

Increasing Efficiency of Fuel Ethanol Production from Lignocellulosic Biomass by Process Integration

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ABSTRACT: The conversion of lignocellulosic biomass to ethanol is currently one of the most popular options for sustainable production of transportation fuel from renewable resources. Due to the resistance of lignin compounds to biological degradation and the important heat requirements for distillation, conventional process designs for the combined production of ethanol and power are yet limited to a modest total energy efficiency of 50% to 55%. This paper investigates how to overcome this limitation by thermochemically converting the residues in order to increase the total energy yield by a combined generation of several fuels and power. Comparing a conventional design with different technological alternatives for thermochemical processing and heat and power recovery, the paper shows that the fuel yield can be more than doubled to reach total energy and exergy efficiencies of up to 72% and 78%, respectively. From a methodological point of view, the paper demonstrates that the combination of process integration and exergy recovery techniques in a site-scale approach is key for tapping the full potential of the limited biogenic resources in future biorefineries.

1. INTRODUCTION

1.1. Background. In the public and scientific debate, the production of ethanol from lignocellulosic biomass is one of the most popular options for biofuel production since the feedstock does a priori not directly compete with food production and ethanol is compatible with conventional petrol-fuelled cars.^{1–4} Since lignin resists biological degradation and hemicellulose can only be partially hydrolyzed, ethanol fermentation yet suffers from a relatively low fuel yield and requires a high amount of heat for its distillation across the azeotrope to reach the required quality for its use as automotive fuels (the required heat equals approx. 45% of the product's heating value, cf. Figure 2(c)). In the absence of another valorization of the residues as commodities or bioproducts, the process efficiency and productivity of the resource is therefore essentially dependent on the internal use of the residues and the quality of the process integration. The conventional intention envisaged in the early and still popular design proposed by Aden et al.⁶ is to dry and burn the residual lignin slurry in order to provide heat for the distillation and power cogeneration, which reaches an overall energy efficiency of around 40 to 53% (Table 1). Since the chemical energy contained in the residuals is considerably higher than what is needed for distillation, this

kind of process integration yet results in an important surplus of heat that is converted at low thermodynamic efficiency in a steam cycle.⁵ For this reason, thermochemical processing⁷ is a promising alternative to combustion since it also completely converts the residues but maintains part of their energy content in chemical form and releases useful heat at high temperature.

1.2. Previous Work. In the scientific literature, the gasification of the unfermented residues from bioethanol production, and thus the integration of biological and thermochemical conversion technologies, has been repeatedly proposed and analyzed.^{8–13} Most of these studies have either investigated conversion concepts on a macroscopic level⁹ or provided detailed techno-economic analyses of some flowsheet scenarios based on engineering knowledge and intuition.^{8,10,11} Usually, the scenarios are developed by hand and systematic process integration methods for optimizing the design (e.g., pinch and exergy analysis) are not routinely applied.^{8–10} To our knowledge, the thermal integration of ethanol fermentation and thermochemical conversion of its residues has only been investigated for ethanol production from sugar cane and power cogeneration from the by-produced bagasse with an integrated gasification combined cycle (IGCC) instead of a conventional single cycle.^{12,13} Together with ref 14 that targets to maximize the energy efficiency of an ethanol plant converted from a kraft pulp mill, these works are exemplary in their successful use of heat and process integration approaches, which are rare in the bioethanol sector.¹⁵ In particular, the integration of processes based on lignocellulosic feedstock and further conversion of the thermochemically generated gas to synthesis fuels has never been analyzed yet.

In the literature that particularly emphasizes methodology, some systematic approaches for the optimal synthesis of

Table 1. Typical Conversion Efficiencies When Combusting the Unconverted Residues for Power Cogeneration in a Steam Rankine Cycle^a

	ethanol	power	total
Aden et al. ⁶	49%	4%	53%
Hamelinck et al. ⁸	35–40%	5–10%	40–50%
Zhang et al. ⁵	32%	17%	49%

^aNote: refs 6 and 8 report in higher and ref 5 in lower heating values. Considering that the ratio between these values is similar for biomass and ethanol, the numbers are comparable. Differences are mainly due to the macromolecular composition and assumed conversion yields.

Received: November 29, 2012

Revised: March 9, 2013

Published: March 12, 2013

integrated bioethanol production processes have recently been proposed.^{16–18} These studies have focused on aspects like product separation, water use, and energy targeting but have not considered in detail important elements like the valorization of byproducts or the actual integration of the utility and heat recovery system with the process. As noted in recent reviews, systematic process optimization considering process integration and the cogeneration of other fuels from the residues still represents a major research challenge and is mandatory for the successful commercial implementation of plants based on lignocellulosic matter.^{7,15,19}

1.3. Objective and Scope. In the context outlined above, the objective of the present paper is to analyze the potential benefit of using systematic process integration methods for polygeneration plants that produce multiple fuels, power, and heat. In particular, it discusses the prospects for increasing the conversion efficiency of biomass to fuel by the polygeneration of ethanol, synthetic natural gas (SNG), and power. SNG is selected here as the coproduced fuel since the generation of excess heat seems to match well with the requirement for ethanol production,⁵ and because it also emerges as a particularly efficient stand-alone process that outperforms Fischer–Tropsch (and other liquid) fuels by roughly 15%–points in terms of overall conversion efficiency^{20–24} and is technically mature to supply natural-gas driven cars in the near future at commercial scale.

