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Assessment of Combinations between Pretreatment and Conversion Configurations for Bioethanol Production

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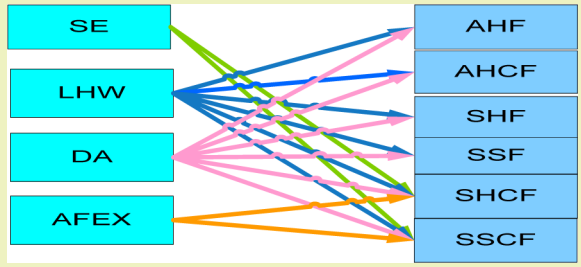
Supporting Information

ABSTRACT: The bioethanol production from lignocellulosic materials is a socially and environmentally well-accepted option; however, its technical and economic feasibility needs to be established. In order to know if the bioethanol production from this feedstock has a potential for implementation, we developed a comparison of 16 process configurations based on four pretreatment methods and six conversion options. Indexes that relate to energy consumption, amount of bioethanol produced, water consumption, and final bioethanol composition were used to compare the processing options. Seven alternatives were selected for further analysis with the implementation of a separation process. It was found that the process based on dilute acid pretreatment and enzymatic hydrolysis and co-fermentation combination shows the best economic potential. On the other hand, the cellulose hydrolysis based on an enzymatic process showed the best energy efficiency, but the final economic incentive for industrial implementation depends strongly on a fairly low enzyme cost.



KEYWORDS: *Lignocellulosic materials, Pretreatment methods, Conversion configuration, Hydrolysis, Saccharification, Fermentation, Conventional distillation*

INTRODUCTION

Today, the principal sources to bioethanol are corn and sugar cane molasses; because of their high sugars content, these materials produce relatively high bioethanol yields. Unfortunately, these materials are important food sources, which have sparked the search for alternative sources. One such option is the use of lignocellulosic materials (LCM). However, the production of bioethanol from LCM seems more difficult because more processing stages and higher energy consumption might be required.

On the basis of a biochemical platform, the bioethanol production process using LCM has three steps, namely, pretreatment, conversion, and separation. For the conversion step, two principal processes are required, cellulose hydrolysis and fermentation. There are two ways for the cellulose hydrolysis implementation. One case is based on acid hydrolysis, and the second is based on enzymatic hydrolysis. In the fermentation case, six and five carbon sugars could be fermented either in separate single processes or in a co-fermentation process, depending on the microorganisms used. From these options, different conversion configurations have been proposed, with the typical objective of achieving maximum yields. Therefore, useful alternatives can be generated, although additional factors need to be considered.

Several works on bioethanol production have been reported. Of particular interest are the review papers by Naik et al.[1] on first and second generation biorefineries for biofuels production, Menon and Rao[2] on the trends of bioconversion of lignocellulosic materials, Brethauer and Wyman[3] on the use of hydrolysis and fermentation processes, Gnansounou and Daurial[4] on tecno-economic aspects for the production of lignocellulosic ethanol, and Kumar et al.[5] on the separation options for anhydrous bioethanol production. An interesting design work on the production of bioethanol from corn and switchgrass using optimization techniques has been reported by Grossmann et al.[6] in which one of the objectives was the reduction of energy and water consumption for the overall process. Kim and Dale[7] and Singh et al.[8] included environmental aspects for biofuels and bioethanol production through the implementation of life cycle analysis. Experimental works on several conversion configurations for bioethanol production have been reported by Öhgren et al.[9] and Olofsson et al.[10] Economic analysis of some configurations for bioethanol production from sources such as softwood, corn stover, and lignocellulosic materials have been reported.[11−14] Recently, Morales-Rodriguez et al.[15] presented an evaluation of configurations for lignocellulosic bioethanol production based on dynamic models.

Because there are several pretreatment options that have been developed as well as a good number of conversion options for bioethanol production, the objective of this work is to carry

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out an analysis of their potential integration to detect the most promising combinations to be implemented as part of an overall bioethanol production process.

GENERAL METHODOLOGY

The methodology we used follows the logics of a hierarchical approach for the design problem, such that the overall problem is decomposed into individual tasks for their sequential implementation. The overall problem consists of the integration of pretreatment, conversion, and separation stages, which will be taken in that order for their analysis. For the pretreatment stage, we have analyzed in a previous work six pretreatment alternatives,[16] namely, those based on steam explosion (SE), liquid hot water (LHW), dilute acid (DA), ammonia fiber explosion (AFEX), alkali extraction with lime (LIME), and the use of organosolvents (OS). We found that the OS option had high energy requirements and that the LIME pretreatment method did not present any opportunity for mass integration using direct recycle. On the basis of such analysis, four pretreatment methods (SE, LHW, DA, and AFEX) are selected in this work for their potential combination with conversion configurations. The alternatives considered for conversion steps include acid and enzymatic hydrolysis, fermentation and co-fermentation processes, and a combined hydrolysis and fermentation process. The resulting configurations are implemented in the Aspen Plus process simulator for their analysis. In this case, the four pretreatment methods and six conversion configurations give rise to 16 possible processing configurations. The simulation results will be taken as a basis to evaluate a series of performance parameters that are related to energy and mass efficiency aspects from which a reduced set of processing options should be identified. Finally, such arrangements will be analyzed in terms of the energy required in the separation stage to purify the ethanol product in order to identify the most promising options.

