

Process Modeling and Integration of Fuel Ethanol Production from Lignocellulosic Biomass Based on Double Acid Hydrolysis

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Lignocellulosic biomass is considered as one of the most promising feedstocks for producing fuel ethanol because of its global availability and environmental benefits of its use. In this paper, the process of lignocellulosic ethanol production was investigated at its present state of development. The experimental data from the East China University of Science and Technology were used to develop a process model and evaluate the performance of the whole process design. For the process simulation, all relevant information about the process streams, physical properties, and mass and energy balances were also considered. Energy integration is investigated to identify the best ways to supply heat to the process, realizing also combined heat and power production from wastewater and residue treatment. The sensitivity on ethanol yield and the overall system performance are also investigated.

1. Introduction

Fuel ethanol, which can be produced from biomass via hydrolysis and fermentation, finds its application in powering engines as fuel either substituting gasoline or as a blend with gasoline for mitigating fossil greenhouse gas emission.^{1–3}

Nowadays, the commercial fuel ethanol sold in the market is mostly made from corn or sugar cane. Starch processing is a fairly mature technology.⁴ The top five ethanol producers in 2006 were the United States [18.38 billion liters per year (GI/y)], Brazil (17.00 GI/y), China (3.85 GI/y), India (1.90 GI/y), and France (0.95 GI/y).⁵

However, a dramatic increase in ethanol production using the current cornstarch-based technology may not be practical because corn production for ethanol will compete for the limited agricultural land needed for food and feed production.⁶ Studies show that the reduction of greenhouse gases resulting from the use of sugar- or starch-based ethanol is not as high as desirable because corn ethanol reduces greenhouse gas emissions only by about 13%.^{7,8} However, abundant biomass resources should be used without creating an environmental burden. In this respect, lignocellulosic materials such as crop residues, wood, grasses, etc., appear to be a more sustainable feedstock for ethanol production.

Lignocellulosic biomass is abundant in many countries. In China, for example, crop stalks or other agricultural waste amount to 700 million tons per year.⁹ The material resource, at least at present, has not found its way of full use. Facing the increasing demand from the fuel market, the development of the technologies for efficient fuel ethanol production from lignocellulosic biomass is of practical significance.

There are technical and economical impediments to the development of commercial processes using lignocellulosic biomass. However, many advances^{10,11} made over the past few years make commercialization more promising, and many projects are now running to realize commercial production.

In China, a 600 ton/year demonstration plant for the production of fuel ethanol from lignocellulosic biomass has been constructed in the Fengxian District, Shanghai, in 2005 (National “863” project). A team from East China University of Science and Technology (ECUST) is in charge of this project. The demonstration plant (Figure 1) was constructed using dilute acid hydrolysis technology, whereas research has also been carried out in enzymatic hydrolysis.

2. Process Description

2.1. Feedstock and Its Composition. Lignocellulosic biomass contains a complex mixture of carbohydrate polymers from the plant cell walls known as cellulose, hemicellulose, and lignin. The cellulose and hemicellulose are polysaccharides that can be hydrolyzed to sugars and eventually fermented to ethanol. Because lignin is indigestible by enzymes, it cannot be converted to ethanol and represents a major residue of the process. In the ECUST plant, the raw materials studied for ethanol production are shown in Table 1.

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(1) Lugar, R.; Woolsey, R. J. *Foreign Affairs* **1999**, *78* (1), 88–102.

(2) Champagne, P. *Resour. Conserv. Recycl.* **2007**, *50* (3), 211–230.

(3) Lavigne, A.; Powers, S. E. *Energy Policy* **2007**, *35*, 5918–5930.

(4) Gray, K. A.; Zhao, L. H.; Emptage, M. *Curr. Opin. Chem. Biol.* **2006**, *10*, 141–146.

(5) Industry Statistics, <http://www.ethanolrfa.org/industry/statistics/>.

(6) Sun, Y.; Cheng, J. Y. *Bioresour. Technol.* **2002**, *83*, 1–11.

(7) Farrell, A. E.; Plevin, R. J.; Turner, B. T. *Science* **2006**, *311* (5760), 506–508.

(8) Zah, R. *Schlussbericht*; EMPA: St. Gallen, Switzerland, 2007.

(9) Yuan, Z. H. *Int. J. Energy Technol. Policy* **2002**, *1*, 1–15.

(10) Zhang, S. P.; Yan, Y. J.; Ren, Z. W.; Li, T. C. *Prog. Chem.* **2007**, *7*, 1129–1133.

(11) Prasad, S.; Singh, A.; Joshi, H. C. *Resour. Conserv. Recycl.* **2007**, *50*, 1–39.



Figure 1. Demo-plant of ethanol production from lignocellulosic biomass.