2. METHODOLOGY

2.1. Process Modeling and Integration. This paper applies a previously developed systematic methodology for the optimal process design and integration for the conversion of lignocellulosic biomass to fuel(s), power, and heat.^{25–27} In the proposed approach, the energy and mass integration of the process is combined by formulating a mixed integer linear programming (MILP) problem in which both the mass balances between the subsystems and the heat cascade of the corrected temperature–enthalpy profiles act as constraints. After a preliminary analysis of the energy integration and the minimum energy requirement (MER) of the principal conversion route, appropriate technologies for supplying the required energy and recovering the excess heat are chosen. Depleted residuals like off-gases, and in the present case also the lignin slurry (cf. Section 3), are thereby considered as possible heat or energy sources. If these are not sufficient, they are completed by intermediate product streams to balance the heat requirement of the process. Since this directly affects the fuel yield and the heat and power cogeneration, its selection is implemented in a MILP formulation that determines the optimal process integration by maximizing the total value of the combined production of fuel(s) and the cogenerated power from excess heat, which is equivalent to minimizing the exergy depletion in the heat recovery and energy conversion system.^{25–27}

2.2. Selection of Energy Conversion Technology. Applying the same methodology, the present work focuses on the identification of appropriate energy conversion technology to maximize the combined product yields through process integration. Starting with a conventional process as a reference case (Section 4.1), the heat transfer requirements defined by the temperature–enthalpy profiles are first analyzed with standard heat integration principles (i.e., amount and temperature levels of the hot and cold streams). Based on some experience and knowledge of candidate technologies, the energy conversion efficiency of the process is then improved by introducing fuel and power cogeneration technologies that better fit the heat requirements while making use of the available residues (Sections 4.2–4.3). A further analysis of these solutions based on exergy considerations yet shows that the conventional integration approach falls short in the attempt of completely extracting the available thermodynamic potential as useful energy (Section 4.4). Figure 1 illustrates that setting up the hot (a) and cold (c) composite curves

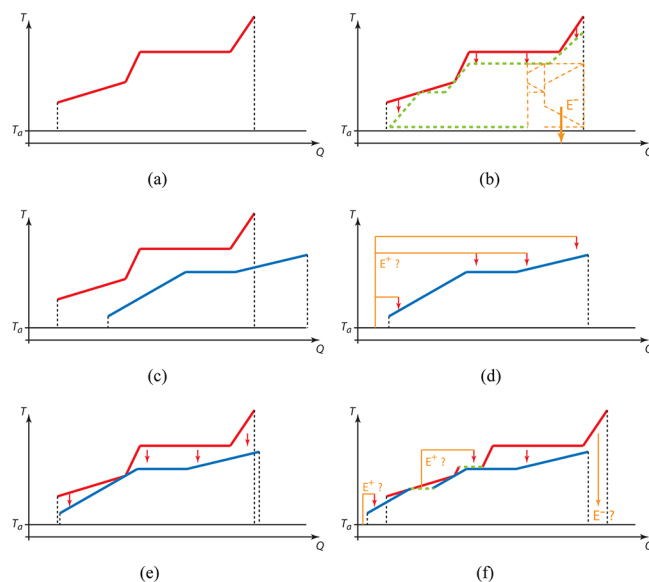


Figure 1. Conventional energy integration (left) and systematic exergy recovery (right). (a) Hot streams. (b) Exergy recovery from hot streams. (c) Hot & cold streams. (d) Exergy supply to cold streams. (e) MER as obtained by conventional energy integration. (f) Exergy recovery potential.

and matching them (e) yields a solution with an activated pinch point that maximizes the heat recovery and recommends the use of utilities to balance the heat requirement. However, this procedure in itself cannot avoid resulting in substantial exergy losses in the heat exchange that limit the useful energy yield. A more detailed analysis of the integration of the energy conversion system is therefore needed to reduce the exergy losses and increase the system conversion efficiency (Sections 4.4.1 and 4.4.2). If an ad-hoc approach is risky to reach a solution as illustrated in Figure 1(f) directly from (e), a more systematic way is to first consider all possible energy exchanges of the hot (b) and cold (d) streams with the atmosphere. This provides a range of potential improvements based on conventional thermodynamic cycles (i.e., power cogeneration and heat pumping (Section 4.4.2)), although other solutions that are specific to the process under investigation are obviously limited by the auxiliary technologies that are considered applicable (Section 4.4.1).

2.3. Performance Indicators. In order to characterize the relative outputs of a polygeneration plant that uses a single, principal resource, it is convenient to normalize the net yields of useful products as partial efficiencies of this input. In our case, partial fuel and electric efficiencies ϵ_{fi} and ϵ_{el} are defined as²⁷

$$\epsilon_{fi} = \frac{\Delta h_{fi}^0 \dot{m}_{fi}^-}{\Delta h_{biomass, dry}^0 \dot{m}_{biomass, dry}^+} \quad (1)$$

$$\epsilon_{el} = \frac{\dot{E}^-}{\Delta h_{biomass, dry}^0 \dot{m}_{biomass, dry}^+} \quad (2)$$

in which Δh^0 represents the lower heating value (LHV) of the dry fuels f_i and the biomass feed, \dot{m} is its mass flow, and \dot{E}^- is the net production of electrical power. The superscripts $-$ and $+$ designate net output and input flows, respectively.

The overall performance of the conversion can be expressed by the total energy and exergy efficiencies ϵ and η

$$\epsilon = \frac{\sum \Delta h_{fi}^0 \dot{m}_{fi}^- + \dot{E}^-}{\Delta h_{biomass, dry}^0 \dot{m}_{biomass, dry}^+ + \dot{E}^-} \quad (3)$$

$$\eta = \frac{\sum \Delta k_{f_i}^0 \dot{m}_{f_i}^- + \dot{E}^-}{\Delta k_{\text{biomass}}^0 \dot{m}_{\text{biomass,dry}}^+ + \dot{E}^+} \quad (4)$$