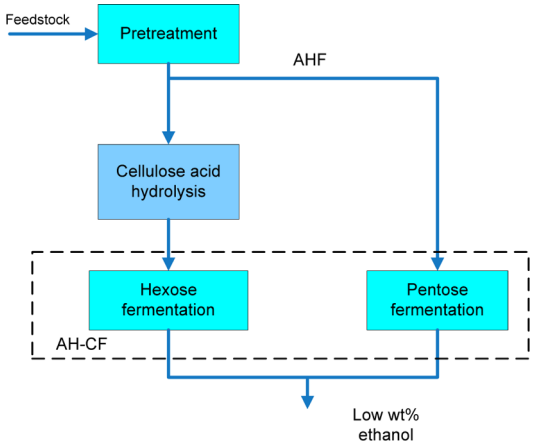

Figure 1. Processes based on acid hydrolysis.

CONVERSION CONFIGURATIONS

A description of the conversion configurations considered in this work is given here. The hydrolysis acid of cellulose is considered to occur at very low acid concentrations (0.07 wt %) to avoid the acid recovery requirements and equipment corrosion problems operating at high temperatures (220 °C).[17] The xylose degradation to furfural occurs significantly under these conditions, so it is better to separate the xylose liquor produced in the pretreatment from the solid fraction before the acid hydrolysis. Two routes are considered. In the first configuration, the cellulose acid hydrolysis is followed by glucose fermentation, and the xylose liquor coming from pretreatment is used in a xylose fermentation process. This configuration is called acid hydrolysis and fermentation (AHF). In the other case, the co-fermentation of both sugars occurs simultaneously; the process is referred to as acid hydrolysis and co-fermentation (AHCF). Both cases are represented in Figure 1.

As for the enzymatic hydrolysis, four configurations are considered. Two of them require a solid−liquid separation step after pretreatment (Figure 2a). In the first option, the enzymatic hydrolysis is followed by glucose fermentation, and the xylose liquor coming from pretreatment is fermented in a separate process. This case is called separated enzymatic hydrolysis and fermentation (SHF). The second option where the solid−liquid separation is implemented after pretreatment is the simultaneous saccharification and fermentation (SSF) process, in which the cellulose enzymatic hydrolysis and the glucose fermentation are integrated, and the xylose fermentation is implemented in a separate process. When co-fermentation is used, the solid−liquid separation after pretreatment is not required, and the solid−liquid mixture can be sent to the next step (Figure 2b). In one option, the enzymatic hydrolysis process is first completed and is followed by the co-fermentation of

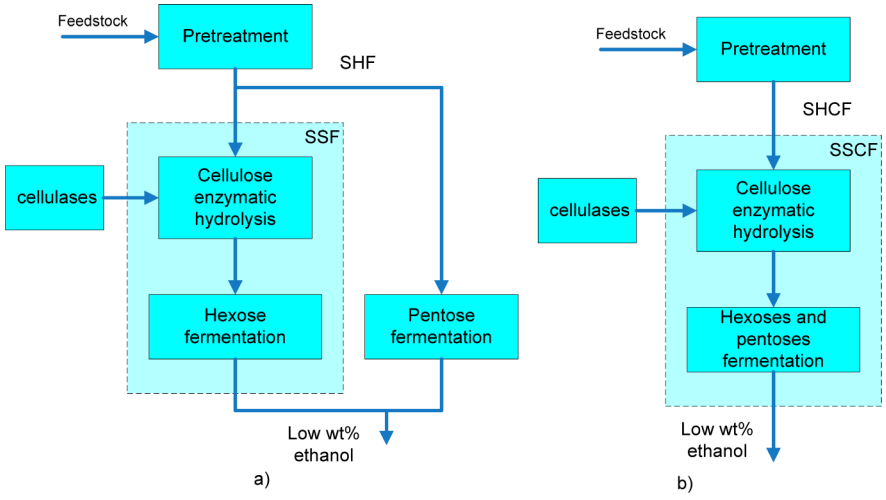

Figure 2. Processes based on enzymatic hydrolysis.

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five and six carbon sugars (separated enzymatic hydrolysis and co-fermentation process, SHCF). In the other option, the simultaneous saccharification and co-fermentation (SSCF) process integrates the cellulose enzymatic hydrolysis and the co-fermentation in a simultaneous process.

COMBINATIONS BETWEEN PRETREATMENT AND CONVERSION CONFIGURATIONS

In the case of SE, we previously found that the solid−liquid separation is not recommended.[16] This pretreatment is implemented with a relatively high solid wt % composition, and the inhibiter compositions (furfural and acetic acid) in the exit stream are usually higher than the recommended values. Any conversion configuration involving xylose fermentation separately from glucose fermentation will produce low bioethanol yields from xylose. Therefore, the most appropriate conversions to combine with SE are SHCF and SSCF. For the LHW and DA methods, significant inhibition is not observed when the solid−liquid separation is implemented; therefore, these methods can be combined with all conversion configurations. For the AFEX pretreatment, the appropriate combinations are SHCF and SSCF. In the case of AFEX, an important solid fraction is not solubilized, such that xylose liquor is not produced. Therefore, the conversion configurations involving xylose fermentation separately from glucose fermentation are not possible unless a second pretreatment step after AFEX is used, an option that does not seem economically appealing. As result of this analysis, we identify 16 candidate combinations between pretreatment methods and conversion configurations, as shown in Figure 3.