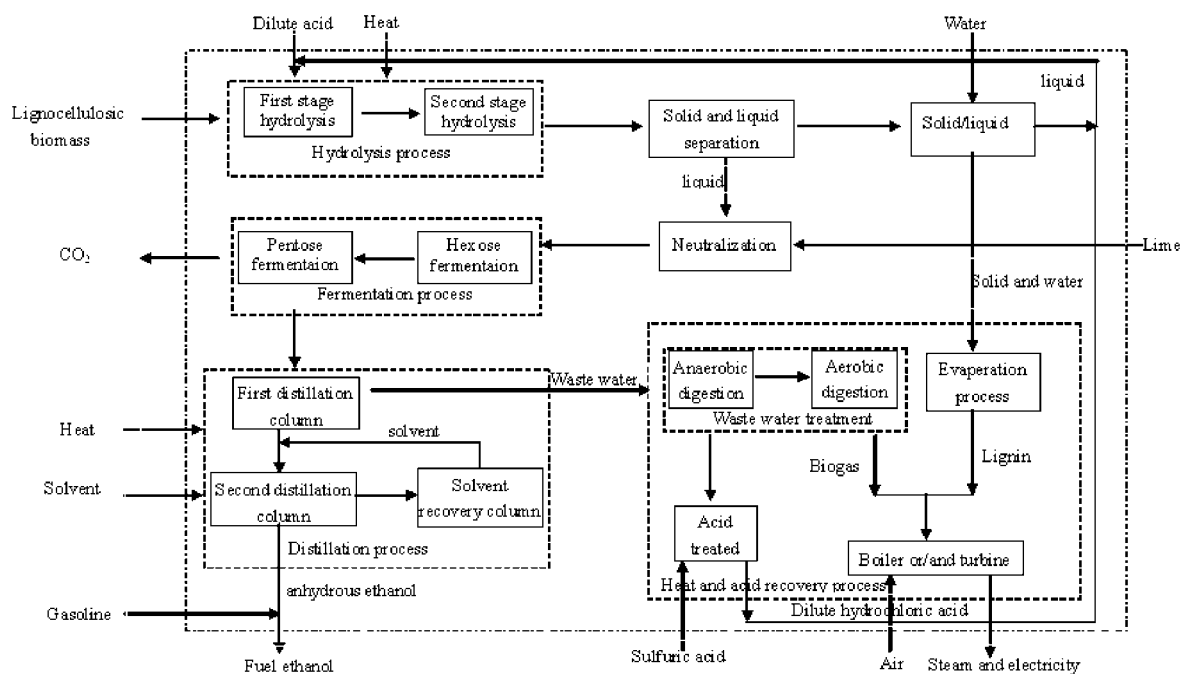


Figure 2. Fuel ethanol production process from lignocellulosic biomass.

Table 1. Typical Composition of Lignocellulosic Feed Materials

lignocellulosic biomass	water (%)	hemicellulose (%)	cellulose (%)	lignin (%)	ash and others (%)
sawdust	15	21.09	36.61	26.48	0.82
rice husk	15	27.22	24.30	12.59	20.89
corn stalk	15	24.87	34.51	14	11.62

For the base case simulation, the material used is assumed to contain 35% cellulose, 25% hemicellulose, 25% lignin, and 15% moisture, as presented in Table 2. Its lower heating value (LHV) is of 16.95 MJ/kg.

2.2. Process Steps. Fuel ethanol production from lignocellulosic biomass includes six major steps (shown in Figure 2): hydrolysis of hemicellulose and cellulose to sugar, fermentation of sugar to ethanol, ethanol recovery from the fermentation broth, mixing of ethanol and gasoline to production of fuel ethanol, and lignin and wastewater treatment for the energy recovery and environmental protection. These major steps will be discussed hereafter, and the technological improvement and research status will be presented.

Table 2. Lignocellulosic Feed Material for the Base Case Simulation

composition analysis	cellulose	hemicellulose	lignin	moisture
value (wt %)	35	25	25	15
chemical formula	$C_6H_{10}O_5$	$C_5H_8O_4$	$C_6H_{11}O_2$	
HHV of component ¹¹ (MJ/kg)	17	17	27	
elemental analysis	C	H	O	N
value (wt %)	49.13	6.93	43.9	0

2.2.1. Hydrolysis. In this study, we considered only the dilute acid hydrolysis because our research results suggest that^{12,13} (1) the process is the closest to commercial operation, (2) the dilute acid hydrolysis could be used as a pretreatment step for enzyme hydrolysis when the enzyme cost will become acceptable, (3) higher sugar yields and a higher sugar concentration could be obtained by a two-stage process, and (4) the energy consumption could be minimized using process and energy integration.

(12) Yuan, C. M. PhD Thesis, East China University of Science and Technology, Shanghai, China, 2004.

(13) Li W. Z. PhD Thesis, East China University of Science and Technology, Shanghai, China, 2008.

2.2.2. *Fermentation.* Contrary to starch-based ethanol production, lignocellulosic biomass ethanol production is a mixed-sugar fermentation in the presence of inhibiting compounds. The different sugars require different organisms for fermentation. Six carbon sugars (hexose) are readily fermented to ethanol by many naturally occurring organisms with high yields, but the five-carbon sugars (pentose) are more difficult to ferment to ethanol and usually only at a relatively low yield.

The glucose is first fermented to produce ethanol, followed by the fermentation of xylose at a slower rate and with a lower yield. The future overall performance strongly depends upon the development of cheaper and more efficient microorganisms for fermentation.¹⁴ In our model, the sugar consumption for organism growth has been neglected.

