanol produced from corn. As a result, the production cost of ethanol is 0.8 \$/gal including the cost of the equipment for the generation of steam from the combustion of lignin.

Acknowledgments

The authors acknowledge NSF Grant CBET0966524 and Dr. M. Martín also acknowledges the financial support from the Ministry of Education and Science of Spain and Fulbright commission providing a MICINN—Fulbright Postdoctoral fellowship.

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Manuscript received Mar. 22, 2011, and revision received Jun. 7, 2011.