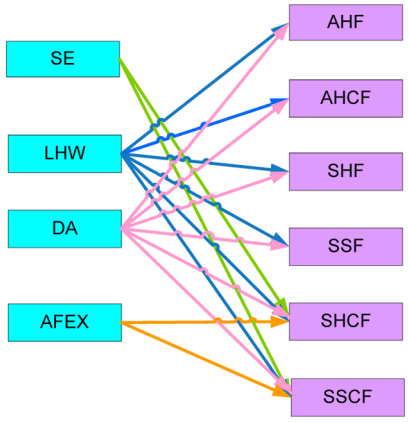

Figure 3. Potential combinations between pretreatments and conversion configurations.

SIMULATION APPROACH

The 16 flowsheet options were implemented in the Aspen plus process simulator, using conceptual design. The simulations for pretreatments with direct recycle were taken as an initial basis.[16] All simulations were based on 42 tonne per hour of feedstock, which represents approximately 1000 tonne per day of dry biomass entering the process.

COMPONENTS INVOLVED IN PRETREATMENT AND CONVERSION PROCESSES

The list of components for the pretreatment simulations used in Conde et al.[16] was complemented with the components generated in the fermentation step: ethanol, glycerol, succinic acid, and lactic acid. Yeast is used as feed for the glucose fermentation process, and zymo is used for the xylose fermentation process or a cofermentation process. Enzyme is used as feed for the enzymatic hydrolysis process, and urea is used in the fermentation process as ammonia source. Table 1 shows the components that were added to the pretreatment list. It should be noted that some of them are not available in Aspen; for those cases, the properties were taken from Wooley and Putsche[18] and implemented into the process simulator. A complete list of components not available in the Aspen process simulator and their property values are included in the Supporting Information.

Table 1. Components Added to the Pretreatment Simulations

cellulase (enzyme)*
ethanol
glycerol
S. cerevisiae (yeast)*
succinic acid
latic acid
urea
Z. mobiliz (zymo)*

*Component originally not available in the Aspen process simulator.

CONVERSION INPUT DATA

A stoichiometric reactor unit was used to implement single conversion steps, such as acid hydrolysis, enzymatic hydrolysis, xylose fermentation, and glucose fermentation, as well as the integrations between these single processes, such as co-fermentation, simultaneous saccharification and fermentation, and simultaneous saccharification and co-fermentation. The conversion percent for the sugars and bioethanol, which were used as a basis for the simulations, are reported in Table 2. The enzymatic conversion values were estimated based on the amount of cellulose and hemicellulose that remain after pretreatment. In the AFEX case, these amounts are equal to the hemicellulose and cellulose amounts at the beginning of the pretreatment. For the cellulose acid hydrolysis, glucose fermentation and co-fermentation process, the conversion values were taken directly from the listed reference.

SE pretreatment is generally implemented with SSF, as reported in several experimental works,[22−25] where SSF yields are usually estimated for cellulose and glucose, but no explicit data for hemicellulose and xylose are available. As conversion percent values for hemicellulose and cellulose for the enzymatic hydrolysis process were needed, we assumed the same yield reported for LHW when followed by enzymatic hydrolysis because both SE and LHW are hydrothermal methods.[25] A summary of pretreatment yields can be found in Conde et al.[16]

The conversion percent for the most representative by-products generated in acid hydrolysis, glucose fermentation, and co-fermentation are presented in Table 3.

The following assumptions were made:

(1) The different five carbon sugars are integrated into a single fraction as hemicellulose.
(2) The sugar products during hydrolysis are just monomers, glucose, and xylose.
(3) No amount of lignin is solubilized during any of the conversion process, acid hydrolysis, enzyme hydrolysis, or fermentation.
(4) The yeast microorganism is only able to ferment glucose sugar. *Z. mobiliz* can ferment both xylose and glucose,

Table 2. Conversion Data to Sugars and Bioethanol

step	reference	conversion
cellulose acid hydrolysis	Qian et al.[17]	76.50% cellulose to glucose
		99.00% hemicelluloses to xylose
enzymatic hydrolysis after:		
LHW	Wyman et al.[19]	30.30% hemicellulose to xylose
		90.00% cellulose to glucose
DA		16.44% hemicellulose to xylose
		91.12% cellulose to glucose
AFEX		67.14% hemicellulose to xylose
		96.01% cellulose to glucose
enzymatic hydrolysis after SE*		30.30% hemicellulose to xylose
		90.00% cellulose to glucose
glucose fermentation by yeast	Brethauer and Wyman[3]	94.00% glucose to bioethanol
xylose fermentation by *Z. mobiliz* at low glucose compositions	Lawford et al.[20]	85.00% xylose to bioethanol
co-fermentation by *Z. mobiliz*	Dimian and Sorin[21]	92.00% glucose to bioethanol
	Kazi et al.[14]	75.60% xylose to bioethanol

*Values assumed equal to LHW option.