After the fermentation reactors, the fermentation broth is sent to the ethanol recovery and purification.

2.2.3. *Distillation.* Distillation is a mature process for ethanol recovery. The first part is distilling the fermentation broth to separate ethanol from water to reach an ethanol concentration of 95%, and the bottom liquid is sent to the wastewater treatment.

The ethanol–water azeotrope is broken by adding a small amount of benzene or cyclohexane. In the process under study, cyclohexane was used as an entrainer to achieve an ethanol concentration of 99.5 wt %. The solvent is recovered using a phase separator tank followed by a distillation column. After this concentration step, the ethanol is ready to be used as a fuel blended with gasoline.

2.2.4. *Wastewater Treatment.* The bottom water of the first distillation column contains some chemicals, such as furfural, from the hydrolysis byproduct, a small part of the nonconverted sugar, some ethanol not recovered in the column, and some of the microorganisms. Therefore, wastewater treatment by anaerobic and aerobic digestion is necessary and allows one to by-produce biogas from the residues.

In the acid recovery unit, hydrochloric acid is recovered by treating the wastewater with sulfuric acid. As stated above, the energy consumption for hydrochloric acid hydrolysis is less than that of sulfuric acid hydrolysis. However, hydrochloric acid is more expensive than sulfuric acid.

In this way, the wastewater treatment process allows for recycling of the water required as a production support, recovers the hydrochloric acid, and provides at the same time some biogas that can be a utility for the process.

2.2.5. *Lignin Treatment.* Lignin is present in all lignocellulosic biomass, and it cannot be hydrolyzed to fermentable sugars. Therefore, any ethanol production process will have lignin as a residue, which can either be sold or used as fuel to supply the energy requirement of the process while by-producing electricity.

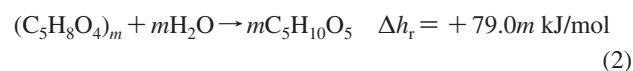
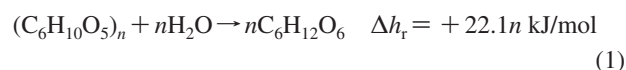
2.2.6. *Utility and Heat Recovery System.* The scale-up from demo-scale production of lignocellulosic ethanol to competitive commercialization production requires an efficient utility and heat recovery system to further reduce the operating cost. One approach to supply the necessary heat for the ethanol production chain is to install a combined heat and power production unit fired by the by-produced biogas and lignin. In our study, we considered the use of a steam Rankine cycle to convert the energy of the byproduct into heat and electricity for the process as a reference case. This is compared to alternative ways of converting the co-products by either increasing the efficiency of the co-production of electricity using an integrated gasification

combined cycle¹⁵ or co-producing additional biofuels by thermochemical processes.

3. Process Modeling

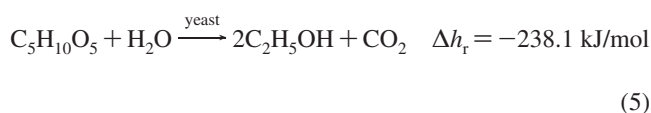
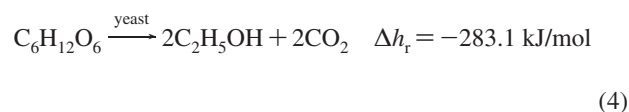
3.1. *Methodology.* Using the experimental data from East China University of Science and Technology and physical property data of the lignocellulosic raw materials and products, a thermodynamic model has been developed using the commercial flowsheeting software Belsim-VALI,¹⁶ which can be applied for both design and data reconciliation purposes. From this energy-flow model, the heat-transfer requirements of the process are determined as hot and cold streams and passed to the in-house energy integration software EASY that calculates the optimal combined heat and power production based on pinch analysis and heat cascade models.¹⁷

3.2. *Description of the Energy-Flow Model.* 3.2.1. *Hydrolysis.* Hydrolysis with hydrochloric acid as a catalyst is modeled. It requires a low reaction temperature of about 155–165 °C compared to 205–215 °C in sulfuric acid hydrolysis.¹³ To reduce the sugar degradation and increase the monosaccharide concentration, a two-stage hydrolysis is used. According to reactions 1–3, cellulose is converted to glucose and hemicellulose to xylose, with the latter being then partly degraded to furfural. The observed conversion rates of the reactions are 80, 70, and 10%, respectively.



After solid separation, the hydrolyzed solids are washed and pressed to extract the remaining liquid portion of the hydrolyzate, including acid and sugars. In this step, it is assumed that 100% of the solubilized materials are recovered and recycled to the hydrolysis part for dilute acid preparation. The solid stream leaving the filters contains up to 75% water and is fed to the lignin treatment process to recover the lignin product.

3.2.2. *Fermentation.* According to reactions 4 and 5, glucose is first fermented to ethanol with 95% conversion, followed by the fermentation of xylose at a slower rate and with a lower yield of 60%.



It should be noted that the sugar consumption for the inoculate of the organism is neglected in this model.