in which Δk^0 refers to the exergy value of a material stream,²⁸ and only the positive term of the plant's electricity balance is retained as \dot{E}^- or \dot{E}^+ . Although providing a strictly physical measure of the energy conversion and its quality degradation, ϵ and η do yet not satisfactorily assess the relative value of the fuel products and electricity with respect to the technical feasibility of their further conversion into final energy services.²⁷ For this purpose, it is more convenient to define an efficiency based on the substitution of fuel-equivalents for the consumed or by-produced power. A consistent weighting is thereby obtained if electricity is represented by the equivalent amount of fuel required for its generation in a (synthetic) natural gas combined cycle (NGCC) at an exergy efficiency η_{NGCC} of 55%:

$$\epsilon_{\text{chem}} = \frac{\sum \Delta h_{f_i}^0 \dot{m}_{f_i}^- + \frac{1}{\eta_{\text{NGCC}}} \frac{\Delta h_{\text{SNG}}^0}{\Delta k_{\text{SNG}}^0} \dot{E}^-}{\Delta h_{\text{biomass,dry}}^0 \dot{m}_{\text{biomass,dry}}^+} \quad (5)$$

Note that \dot{E}^- represents the net electricity balance in eqs 1, 2, and 5 and may be negative therein, while only the positive term of \dot{E}^- or \dot{E}^+ is used in eqs 3 and 4. This approach is more extensively discussed in ref 27 and has been successfully applied for analyzing and optimizing the polygeneration of SNG, power, and heat with several dry and wet gasification technologies.^{22–24}

3. PROCESS MODEL FOR ETHANOL PRODUCTION FROM LIGNOCELLULOSIC BIOMASS

Motivated by the results of Zhang et al.,⁵ the present paper investigates the potential benefit of process integration on performance with their process model for fuel ethanol production from lignocellulosic biomass, which has been developed based on design and operation experience from a 600 ton/year demonstration plant commissioned in 2005 in the Fengxian District, China. As outlined by the principal process steps depicted in the block flow diagram of Figure 2(a), the biomass with properties as shown in Table 2 is first decomposed by two-step dilute acid hydrolysis at 155 to 165 °C with overall conversion yields of 80%, 70%, and 10% for the degradation of cellulose to glucose, hemicellulose to xylose, and further to furfural, respectively. After removing the suspended solids, glucose and xylose are then fermented at 38 °C to ethanol at conversion yields of 95% and 60%, respectively. Overall, these rates result in conversion yields of 76% for cellulose and 42% for hemicellulose to ethanol, which leaves the reactor diluted in mainly water to a concentration of 2.7 wt%.

The subsequent distillation is carried out in three columns, where ethanol is concentrated to 40% and further to the azeotrope at 95 wt%, from which it is rectified with cyclohexane as entrainer to 99.5 wt%. This distillation sequence and the column pressures, which have been adjusted to achieve a good heat integration of the columns, are summarized in Figure 2(b). After recovery of the residual ethanol and cyclohexane by stripping, 90% of the organic matter in the wastewater is recovered as biogas by anaerobic digestion. For these conversions, the composite curve in Figure 2(c) assesses a minimum energy requirement (MER) of roughly 15% of the biomass input at 130–170 °C, which also includes the multieffect evaporation from 75 to 35 wt% humidity of the lignin-rich slurry recovered from hydrolysis. With a dry biochemical composition of 12.3 wt% hemicellulose, 25.9 wt% cellulose, and 61.8 wt% lignin, this residue represents more than 50% of the feedstock's chemical energy due to the relatively modest conversion yields assumed in hydrolysis and

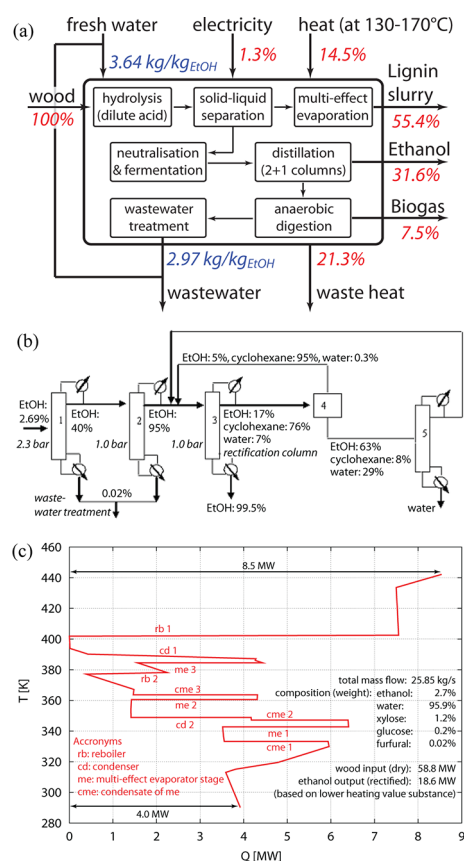


Figure 2. Overview and principal energy balances of the ethanol production process according to the model of Zhang et al.⁵ (a) Block flow diagram and principal energy balances based on lower heating value of dry species. (b) Distillation sequence. 1–3: concentration, rectification and azeotropic columns, 4: liquid-liquid separator, 5: stripper. (c) Grand composite curve of the process streams.

Table 2. Flow and Composition of Wood and Ethanol and Its Byproducts According to the Process Model⁵

		input				outputs			
		wood	ethanol	lignin slurry	biogas	wood	ethanol	lignin slurry	biogas
mass flow	kg/s	3.47	0.697	2.16	0.328				
energy flow	MW	58.8 ^a	18.6	32.6	4.42				
LHV (Δh^0) ^a	MJ/kg _{dry}	19.9	26.8	23.2	13.5				
composition ^b									
hemicellulose	wt%	25.0	-	8.0	-				
cellulose	wt%	35.0	-	16.9	-				
lignin	wt%	25.0	-	40.1	-				
ethanol	wt%	-	99.5	-	-				
methane	wt%	-	-	-	27.1				
carbon dioxide	wt%	-	-	-	72.9				
water	wt%	15.0	0.5	35.0	-				

^aZhang et al.⁵ have assumed LHV's of biomass based on its dry macromolecular composition with 17 MJ/kg for hemicellulose and cellulose and 27 MJ/kg for lignin. They have reported energy flow based on the heating value of the wet substance considering the 15% bound moisture to decrease the LHV by 0.43 MW/kg_{dry}. This has resulted in an energy flow of 57.6 MW for the wood input, which is reported here as 58.8 MW based on the dry composition. ^bMolecular compositions: hemicellulose: C₅H₈O₄, cellulose: C₆H₁₀O₅, lignin: C₆H₁₁O₂

fermentation. A summary of the overall mass balance of the process and the associated chemical energy transformation is provided in Table 2.