Table 3. Conversion Data for Byproducts

acid hydrolysis		
byproduct	reference	conversion
furfural	Dias et al.[26]	80.00% from Xylose
glucose fermentation		
byproduct	reference	yield
glycerol	Dias et al.[26]	2.67% from glucose
succinic acid		0.29% from glucose
acetic acid		1.19% from glucose
yeast		1.37% from glucose
co-fermentation		
byproduct	reference	yield
Z. mobiliz	Dimian and Sorin[21]	2.70% from glucose
		2.90% from xylose
glycerol		0.20% from glucose
		2.90% from xylose
succinic acid		0.80% from glucose
		0.90% from xylose
acetic acid		2.20% from glucose
		2.40% from xylose
lactic acid		1.30% from glucose
		1.40% from xylose

but when the glucose composition is high, the xylose conversion to ethanol is low (75.60%), and when the glucose composition is low, the xylose conversion to ethanol is high (85.00%).

(5) In the acid hydrolysis case, we assumed that cellulose hydrolysis is slower than hemicellulose hydrolysis. Also, xylose degradation to furfural is modeled to occur in series with hemicellulose hydrolysis; therefore, the xylose generated in hemicellulose hydrolysis is available for furfural production. Figure 4 shows both hydrolysis reactions.

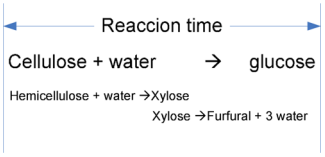

Figure 4. Acid hydrolysis reactions.

(6) For the SSF and SSCF cases, saccharification reactions are modeled in series with the fermentation reactions; therefore, glucose and xylose generated in enzymatic hydrolysis are available for the fermentation process. In the stoichiometric reactor unit, the conversion percents to final products were based on cellulose and on cellulose and hemicellulose available as solids after pretreatment (Figure 5). The estimation of these values was based on the stoichiometric relations with glucose and xylose as intermediate products.

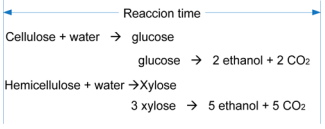

Figure 5. Saccharification and fermentation reactions.

OPERATING CONDITIONS

The experimental conditions for conversion processes vary from different sources, but the conditions presented in Table 4 are fairly representative. Although, temperatures up to 28 °C have been reported for optimum fermentation temperature,[27] we assume fermentation temperatures of 35 °C to ensure the use of cooling water. Table 4 gives the temperatures used for our simulations. The experimental solid weight percent is usually around of 5 wt % for acid hydrolysis and 10 wt % for enzymatic hydrolysis.[17,28] However, these values might not be suitable for industrial implementation, so we used them as parameters in our simulations. When the enzyme feed was required, we used the equivalent amount to 15 FPU (filter paper units) in all cases. A filter paper unit is a measure of enzymatic activity; it represents the point when an amount of enzyme (cellulase) releases 2.0 mg of reducing sugars (glucose) in 1 h at 50 °C.[29] We expressed the enzyme feed as kg of cellulase per kg of cellulose according to the method reported by Douglas et al.[30]

Table 4. Experimental Operating Conditions

step	*T* (°C)	wt % solids or wt % sugars	enzyme consumption FPU/g cellulose
acid hydrolysis	220	5.0%	
enzymatic hydrolysis	45	10.0%	15
xylose fermentation	37	4.0%	
glucose fermentation	35	10.0%	
SSF	35	10.0%	10
SSCF	34	11.5%	14

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INHIBITION AND FRESH WATER CONSUMPTION

Furfural and acetic acid are the most representative inhibiter components produced during a pretreatment step and during a hydrolysis process. The inhibition performance of these components has been studied by different authors;[9,31−35] however, it is difficult to define the conversion of these components through all different conversion steps. In the furfural case, it is known that when acid hydrolysis is used an important percent of xylose is degraded to furfural.[26] Also, it has been reported that fermentation microorganisms are able to degrade furfural to others components.[31,34,35] During pretreatment and hydrolysis steps, the main amount of acetic acid is not produced by degradation; instead, it is postulated that acetic acid generation comes from the liberation of the acetyl groups present in hemicellulose.[32,33] Moreover, the amount of acetyl groups liberated during a pretreatment step depends on the pretreatment conditions (temperature, residence time, and chemical usage). Therefore, the acetic acid production before a fermentation step highly depends of the acetyl amount contained in the initial material. On the other hand, when fermentation is performed, the degradation of sugars to acetic acid has been observed.[21,26]

For the simulation of the different combinations, the production of furfural was included only when acid hydrolysis is used (Table 3), and degradation of furfural to other products was not considered during a fermentation process. In the acetic acid case, additional assumptions were made. First, we defined the acetyl fraction content in hemicellulose for the initial material. We took 3.2 wt % of acetyl group in the initial feedstock because materials such as corn stover and sugar cane bagasse usually contain between 3.2 and 3.5 g of acetyl in 100 g of material.[19,36] We assumed that the amount of acetyl is part of the hemicellulose fraction.[32,33] Hemicellulose content in the feedstock was assumed as 27 wt %; therefore, the equivalent content of acetyl within the hemicellulose fraction was estimated as (3.2/27)100% = 11.85 wt %. As a result, 11.85 wt % of hemicellulose was converted to acetic acid during pretreatment and hydrolysis steps, out of which 1.25% corresponds to pretreatment and 10.6% to any hydrolysis step. For the fermentation and co-fermentation steps, the production of acetic acid was estimated with the conversion values from glucose and xylose given in Table 3.