3.2.3. *Distillation.* In the concentration column, the feed stream with 2.69 wt % ethanol is separated into a distillate with 40 wt % ethanol and a bottom stream of 0.02 wt %. The ethanol is concentrated in a rectification column to reach 95 wt % ethanol. The distillate of this column is fed to an azeotropic

(15) Hamelinck, C. N.; van Hooijdonk, G.; Faaij, A. P. C. *Biomass Bioenergy* **2005**, *28*, 384–410.

(16) www.belsim.com.

(17) Kemp, I. C. Personal communication, Oxford, U.K., 2007.

(14) Lynd, L. R. *Annu. Rev. Energy Environ.* **1996**, *21*, 403–465.

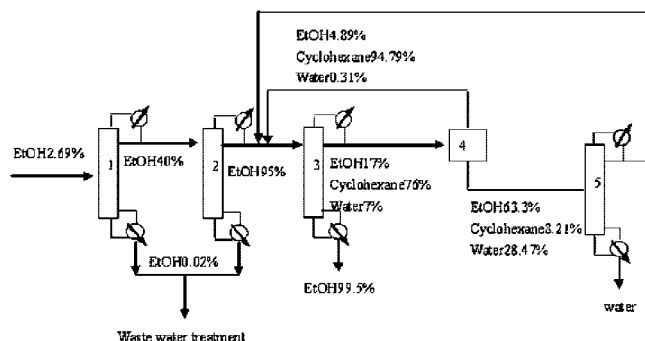


Figure 3. Diagram of recovery of fuel ethanol based on azeotropic distillation.

Table 3. Compositions of Ternary Azeotrope and Separated Phases (wt %)

composition	cyclohexane	ethanol	water
azeotrope	76	17	7
light phase	94.79	4.89	0.31
heavy phase	8.21	63.30	28.47

Table 4. Thermodynamic Models Used for the Distillation Simulation

methods	vapor	liquid
fugacity	VIRIAL	NRTL
enthalpy	Peng–Robinson	Peng–Robinson
volume	LASSC	LASSC
conductivity	Stiel–Thodos	Robbins–Kingrea
viscosity	Chapman–Enskog	Van Velzen
volume pressure drop	LASSC	LASSC

Table 5. Binary Parameters for the Ethanol–Water System

method	parameter	value
VIRIAL	ETA	-0.931447
NRTL	ijCO	-331.85
NRTL	jiCO	462.79
NRTL	ijAO	-0.396804
NRTL	ijCT	1.2928
NRTL	jiCT	0.214686
NRTL	ijAT	0.00275277

column with cyclohexane as an entrainer, from which 99.5 wt % pure ethanol is recovered at the column bottoms. The distillate is directed to a separator where its light phase (cyclohexane enriched) and heavy phase (ethanol and water enriched) are separated. The composition of the streams involved in this separation are shown in Table 3. The light phase is taken back to the azeotropic column as reflux stream, and the other one is fed to the stripper, where most of the water is collected and the distillate is recycled to the azeotropic column (see Figure 3).

The thermodynamic models and the binary interaction parameters for the ethanol–water mixture are shown in Tables 4 and 5. The methods from Fenske, Underwood, and Gilliland^{18–20} are used for the preliminary column design.

3.2.4. Wastewater Treatment. Wastewater is conveniently treated by anaerobic and aerobic digestion. Anaerobic digestion produces biogas that is rich in methane and can be recovered or used as utility for the process. Within anaerobic digestion, 90% whole organic component is converted to methane and carbon dioxide. Therefore, a subsequent aerobic digestion step is needed to complete the treatment and obtain a relatively clean water stream that will be recycled in the process. Sulfuric acid is used to recover the dilute hydrochloric acid.

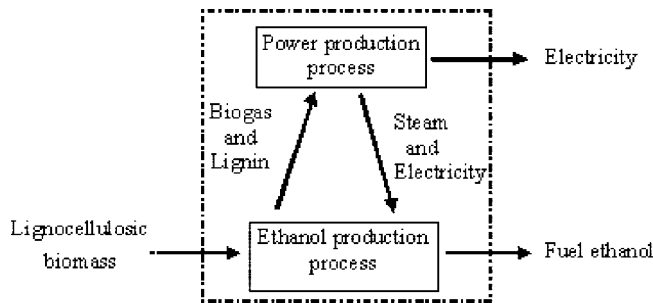


Figure 4. Integration of the ethanol production process with combined heat and power production.

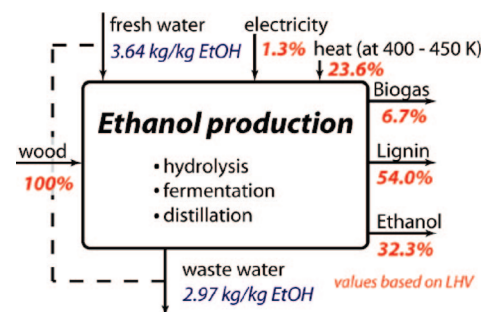


Figure 5. Overall balance of the plant.