4. PROCESS INTEGRATION ALTERNATIVES

Considering the energetic value of the byproducts in Table 2 and the important heat requirement for distillation and rectification of the raw product to fuel quality of Figure 2(c), this section compares different alternatives for integrating the fuel production and the energy and exergy recovery processes. Starting from conventional combustion and power generation in a single cycle, more efficient thermochemical process alternatives for converting the residual lignin slurry into power and SNG are developed by combining energy integration and exergy recovery technologies.

4.1. Combustion and Power Generation in a Single Cycle. The most straightforward use of the residual lignin slurry and biogas is to supply the heat requirement of the process streams by combustion and cogenerate power from the excess heat in a steam Rankine cycle, which is the conventional solution as proposed in the design of Aden et al.⁶ Assuming a steam cycle with a single production level at 80 bar (300 °C), superheating to 550 °C, steam utilization at 14.9 and 3.6 bar (198 and 140 °C), and condensation at 0.02 bar (20 °C), the resulting integrated Carnot composite curve for the process configuration of Zhang et al.⁵ shown in Figure 3(a) highlights that the combustion of the residues generates 3.7 times more heat than the already considerable amount that is required for distillation. As assessed by the energy balance of Table 3, the steam cycle recovers this excess heat at a very modest efficiency. Overall, a net partial electric efficiency ε_{el} of 16.7% based on the biomass input to the plant is achieved. In this configuration, the Rankine cycle operates largely independent of the ethanol plant, and 25% of the chemical energy fed to the process is evacuated as waste heat by the cooling water due to the exergy losses in the recovery of the high temperature heat.

4.2. Integrated Gasification Combined Cycle. Compared to the chemical energy potential of the residuals, the process heat demand is relatively small, and cogeneration technologies with a low heat to power ratio are thus preferable. This motivates the use of an integrated gasification combined cycle (IGCC), which has already been proposed by Hamelinck et al.⁸ and later also by Laser et al.²⁹ In such a configuration, the dried residuals are gasified and the producer gas is fired in a gas turbine, whose excess heat is recovered in a bottoming steam cycle.

Due to its demonstrated ability to efficiently operate in pressurized conditions, directly heated gasification with a mixture of oxygen and steam as gasifying medium is considered, whose performance is calculated with a previously developed process model.²⁰ In order to limit the exergy losses in the gasifier, the dewatered lignin slurry is first dried with hot air (200 °C) to 20% humidity before pressurization and gasification at 15 bar, 850 °C, and a steam-to-dry-biomass ratio of 0.5. The producer gas is directly fed to a gas turbine that is operated at the same pressure and whose performance is calculated with the assumptions of Brown et al.³⁰ For consistency of the results, the same conditions for the bottoming steam cycle than for the single cycle outlined in Section 4.1 are considered.

Compared to a single steam cycle, this combined cycle architecture reduces the exergy losses at high temperature and increases the total power output. As shown in Figure 3(b), the