During the simulations we kept the composition of furfural and acetic acid below 3.75 and 6 g/L after any step that involves enzymatic hydrolysis, fermentation, or co-fermentation; we took these limits from the experimental report by Larsson et al.[31] Different solids wt % were tried to estimate the fresh water consumption and the composition of furfural and acetic acid. The fresh water consumption and the solids wt % are closely related to the inhibition problem. Moreover, when acid hydrolysis is used, the furfural composition is the most significant factor for inhibition, and when enzymatic hydrolysis is used, acetic acid is the limiting factor. In order to reduce the fresh water consumption, the xylose wine, coming from xylose fermentation, was used instead of fresh water. For the cases, AHF, AHCF, and SHF, the wine was mixed with the stream coming from cellulose hydrolysis and sent to the next fermentation step. In SSF configuration, the wine was mixed with the solids coming from pretreatment and fed to the simultaneous saccharification and fermentation process. In Table 5, the final values used in the simulations for solids wt % are given; the acetic acid and furfural compositions after the reactions steps are included.

Table 5. Solids Content and Furfural or Acetic Acid Composition

combinations	solids wt %	[significant component] kg/L
SE-SHCF	12.0	$[\text{acetic acid}]_{EH}$ =0.00405
		$[\text{acetic acid}]_{CF}$ = 0.00583
SE-SSCF	12.5	$[\text{acetic acid}]_{SSCF}$ = 0.00585
LWH-AHF	9.5	$[\text{furfural}]_{F}$ = 0.00344
LWH-AHCF	10.5	$[\text{furfural}]_{CF}$ = 0.00370
LWH-SHF	20.0	$[\text{acetic acid}]_{EH}$ = 0.00566
		$[\text{acetic acid}]_{F}$ = 0.00404
LWH-SHCF	12.5	$[\text{acetic acid}]_{EH}$ =0.00387
		$[\text{acetic acid}]_{CF}$ = 0.00581
LWH-SSF	14.5	$[\text{acetic acid}]_{SSF}$ = 0.00563
LWH-SSCF	13.0	$[\text{acetic acid}]_{SSCF}$ = 0.00584
DA-AHF	10.0	$[\text{furfural}]_{F}$ = 0.00370
DA-AHCF	10.0	$[\text{furfural}]_{CF}$ = 0.00370
DA-SHF	20.0	$[\text{acetic acid}]_{EH}$ = 0.00399
		$[\text{acetic acid}]_{F}$ = 0.00432
DA-SHCF	14.0	$[\text{acetic acid}]_{EH}$ = 0.00315
		$[\text{acetic acid}]_{CF}$ = 0.00589
DA-SSF	17.0	$[\text{acetic acid}]_{SSF}$ = 0.00586
DA-SSCF	14.0	$[\text{acetic acid}]_{SSCF}$ = 0.00585
AFEX-SHCF	11.5	$[\text{acetic acid}]_{EH}$ = 0.00427
		$[\text{acetic acid}]_{CF}$ = 0.00597
AFEX-SSCF	13.0	$[\text{acetic acid}]_{SSCF}$ = 0.00583

*EH: enzymatic hydrolysis. CF: cofermentation. F: glucose fermentation. SSF: simultaneous saccharification and fermentation. SSCF: simultaneous saccharification and co-fermentation.

RESULTS AND DISCUSSION

In order to compare the 16 combination alternatives, several parameters were considered. The energy cost, total gallons of bioethanol produced, and total water consumed were obtained per one tonne of dry biomass; from these estimations, the energy cost per gallon of bioethanol produced (unit energy cost) was obtained. Energy costs were estimated using utility prices of $6/MMBtu heating, $4/MMBtu cooling, and $0.07 KWh. On the basis of the mass of ethanol produced, we calculated two indexes defined by El-Halwagi:[37] mass intensity index [(mass of raw materials − mass of ethanol)/mass of ethanol] and water intensity index (mass of fresh water used/mass of ethanol). The bioethanol composition before the separation step was also estimated. Table 6 summarizes the values for these parameters.

In order to select the alternatives with better potential, we assigned a priority order for three of the parameters shown in Table 6. The first one is the unit energy cost because it is related to the economic performance. As a second criterion, we used the mass intensity index (MII), which represents a feedstock efficiency usage. The third criterion was the water intensity index (WII), which is a measure of water efficiency usage. One can observe that the bioethanol composition shows a fairly clear dependence on the MII and WII indexes, such that the best indexes yield the highest bioethanol composition. It should be mentioned that the enzyme cost was not included in the analysis of the options based on enzymatic hydrolysis; consequently, a direct comparison between options based on acid hydrolysis and options based on enzymatic hydrolysis cannot be developed at this point. Therefore, we compared two independent sets of arrangements: one with the four options based on acid hydrolysis and the other one with 12 combinations based on enzymatic hydrolysis.