Table 6. Residue Composition

water (%)	hemicellulose (%)	cellulose (%)	lignin (%)	LHV (MJ/kg)
35	8.02	16.85	40.12	14.21

Table 7. Conditions of the Steam Cycle

header	T (K)	p (bar)
high pressure	823	80.0
medium pressure	450	9.31
low pressure	425	5.00
condensation	293	0.02

Table 8. Comparison of Energy Balances for the Different Residue Usage Alternatives

		base case	IGCC	SNG
input	wood	57.55 MW	57.55 MW	57.55 MW
	electricity			1.73 MW
intermediates	total	57.55 MW	57.55 MW	59.28 MW
	biogas	3.86 MW	3.86 MW	3.86 MW
	lignin slurry	31.08 MW	31.08 MW	31.08 MW
output	ethanol	18.57 MW	18.57 MW	18.57 MW
	SNG			23.19 MW
efficiencies	electricity	9.84 MW	12.37 MW	
	total	28.41 MW	30.94 MW	41.76 MW
	η_{etoh}	32.3%	32.3%	32.3%
	η_{SNG}			40.3%
	η_{elect}	17.1%	21.5%	-3.0%
	η_{total}	49.4%	53.8%	70.5%

3.2.5. Lignin Treatment. The lignin and nonconverted residues leaving the fermentation and separation steps with 75% moisture are dried in a three effects evaporator to reach a targeted moisture content of about 35%. The presence of lignin thereby delays the boiling of the liquid, whose boiling point can be adjusted according to eqs 6 and 7²¹

$$T_{\text{EB}} = T_{\text{BP}}(P) + \Delta T_{\text{BP}}(\% \text{ Sicc}) \quad (6)$$

where $T_{\text{BP}}(P)$ designates the boiling point of pure water, T_{EB} designates the boiling point of the lignin slurry, and ΔT_{BP}

(18) Fenske, M. R. *Ind. Eng. Chem.* **1932**, *24* (5), 482–485.

(19) Underwood, A. J. V. *Chem. Eng. Prog.* **1948**, *44* (8), 603–614.

(20) Gilliland, E. R. *Ind. Eng. Chem.* **1940**, *32* (9), 1220–1222.

(21) Palese, V. Diploma Thesis, Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland, 2007.

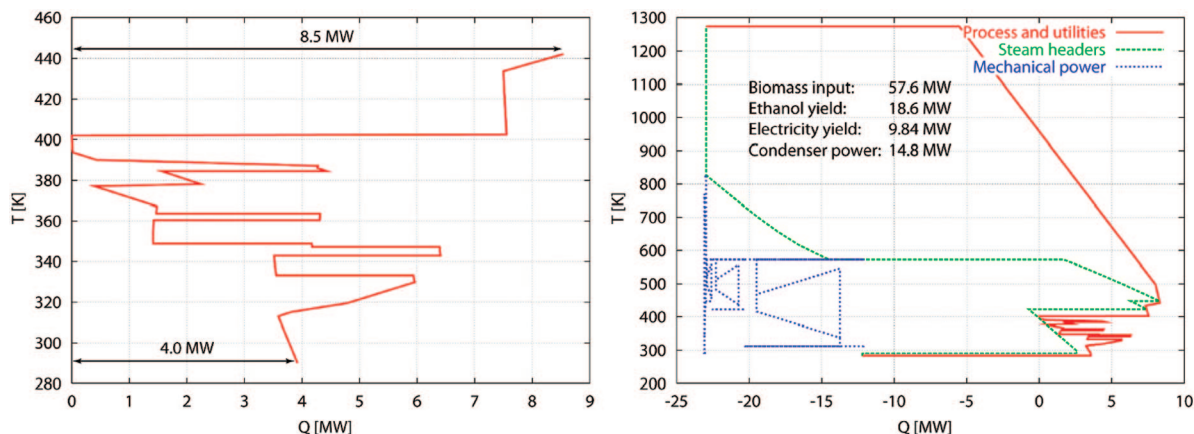


Figure 6. Composite curve (left) and integrated composite curve (right) of the lignocellulosic ethanol production process.

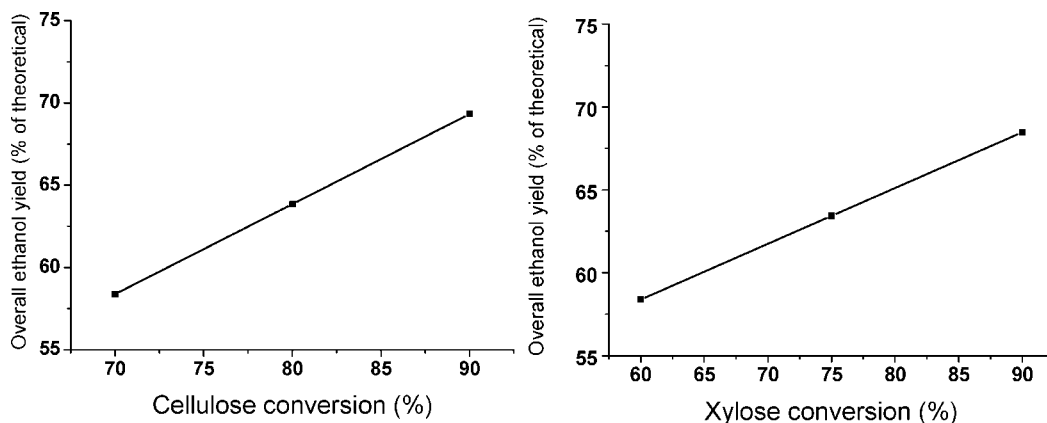


Figure 7. Effect of cellulose (left) and xylose (right) conversion on ethanol yield.