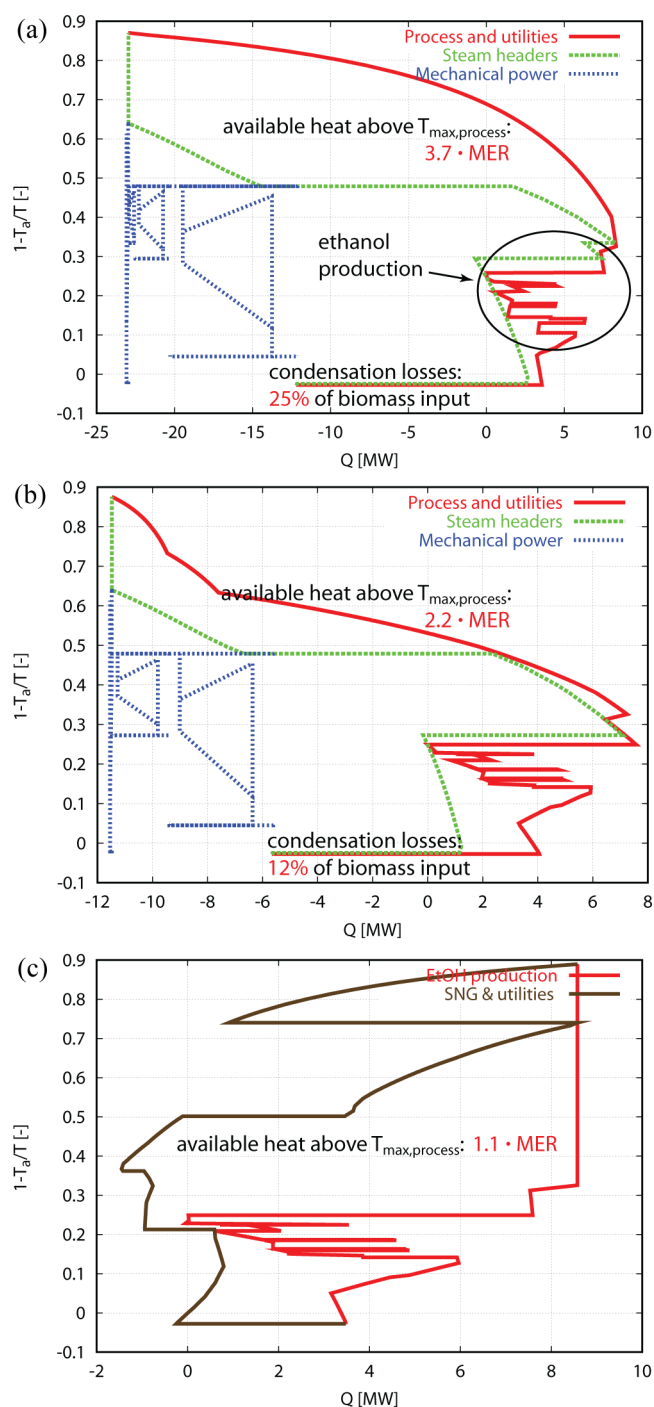


Figure 3. Integrated Carnot composite curves for different alternatives of lignin valorization in the production of ethanol from wood (biogas is combusted in all cases). (a) Combustion and steam cycle. (b) IGCC (gasification, gas turbine and steam cycle). (c) SNG production (gasification and methanation).

addition of a topping cycle based on gasification reduces the heat that is generated from the byproducts from 3.7 to 2.2 times more than required for the distillation of ethanol and increases the net electric efficiency from 16.7% to 21.0% based on the total biomass input compared to the single steam Rankine cycle (Table 3).

4.3. Thermochemical Conversion to SNG. Instead of combusting the producer gas obtained by gasification of the residual lignin slurry to cogenerate power, a second

Table 3. Overview of Partial and Total Efficiencies As Defined in Eqs 1–5 for Different Lignin Valorization and Process Integration Options

parameter	remarks				
lignin conversion	combustion	gasification	SNG ^a (gasification and methanation)		
power cogeneration	steam cycle	IGCC	none	steam cycle	and heat pumps
composite curve	Figure 3(a)	Figure 3(b)	Figure 3(c)	Figure 4(b)	Figure 4(c)
discussed in Section	4.1	4.2	4.3	4.4.1	4.4.2
ϵ_{EtOH}	31.6%	31.6%	31.6%	31.6%	31.6%
ϵ_{SNG}	-	-	39.4%	34.4%	41.0%
ϵ_{el}	16.7%	21.0%	-2.9%	1.9%	-0.5%
ϵ	48.3%	52.6%	68.1%	67.9%	72.1%
ϵ_{chem}	60.9%	68.5%	65.9%	69.3%	71.7%
η	51.3%	55.6%	73.5%	73.0%	77.5%

^aSNG is produced as 96%mol CH₄, 1.2% H₂, 0.1% CO, 1.1% CO₂, 1.6% N₂. Pressure: 50 bar, LHV (Δh^0): 47.2 MJ/kg.

thermochemical process alternative is its further conversion to other liquid or gaseous (fuel) products and thus to increase the overall fuel yield. The amount of excess heat from such thermochemical reforming processes is generally lower than from power generation in a single or combined cycle, which should reduce the exergy losses in the waste heat recovery. While Laser et al.¹⁰ discuss scenarios for the coproduction of Fischer–Tropsch fuels, dimethyl ether or hydrogen, we have explored the coproduction of SNG as modeled in ref 20 since a higher conversion efficiency can be expected.

Our calculations are based on the model of an indirectly heated gasifier with steam as gasifying medium²⁰ since its overall excess heat has shown to better match the requirement for ethanol production considered in this work than the pressurized gasifier for IGCC of Section 4.2. As in the latter, the incoming lignin is dried with hot air (200 °C) to 20% humidity and gasified at atmospheric pressure, 850 °C, and a steam-to-dry-biomass ratio of 0.5. The raw producer gas is cooled and cleaned from dust and tar by filtering and scrubbing before catalytic isothermal methanation in a fluidized bed at 320 °C.²⁰ For injection into the natural gas grid, the crude mixture of methane, carbonyl dioxide, and some residual hydrogen is then upgraded to the required methane purity (96%mol) by a three-stage membrane system with one recycle loop.³¹

The integrated Carnot composite curve of Figure 3(c) for this process configuration illustrates that the excess heat available from the conversion of the residual lignin slurry into SNG matches well with the requirement for ethanol distillation. Together with the sensible heat of the producer gas and the fumes from the gasifier's combustion chamber, the excess heat from the exothermal methane synthesis exactly balances the overall demand for ethanol production, and the total cooling requirement equals the strict cold MER of 4.0 MW_{th} assessed in Figure 2(c). In this setup, SNG production allows for an increase of the combined fuel yield to over 70%. However, no more excess heat is available to cogenerate power, and the electricity consumption of the process that is equivalent to 2.9% of its biomass input must be supplied by the grid (Table 3).

4.4. Process Integration Analysis for Combined Production of Ethanol, SNG, and Power. Transforming the integrated section composite curves of Figure 3(c) into a balanced Carnot composite curve as shown in Figure 4(a) reveals an uncommon situation in heat recovery and energy conversion problems, which usually suffer from low quality but not low quantity of heat. The area between the balanced Carnot composite curve of Figure 4(a) and the temperature axis corresponds to the exergy loss of the heat exchange system.

However, there is no heat excess below the high temperature pinch at 875 °C, which makes it impossible to convert the available exergy into mechanical power by integrating a steam cycle. Indeed, the combined production of power is limited by the activation of the pinch point at a low temperature of 104 °C. In order to extract mechanical power from the available exergy at high temperature, heat needs to be added to the system at a temperature between 875 and 104 °C. This can be done either by additional combustion of producer gas or by heat pumping from below the low-temperature pinch. Note that heat pumping is thereby only meaningful if the heat pocket offers more exergy than the additionally generated losses in the heat pumping and power recovery cycles.