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Table 6. Comparison of 16 Combination Alternatives

	based on one tonne of dry biomas			unit energy cost	based on total mass of bioethanol produced		bioethanol composition before separation
combination	energy cost ($)	bioethanol gallons	water consumption (kg)	$/gallon (spent in energy)	mass intensity index (MII)	water intensity index (WII)	wt % kg/kg of mixture
SE-SHCF	13.40	78.92	4973.72	0.1697	3.25	21.13	4.02
SE-SSCF	12.42	81.49	4708.11	0.1524	3.11	19.37	4.20
LWH-AHF	53.95	66.47	9340.28	0.8118	4.04	47.12	2.41
LWH-AHCF	49.44	68.19	8586.75	0.7251	3.92	42.22	2.64
LWH-SHF	13.45	72.38	5186.55	0.1858	3.63	24.03	3.75
LWH-SHCF	13.74	81.85	4345.53	0.1679	3.10	17.80	4.68
LWH-SSF	13.71	72.66	3506.88	0.1886	3.61	16.18	4.96
LWH-SSCF	13.92	81.43	4114.25	0.1709	3.12	16.94	4.89
DA-AHF	46.07	72.45	7147.48	0.6358	3.63	33.08	3.41
DA-AHCF	46.17	72.79	7147.48	0.6343	3.61	32.92	3.43
DA-SHF	9.72	79.07	3667.27	0.1229	3.24	15.55	5.13
DA-SHCF	9.95	85.05	3284.88	0.1170	2.94	12.95	6.07
DA-SSF	9.94	77.18	2408.60	0.1287	3.34	10.46	6.97
DA-SSCF	10.09	84.80	3284.88	0.1190	2.95	12.99	6.08
AFEX-SHCF	27.48	90.87	6673.80	0.3024	2.69	24.63	3.79
AFEX-SSCF	24.54	90.33	6047.71	0.2716	2.71	22.45	4.15

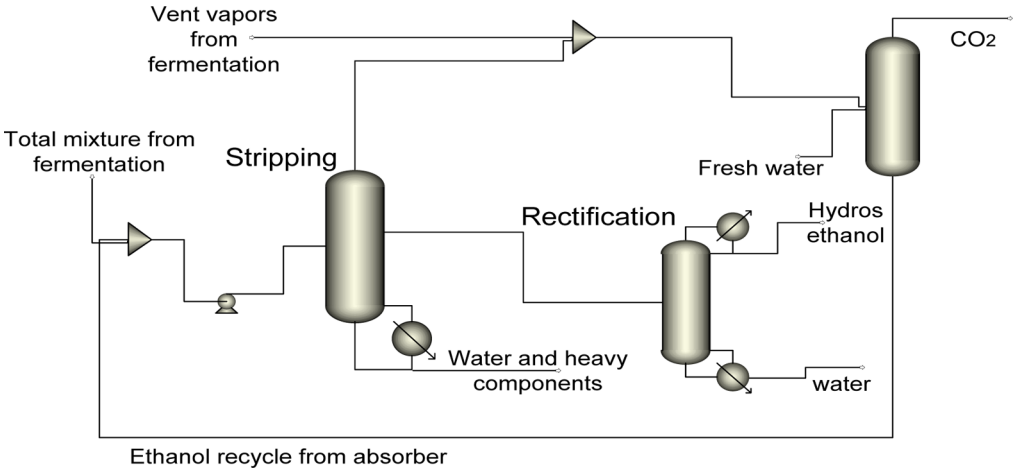

Figure 6. Distillation scheme.

For the options based on acid hydrolysis, DA-AHF and DA-AHCF show lower unit energy cost and lower values of MII and WII than the two alternatives with the use of LHW; therefore, we chose them as the best options. From the 12 combinations based on enzymatic hydrolysis, the options with DA pretreatment have the lowest values of unit energy costs; therefore, we selected them for further analysis. By comparing the MII values, it can be observed that the combinations based on AFEX pretreatment show better indexes. From these, AFEX-SHCF has the lowest MII value, but this option shows a higher unit energy cost than the AFEX-SSCF arrangement. Therefore, we took the AFEX-SSCF combination as the best option with AFEX pretreatment usage. As a result, five arrangements based on enzymatic hydrolysis have been identified as suitable for further analysis, which together with the two resulting schemes based on acid hydrolysis provide seven processing alternatives that emerge from this screening process.

ENERGY COST INCLUDING THE SEPARATION STEP BEFORE AZEOTROPIC COMPOSITION

To complement the pretreatment conversion analysis for the most promising seven combinations, a simple distillation scheme that purifies bioethanol close to the azeotropic composition was implemented. The separation process considered here is similar to the one reported by Wooley et al.[38] First, we used a stripping column with a side draw stream to separate the CO_2 that remained after fermentation. In the top of the column, a vapor stream consisting mainly of CO_2 was obtained. The side draw stream had a vapor with more than 50 wt % of ethanol, and the bottoms contained mainly water and heavy components. The second column had a partial condenser and was used to concentrate the ethanol close to the azeotropic composition. An absorber column was implemented in order to recover the ethanol fraction lost in the fermentation and stripping vapors; the absorber bottoms stream with water and ethanol was recycled to the stripping column. Figure 6 shows the distillation scheme.