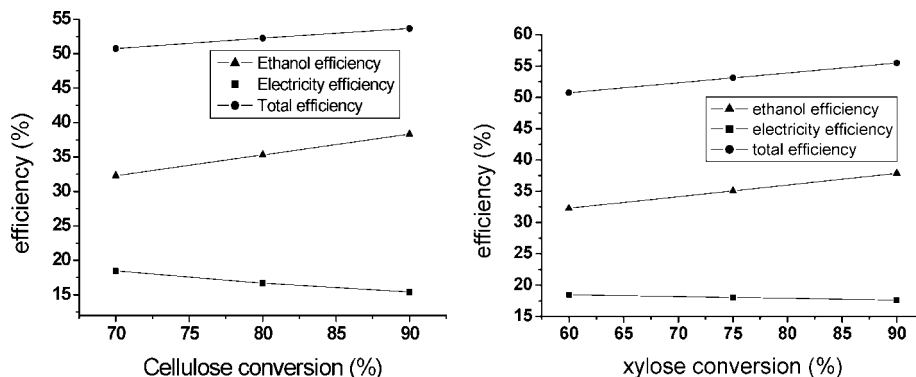


Figure 8. Effect of cellulose (left) and xylose (right) conversion on process efficiencies.

designates the boiling temperature delay. The latter can be correlated with the solid fraction S_{icc} (%) of the slurry (eq 7)

$$\Delta T_{BP} = \frac{8 \times \% S_{icc}}{100 - \% S_{icc}} \quad (7)$$

3.3. Energy Integration. The heat-transfer requirements of the process are obtained from the flowsheet model. Defining the list of hot (to be cooled down) and cold (to be heated up) streams of the process, the minimum energy requirements are determined by applying a pinch analysis and formulating the heat cascade.¹⁷ In a second step, suitable energy conversion technologies, such as combustion, steam cycles, or heat pumps, are identified. Formulating the problem as a mixed integer linear programming problem with the heat cascade as constraints, the

combined heat and power production are optimized and all of the flows in the system are calculated.²²

In the present study, a steam network with one production level at 80 bar ($T_{sat} = 295$ °C) superheated to 550 °C, 2 utilization levels at 9.31 bar (177 °C) and 5.00 bar (152 °C), and 1 condensation level at 0.02 bar (20 °C) has been considered. The efficiencies of the backpressure and condensation steam turbines are assumed to 80 and 70%, respectively. The combustion is assumed to be complete, and the best air preheating temperature is determined by the model. The biogas and the dried lignin slurry also containing the nonconverted residues of cellulose and hemicellulose are recovered from the process and used as a fuel in a recovery boiler. Because their energy content is higher than the heat demand of the process,

(22) Gassner, M.; Maréchal, F. *Comput. Chem. Eng.* **2009**, accepted for publication.

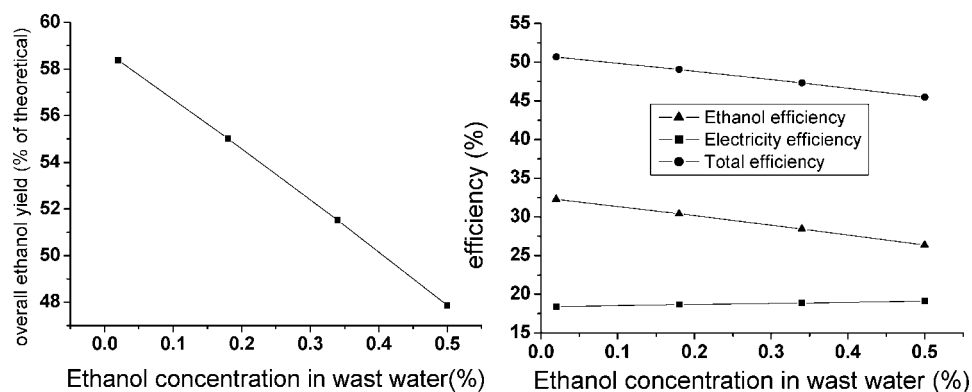


Figure 9. Effect of the ethanol concentration in the bottom product on ethanol recovery (left) and efficiencies (right).