4.4.1. Heat Generation by Partial Combustion of Producer Gas. A first alternative to provide heat for extracting the available exergy is the combustion of an additional amount of producer gas. This solution is illustrated in Figure 4(b), for which the steam production pressure and superheating temperature have been decreased to 75 bar (294 °C) and 537 °C to match the heat profile of the exothermal methanation reactor. By supplying just as much energy as required to extract the exergy potential of the high temperature streams, the heat that is generated from the chemical energy of the intermediate product is entirely transformed into electrical power. This results in a marginal electric efficiency $\Delta\epsilon_{\text{el}}/\Delta\epsilon_{\text{SNG}}$ of 96%, which demonstrates that no additional second-law losses are generated in the system's heat to power conversion, except the thermal and mechanical ones in the boiler and turbomachinery, respectively. However, the consequence is a reduction of the production of SNG. The according energy balances of Table 3 highlight that this allows for a gross power generation of roughly 5% of the total biomass input and results in an overall positive electricity balance of the integrated plant.

4.4.2. Heat Pumping. A second, thermodynamically more efficient alternative is to supply the required energy for extracting the available exergy by pumping heat across the low temperature pinch. While combustion transforms the chemical energy of an intermediate product into power, heat pumping is using the waste heat of the process to generate additional power. As illustrated in Figure 4(c), the exergy available below the pinch at 104 °C is valorized and reduces at the same time the losses at high temperature. This makes it possible to generate a net supplement of power without decreasing the fuel yield and not only for converting chemical into mechanical energy without additional second-law losses as in the previous section.

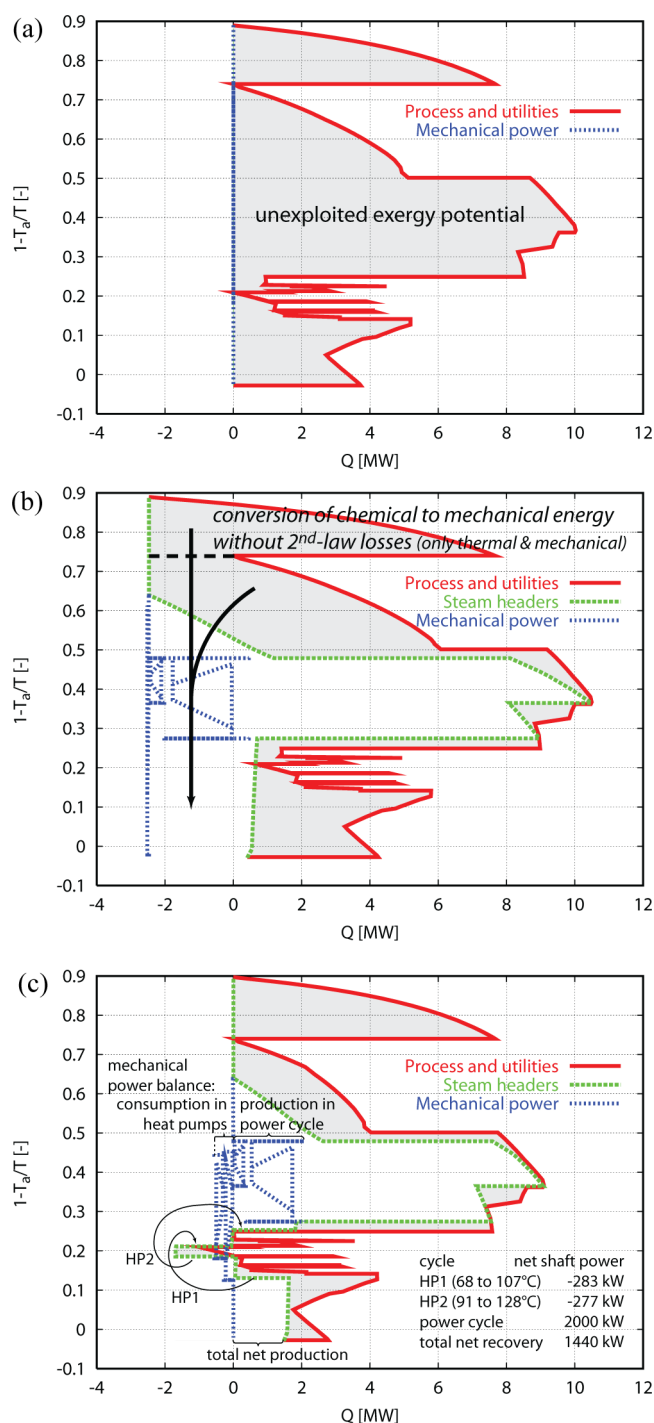


Figure 4. Balanced Carnot composite curves for the exergy recovery alternatives in combined ethanol and SNG production. (a) Without exergy recovery (identical to Figure 3(c)). (b) Steam cycle with partial producer gas combustion. (c) Steam cycle with heat pumping.

The prevailing temperature profiles enable water as a working fluid of two cycles that pump heat from 68 to 107 °C (0.28 to 1.29 bar) and 91 to 128 °C (0.72 to 2.53 bar). The integration with the lignin drying and ethanol distillation processes thereby allows these cycles to work at an excellent coefficient of performance of 7. With a combined shaft power of 560 kW_{el}, they provide 3.9 MW_{th} above the pinch, which enables the power cycle to extract 2.0 MW_{el} from the exergy that is available at high temperature. In this situation, heat

pumping thus generates a net supplement of 1.4 MW_{el} of power. In process integration, this is relatively uncommon since it usually reduces the requirement of thermal energy or fuel by consuming some additional power. Overall, this contribution almost balances the electricity consumption of the biomass conversion plant. In the same time, the SNG yield even increases since the heat pumps also substitute thermal energy from producer gas combustion that has previously been transferred across the high temperature pinch by only partially preheating the combustion air. Table 3 shows that this solution consistently achieves the best overall energy, exergy and chemical efficiencies, which are by 3 to 4%-points higher than in the best previous cases.