In the stripping column, we targeted the ethanol mass recovery for the side draw stream and varied the vapor side stream rate. We started the simulations with a column of 20 stages and then varied the number of stages. From the column composition profile, we selected the tray with at least 50 wt % bioethanol composition and no CO_2 in the vapor phase as the side draw. In the rectification column, we targeted the ethanol mass recovery and the ethanol mass purity for the distillate stream and varied the

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mass reflux ratio. We started the simulations with a column of 30 trays and then varied the number of stages. We also varied the feed stage location. Table 7 gives the resulting characteristics for the stripping and distillation columns for each combination.

Table 7. Column Specifications

	stripping with side draw stream					
	no. stages	feed stage	*P* (atm)	side draw	wt % recovery	wt % purity
DA-AHF	35	1	1	14	99.11	50.52
DA-AHCF	35	1	1	14	99.11	50.61
DA-SHF	22	1	1	11	99.11	52.27
DA-SHCF	22	1	1	10	99.11	55.65
DA-SSF	22	1	1	12	99.11	55.06
DA-SSCF	22	1	1	10	99.11	55.66
AFEX-SSCF	28	1	1	16	99.11	50.60
	rectification column with partial condenser					
	no. stages	feed stage	*P* (atm)	reflux ratio	wt % recovery	wt % purity
DA-AHF	15	11	1	2.95	99.51	92.01
DA-AHCF	15	11	1	2.80	99.51	92.01
DA-SHF	15	12	1	2.60	99.51	92.01
DA-SHCF	15	11	1	2.44	99.51	92.01
DA-SSF	15	13	1	6.89	99.51	92.01
DA-SSCF	15	11	1	2.48	99.51	92.01
AFEX-SSCF	25	17	1	9.96	99.51	92.01

Figure 7 shows the energy cost based on one tonne of dry biomass for the seven combinations. The black color bar represents the energy cost for pretreatment and conversion steps, and the gray color bar represents the energy cost for the distillation step. It should be pointed out that from the alternatives based on DA pretreatment and enzymatic hydrolysis the DA-SSF combination had the highest ethanol composition after fermentation, although the energy consumption in the separation step was the higher. Also, AFEX-SSCF combination, which has the highest yield after fermentation, had the highest energy cost for the separation step.

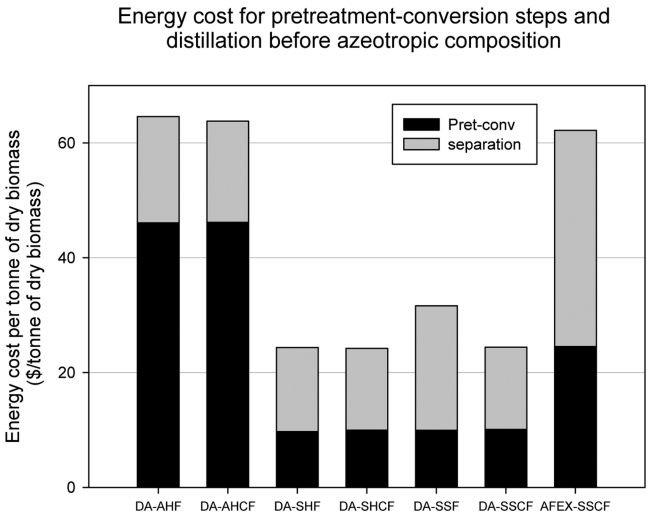

Figure 7. Energy cost for pretreatment conversion and separation steps.

The enzyme costs are still to be considered, but we can compare the options based on acid hydrolysis on one hand and on the other the five combinations based on enzymatic hydrolysis. The DA-AHCF shows a slight advantage with respect to the DA-AHF scheme. For combinations based on enzymatic hydrolysis, DA-SHF, DA-SHC, and DA-SSCF were identified as better combinations than the DA-SSF and AFEX-SSCF arrangements. Therefore, we have reduced our selection to four processing alternatives.

Figure 7 shows that the bioethanol production based on enzymatic hydrolysis has a promising potential from an energy point of view. However, one must keep in mind that the enzyme cost has an important contribution for the enzymatic hydrolysis alternatives; it remains to be seen if the DA-AHCF combination becomes competitive with respect to the enzymatic hydrolysis cases when the enzyme cost is considered. We recalculated the unit energy cost including the separation energy cost for the four alternatives selected above, with results given in Table 8.

Table 8. Unit Energy Cost Including the Distillation Step

	energy cost ($/tonne of dry biomass)	bioethanol gallons in the distillate (gallons/tonne of dry biomass)	unit energy cost [$/gallon (spent in energy)]
DA-AHCF	63.79	72.32	0.8814
DA-SHF	24.38	78.89	0.3090
DA-SHCF	24.20	85.02	0.2847
DA-SSCF	24.41	84.83	0.2877

REACTORS COST ESTIMATION FOR ALTERNATIVES BASED ON ENZYMATIC HYDROLYSIS

The three options based on enzymatic hydrolysis have similar unit energy cost (Table 8), so a fixed cost for the conversion step was estimated for further comparison. Table 9 shows reported residence times and corresponding dilution rates for the reactions systems of co-fermentation, glucose fermentation, enzymatic hydrolysis, and SSCF.