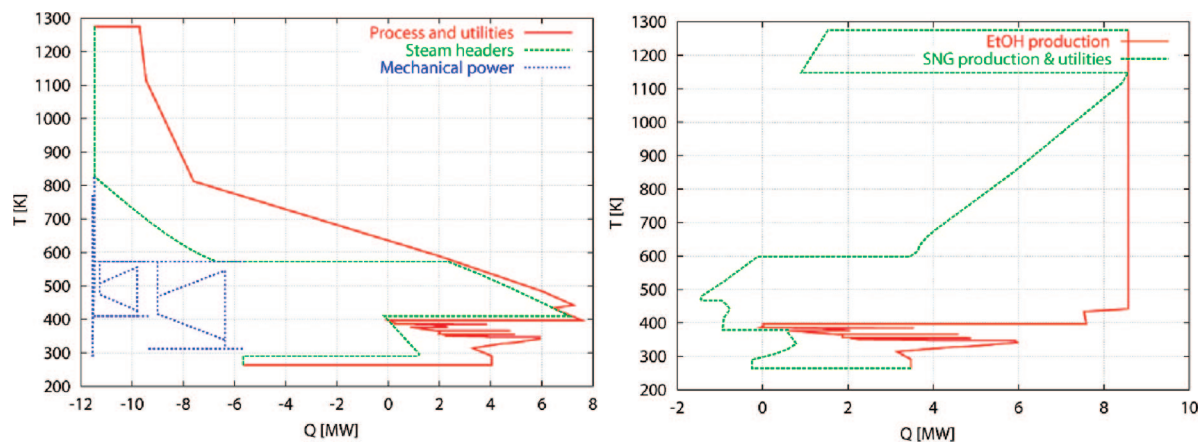


Figure 10. Integrated composite curves of ethanol production with lignin treatment by an IGCC (left) and a SNG plant (right).

the heat recovery system allows for a considerable by-production of electricity to supply the process needs and to feed the excess power to the grid as shown in Figure 4.

4. Simulation Results and Discussion

4.1. Base Case. A plant designed to process 100 000 tons of raw material annually is investigated here as a base case. With an annual operating time of 8000 h, this represents a equivalent capacity of 57.6 MW_{th} of biomass processed. The objective of this paper is maximization of efficiency.

After the hydrolysis, a hydrolyte liquid containing 2.89 wt % xylose concentration and 3.50 wt % glucose concentration is obtained.

For the fermentation, although most of the cellulose can be converted to ethanol (95% glucose can be converted), while the xylose conversion is not so high, conversion of xylose to ethanol is only 60%.

After the fermentation step, the ethanol concentration in the feed of the purification section is 2.69 wt % and the overall ethanol yield is equal to 58.25% of the theoretical yield.²³

Within anaerobic digestion, 90% of each organic compound is converted to methane and carbon dioxide. The biogas, containing about 27.05% methane and having an approximate LHV of 13.53 MJ/kg, represents 6.7% of the energy content of the biomass input and is fed directly into the boiler for steam generation.

Residues were concentrated by three effects of evaporation; the residues composition was shown in Table 6. After evaporation, lignin moisture reaches 35% and a lower heating value of 14.21 MJ/kg.

Waste water was treated using sulfuric acid to recover hydrochloric acid and, at the same time, to reduce water makeup; about 90% hydrochloric acid can be recovered.

In general, this process needs a large amount of water, and therefore, it is important to recover and recycle it as much of as possible to minimize the required fresh water makeup. After our analysis, the water makeup could be reduced (excluding the water required by the makeup of cooling boilers), 3.64 kg to produce 1 kg ethanol, and with the CaCl₂ treatment step, the water needed is only 0.67 kg/kg of ethanol.

The overall balance of the non-integrated process is shown in Figure 5. The minimum energy requirement and the integrated composite curve for the whole process are shown in Figure 6. The corresponding energy balance including the co-generated electricity is shown as a base case configuration in Table 8. The total efficiency of the process suffers from the limited conversion of xylose and the fact that lignin is not digested. In comparison to the heat requirement of 8.5 MW between 129 and 169 °C, 73% of the waste stream has no value for the process and has to be wasted or converted into other useful energy services. The option considered here is the integration of a steam turbine that co-generates heat and produces mechanical power. The counterpressure mode is thereby considered to supply the heat to the process, and the condensing mode is considered to convert the excess heat into electricity. The characteristics of the steam cycle are given in Table 7. The total energy efficiency is defined as the ratio of the energy value of the products to the energy value of the input (eq 8)

$$\eta_{\text{total}} = \frac{\text{energy}_{\text{ethanol}} + \text{energy}_{\text{electricity}}}{\text{energy}_{\text{biomass}}} \quad (8)$$

On the basis of the lower heating values of biomass and ethanol, it amounts to 49.37%.

(23) Vadas, P. A.; Barnett, K. H.; Undersander, D. J. *Bioresearch Energy* 2009, in press, doi: 10.1007/s12155-008-9002-1.