5. DISCUSSION

5.1. Impact of Technological Progress in Ethanol Production. As outlined in Section 3, our analysis is based on a demonstration plant for ethanol production commissioned in 2005. Due to the ongoing technological development, the considered process does not represent the latest state-of-the-art and is unlikely to be implemented as such at large scale. Based on recent technology reviews,^{19,32–35} it is therefore appropriate to discuss the potential impact of technological progress on the integration and performance of a polygeneration setup as investigated in this work.

Dilute acid hydrolysis has been widely used due to its comparatively high conversion yields but generates inhibitors for the subsequent fermentation. Enzymatic hydrolysis does not suffer from this disadvantage and is considered a more promising - although still costly - option for commercialization.¹⁹ Combined with effective pretreatment technologies to dissociate cellulose and hemicellulose from the ligneous structure, higher conversion efficiencies to sugars and further to ethanol can be expected. With respect to heat demand, dilute acid hydrolysis at 165 °C represents less than 12% of the total requirement when appropriately integrated with the distillation (Figure 2(c)). The potential for reducing the process heat demand by alternative pretreatment methods is thus limited, and can even increase if energy-intensive techniques like steam explosion are applied.

With an increasing conversion yield, an improved tolerance of industrial micro-organisms to inhibitors and ethanol, and an accompanied increase of the solids loading in pretreatment, the fermentation broth can reach considerably higher ethanol concentrations than the 2.7 wt % considered here. This reduces the heat load in the reboiler of the first column significantly, which represents the major contribution to the process' heat demand (Figure 2(c)). The same impact can be expected from techniques for reaction-separation integration^{32,35} like in situ removal of ethanol, which have the potential to further reduce or even replace the distillation. For the rectification, molecular sieves instead of azeotropic distillation can be considered as the current industrial choice.^{19,34} Since the heat demand for stripping the entrainer is modest compared to the bulk distillation and satisfied by the heat released from the condensers of the upstream columns, the use of molecular sieves does yet not have a dominant impact on the product yield and the process heat requirements.

According to these considerations, technological progress can be expected to increase the ethanol yield to the expense of the byproducts and to reduce the heat requirement for separation. The impact of these two effects on the process integration is yet attenuated by the fact that a reduction of the byproducts also

reduces the available amount of heat to satisfy the requirements. Although a detailed assessment requires representative models for the technologies, an estimation of its consequences for the internal energy balance is possible.

With an initial lignin composition of roughly 30 wt%_{dry} and an according share of 40% of the lower heating value (cf. Table 2), the maximum ethanol yield from lignocellulosic biomass can be estimated to $\epsilon_{EtOH} = 54.5\%$, assuming complete conversion of the cellulosic compounds to ethanol, lignin not to be accessible and neglecting the small variation of the reaction enthalpy (i.e. $31.6\% + 7.5\% + (55.4\% - 40.0\%) = 54.5\%$ in Figure 2(a)). This results in a reduction of the residues' energy content from 62.9% to 40% of pure lignin, and accordingly decreases the amount of energy that is available from the further conversion of the residues by 36%. When conventionally combusted (cf. Section 4.1), the heat release yet still exceeds the process requirement by a factor of 2.4 if the demand of the process is unchanged (from previously 3.7, cf. Figure 3(a)), and condensation losses from a single cycle remain at approximately 15% of the biomass input. In case of an IGCC, the heat excess amounts to 1.4 of the process requirement and results in condensation losses of 5% of the biomass input. The reduction of the losses is yet likely to be overcompensated by a considerable decrease of the demand of the process itself, and the conversion of the excess heat into power is limited by the efficiency of the steam cycle. If the process were to consume no heat at all, an efficient power recovery system would allow for generating 10% (steam cycle) to 15% (IGCC) of electricity in addition to the 54.5% of ethanol from the biomass input.

When coproducing SNG from the reduced amount of residues (Section 4.3), the gaseous fuel yield decreases from initially 41.0% to 26.2%. With the increase in ethanol to 54.5%, the combined production of fuel thus amounts to 80.7% instead of the 72.6% that can be achieved with pilot plant technology (cf. Table 3). However, the reduction of the excess heat from the exothermal methanation covers no more than 70% of the process requirement (previously 110%, cf. Figure 3(c)). Unless the latter is not reduced, heat pumping thus becomes mandatory, and the overall process performance is sensitively affected by a negative electricity balance. Considering that the investigated distillative separation requires 14.5% of the biomass input as heat, that the conversion of the byproduct to SNG delivers an equivalent of 10%, and that the process consumes 1.3% of electricity (cf. Figure 2(a)) that can be generated in a steam cycle from an equivalent of 4 to 5% of heat, the heat demand for separation needs to be reduced by roughly 2/3 to a total of 5% of the biomass input to make the plant self-sustainable. If separation does not require any heat at all, the net fuel yield of 80.7% is therefore completed by an additional 2% of electricity at best.

Provided that lignin cannot be valorized on a material pathway, these considerations show that the thermochemical conversion of residues, and in particular fuel polygeneration, indeed appears as a promising option to achieve high product yields in large-scale ethanol plants based on lignocellulosic biomass.