Table 9. Residence Time and Dilution Rate

conversion step	residence time (h)	dilution rate (h^{-1})	reference
xylose fermentation	25	0.04	Lawford et al.[20]
co-fermentation			
glucose fermentation	10	0.1	Brethauer and Wyman[3]
enzymatic hydrolysis	120	0.0083	Öhgren et al.[9]
SSCF	168	0.0059	McMillan et al.[39]

Table 10 reports the estimated reacting volume (*Vr*) for each reaction step involved in each configuration, and reactor volumes were taken as 20% above such values. We considered four options for tank volumes to implement such reactors.

The cost for each tank was estimated based on the report by Aden et al.[40] The annual fixed cost was estimated using a linear depreciation for 10 years, assuming 350 operating days/year. Table 11 shows the annual costs, annual production, and cost per gallon based on energy consumption and reactor fixed cost. On the basis of these estimations, the DA-SHCF combination seems to be the most promising synthesis route for bioethanol production.

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Table 10. Reactor Size for Each Configuration

	vol. flow (m^3/h)	Vr (m^3)	reactor volume	tank volume (m^3) 3500	3000	2600	2500
DA-SHF							
EHR	121.72	14665.06	17598.07		5	1	
XFR	83.75	2093.75	2512.50			1	
GFR	199.29	1992.9	2391.48				1
DA-SHCF							
EHR	189.99	22890.36	27468.43	1	8		
CFR	178.89	4472.25	5366.70		1		1
DA-SSCF							
SSCFR	188.15	31889.83	38267.79		13		

Table 11. Annual Costs and Yearly Production

combination	annual energy cost ($/year)	annual reactor fixed cost ($/year)	total cost ($/year)	total annual gallons	$/gallons
DA-SHF	8600780	479944	9080724	27832699	0.3263
DA-SHCF	8539056	682395	9221452	29995775	0.3074
DA-SSCF	8610715	806960	9417675	29928179	0.3147

ESTIMATION OF ENZYME COST CONTRIBUTION

The enzymatic hydrolysis process is characterized by low energy consumption, but an enzyme feed is needed. As we mentioned above, the enzyme contribution is very important for the process economics. One current problem is the absence of enzyme prices for industrial processes. What we can do here is to provide a maximum target value for the enzyme price. The difference between the unit energy costs for DA-AHCF and DA-SHCF combinations (considering only the energy cost for the conversion step) can be used for such estimation. The result is \$0.6343/gallon -\$0.1170/gallon = \$0.5173/gallon. Higher values will make this process unsuitable for implementation.

It should be mentioned that some alternatives to reduce the enzyme costs have been reported. For instance, enzyme recycling has been implemented at an experimental scale. The success of this alternative in a large scale process depends on the reactor design and on an efficient separation of enzymes from the reaction mixture.[41−43] Production in situ of cellulases, instead of purchasing, is another alternative to reduce the enzyme cost. In this case, the main base feedstock is used as a carbon source to generate cellulase enzymes.[44] Another interesting option is the implementation of a consolidated bioprocesing (CBP), a concept similar to the SSCF process, but the enzyme feed is not needed because microorganism are used to convert cellulose into sugars and the sugars into bioethanol.[45,46]

The enzyme hydrolysis-based processes have promising potential from an energy point of view, but the success for industrial implementation strongly depends on a suitable enzyme cost.

CONCLUSIONS

A comparison among pretreatment options and conversion configuration alternatives has been presented. Sixteen process options were evaluated. Simulations based on yield and stoichiometric relations were performed. Several process parameters were used, and the seven best alternatives were identified and subjected to an additional analysis by including a distillation sequence for product purification. From here, four combinations stood as the most promising options: one based on acid hydrolysis (DA-AHCF) and three others based on enzymatic hydrolysis. The three options based on enzymatic hydrolysis were further analyzed by including reactor cost estimations; the results showed that the DA-SHCF combination seems as the best alternative based on enzymatic hydrolysis.

We showed that the bioethanol synthesis based on enzymatic hydrolysis has a promising potential from an energy point of view. The final decision between acid and enzymatic hydrolysis, however, strongly depends on the enzyme cost available.

ASSOCIATED CONTENT

Supporting Information

Additional information containing the flowsheets here analyzed and lists of components and properties defined for the simulations. This information is available free of charge via the Internet at http://pubs.acs.org/

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Notes

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ABBREVIATIONS

AFEX, ammonia fiber explosion
AHCF, acid hydrolysis and co-fermentation
AHF, acid hydrolysis and fermentation
CFR, co-fermentation reactor
DA, dilute acid
EH, enzymatic hydrolysis
EHR, enzymatic hydrolysis reactor
GFR, glucose fermentation reactor
LCM, lignocellulosic materials
LHW, liquid hot water
LIME, alkali extraction with lime
MII, mass intensity index
OS, use of organosolvents
SE, steam explosion
SHCF, separated enzymatic hydrolysis and co-fermentation
SHF, separated enzymatic hydrolysis and fermentation
SSCF, simultaneous saccharification and co-fermentation
SSCFR, Simultaneous sacharification and fermentation reactor
SSF, simultaneous saccharification and fermentation
WII, water intensity index
XFR, xylose fermentation reactor

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