4.2. Sensitivity Analysis on Ethanol Yield. As outlined above, the overall ethanol yield is not so high. One of the main reasons is that the conversion of biomass to fermentable sugar is limited to 70% to avoid the release of possible inhibitors. Another reason is that the conversion of xylose to ethanol is only 60%. If the conversion can be increased by technical development, the overall ethanol yield can be increased.²⁴ The effects of cellulose and xylose conversion on the ethanol yield and the corresponding efficiencies are shown in Figures 7 and 8. With the increase of cellulose conversion from 70 to 90%, the ethanol yield can be increased by 11%, while an increase of the xylose conversion from 60 to 90% results in increasing the ethanol yield by 10%. In terms of efficiency, this corresponds to an increase of 6 and 5.5%, respectively. Because a higher conversion to ethanol decreases the amount of unconverted material available for combustion, this positive effect is attenuated a lower by-production of electricity. If the cellulose conversion is increased from 70 to 90%, this production falls by 3% and the overall efficiency increases by only 3%. In case of an increase of xylose conversion from 60 to 90%, the electric efficiencies decrease by 1% and the overall efficiency increases by 4.5%.

Another important influence on the ethanol recovered is due to the ethanol fraction in the distillation bottom product. Figure 9 shows that an ethanol concentration decrease from 0.5 to 0.02 wt % would increase the overall ethanol recovery by about 10% and increase ethanol efficiency by about 6%.

4.3. Other Options for the Conversion of Residues. As already highlighted in the discussion of the composite curves (Figure 5), the combustion of all of the residues (3.86 MW of biogas and 31.08 MW of lignin slurry) is not a very efficient way of conversion. On one hand, high exergy losses occur because of the large temperature difference between the hot flue gases and the steam production. On the other hand, the amount of heat available from the fumes is much higher than the actual heat required by the process. As indicated by the large cooling water load, the Rankine cycle is thus to a large extent operated independently of the ethanol plant for electricity production and the benefits of process integration are small.

For this reasons, it appears interesting to investigate other options of converting the residual lignin. A first, technically mature one is its use as feedstock in an integrated gasification combined cycle (IGCC), where the feedstock is first gasified and the producer gas is directly burnt in a close-coupled gas turbine. The excess heat from the gas turbine exhausts is further recovered by a steam cycle, which, as before, also satisfies the heat requirements of the process. For the purpose of this study, a process model for this technology²⁵ has been integrated with the ethanol process.

The integrated composite curve of the IGCC case on the left part of Figure 10 shows that the exergy losses because of the high temperature differences between the hot and cold streams decrease. The energy excess is better converted in electricity. Therefore, less cold utility is necessary than in the base case, and less energy is lost to the atmosphere in the condenser of the Rankine cycle. The comparison of the overall energy balance

of Table 8 highlights the advantages of a better process integration. In the IGCC case, the electricity production raises from 0.317 to 0.398 MJ_e/MJ_{th}, which corresponds to a 25% increase.

As a second alternative, the lignin could be gasified and the producer gas converted to methane. After separation of the by-produced CO₂, the gas reaches a quality that allows its injection as synthetic natural gas (SNG) into the natural gas grid. Because the methanation reaction is exothermic and realized at around 300–400 °C, it is possible to use it as a hot utility for the ethanol plant. A thermo-economic model of the SNG production has been developed in refs 26 and 27 and integrated with the ethanol production process model detailed in the present work.

When conversion of lignin to SNG is performed, the heat from the SNG process is just sufficient to satisfy the demand of the ethanol plant and no excess heat is available to co-produce electricity. However, if SNG is considered as a transportation fuel, the biofuel production of 32.3% in the form of ethanol is more than doubled by adding 40.3% SNG and leads to an overall biofuels production of 70.5%, if we consider the electricity requirement for the process.

5. Conclusions

An ethanol production process from lignocellulosic biomass was modeled on the basis of the experimental data obtained from an existing plant. In the pretreatment section, the double acid hydrolysis is used, in which hydrochloric acid catalyst allows for the reaction temperature reduction and where sulfuric acid is used to recover the hydrochloric acid. To reduce the degradation and increase the sugar concentration, a two-stage process operation is used to increase the monosaccharide concentration. A sensitivity study revealed that, with the increase of cellulose conversion from 70 to 90%, ethanol yield can be increased by 11%. With an increase of xylose conversion from 60 to 90%, ethanol yield can be increased by 10%. The study also shows the impact of the raw material on the ethanol conversion and the overall efficiency of the process. The byproduct biogas and lignin are considered to produce heat and electricity to cover the demand of the whole process. Surplus energy was used to generate electricity, which results in a total energy efficiency of 49.4%. The energy integration reveals that there is potential for a much more efficient conversion, if the byproducts are used in another way than a simple steam cycle. When the lignin is fed to an IGCC process, the electric efficiency is increased by 25%, which leads to an overall efficiency of 53.8%. However, the best solution is reached when converting the lignin into synthetic natural gas and using its excess heat for the ethanol process. With this option, the total biofuel production is more than doubled and an overall efficiency of 70.5% is reached.

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(26) Duret, A.; Friedly, C.; Maréchal, F. *J. Cleaner Prod.* **2005**, *13*, 1434–1446.

(27) Gassner, M.; Maréchal, F. *Biomass Bioenergy* **2009**, manuscript submitted.

(24) Byron, C. H.; Lee, C. H. *Biotechnol. Adv.* **2007**, *25*, 425–441.

(25) Brown, D.; Gassner, M.; Fuchino, T.; Maréchal, F. *Appl. Therm. Eng.* **2009**, in press.