5.2. Competing Technologies and Polygeneration. In order to provide a reference point for the process alternatives discussed in this work, Table 4 summarizes the projected thermodynamic performance of the most prominent options to produce fuels and power from lignocellulosic biomass. The values represent reference cases (without optimization) that

Table 4. Projected Energy Efficiencies (in %) of the Major Competing Technologies for the Polygeneration of Fuels and Power from Lignocellulosic Biomass (Without Heat Cogeneration)

fuel product	ϵ_{fuels}	ϵ_{el}	ϵ_{chem}
methanol ²¹	57	−6	47
dimethyl ether ²¹	56	−5	48
Fischer–Tropsch (crude product) ²¹	60	−0.4	59
ethanol	32	17	61
SNG (hydrothermal gasification) ²²	55	7	67
SNG (hydrothermal gasification, high power share) ²²	29	24	70
SNG (conventional atm. gasification) ²⁰	67	3	71
SNG (conventional pressurized gasification) ²⁰	74	2	77
ethanol and IGCC	32	21	69
ethanol and SNG (conventional gasification)	73	−0.5	72

have been obtained in earlier work with the same methodology and consistent assumptions. In particular, the lignocellulosic raw material is considered at 50% moisture, and efficiencies are reported based on the lower heating value of the dry substance as defined in eqs 1–5. It is worthwhile to note that the overall process efficiency may significantly change if excess heat can be used on-site.^{22,24} The values of Table 4 therefore provide only a rough performance comparison of possible fuel products from dry lignocellulosic biomass.

Among the liquid substitute fuels, the production of ethanol emerges as a promising option, although the chemical efficiency that is used for comparison does not account for the difference in performance when using the fuel in combustion engines. Typically, modern spark-ignited engines for gasoline (and its mixture with ethanol) are roughly 5 to 10% less efficient than diesel-fuelled compression ignition engines.³⁶ Since the process technology considered in this work is based on a pilot plant that does not represent the latest state-of-the-art (cf. Section 5.1), further improvements can be expected to overcome this penalty.

Outperforming the conversion to liquid fuels by a significant difference in efficiency, SNG can be considered a promising alternative fuel with an existing distribution grid. Due to its high octane number, dedicated natural gas engines almost reach the efficiency of diesel engines. SNG therefore does not suffer from performance losses in the final use. The main drawback is its gaseous state, which does not provide the same autonomy than liquid fuels. In countries with a dense network of fuel stations, natural gas is yet already becoming a serious competitor to conventional fuels.

By providing part of the output in liquid and gaseous form, fuel polygeneration processes as the one investigated in this work combine the advantages of several products. In our particular case, the production of ethanol as a convenient fuel with high energy density is made more competitive by an efficient valorization of its byproducts as a secondary fuel. Quite obviously, the initial design of such processes is more complex and costly due to the need for more equipment and a higher level of integration. However, a low share of power cogeneration decouples their operation from short-term fluctuations in the power grid, which are getting increasingly important due to the entrance of intermittent wind and solar power at large scale. The according fluctuations of the electricity price can make chemical processes that cogenerate a large amount of power economically vulnerable and result in a competitive advantage for processes that produce easily storable

energy vectors – without yet considering the possibility for adapting its shares to the seasonal variations in market demand.

In the example outlined in this work, the addition of heat pumping and steam cycles to recover 2.4% of the raw material's heating value as electrical power may appear as an exaggerated effort that may not pay off. An estimation of the related capital cost with economic models for the steam cycles, the heat exchanger network,^{20,25} and industrial heat pumps³⁷ suggest a total supplementary investment of 6.4 million USD for the plant considered here. If the generated electricity is considered as green electricity with a market value of 180 USD/MWh, such an investment pays back within 3 years, whereas 9 years are required for a low electricity price of 60 USD/MWh on average.²⁴

6. CONCLUSIONS

Contributing to the challenges outlined by e.g. Kokossis and Yang¹⁵ and supporting similar results for related applications,^{11–14} this paper highlights the potential performance benefits when designing biorefineries as integrated processes that convert biomass resources into a portfolio of commodities, fuels, power, and heat. The system configurations that are proposed in this paper exploit synergies between complementary energy conversion processes that have been identified by systematically computing the flowsheet integration through an MILP formulation, combining mass and energy integration at site-scale and applying exergy analysis to identify suitable technologies that improve the conversion efficiency of the process. Based on a process model that reflects pilot plant experience for ethanol production from lignocellulosic biomass, it is shown that the combined production of ethanol, SNG, and power increases the energy and exergy efficiencies to up to 72.1% and 77.5%, respectively, which is by 24% to 26%-points higher than the 48.3% and 51.3% that are reached with a conventional process design (Table 3). The final potential that can be extracted from the resource can be expected to be even higher since a detailed integration of all process streams (including intermediates and biogas) with a simultaneous optimization of the operating conditions^{13,24–26} has been out of scope of this work. Furthermore, advanced technologies for more efficient biomass pretreatment, hydrolysis, fermentation, and separation^{19,32–35} and alternative gasification technology dedicated to wet substrates^{22,23} have also not been considered yet.

The benefits outlined above are inherently linked to the combined application of energy integration techniques and exergy analysis. Since pinch analysis alone does not inherently quantify the exergy destruction in the heat exchange nor provide solutions for its reduction, it falls short in the attempt of completely extracting the available thermodynamic potential as useful energy. Instead of considering energy integration as a problem of utility minimization or waste heat recovery from the process streams' energy excess, it should therefore be regarded as a problem of exergy loss minimization, in which energy exchanges between both the hot and cold composite curves and the environment are symmetrically considered. As outlined in Section 2, this does not require to reformulate the mathematical MILP problem but an awareness of possibilities to modify the shape of the composite curves by introducing alternative conversion technologies and systematically considering heat exchanges with the environment. As our case has shown, this facilitates the identification of solutions that reduce the exergy losses in the balanced system, which are not

necessarily trivial since it has revealed a way to additionally generate mechanical power by adding heat pumps to the process. The iterative, analysis-driven procedure as applied here is thereby a time-efficient alternative to an entirely computational approach, in which all potential technologies and routes are included in an overall superstructure and processed by optimization.

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Notes

The authors declare no competing financial interest.

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