

Increasing Conversion Efficiency in Fuel Ethanol Production from Lignocellulosic Biomass by Polygeneration – and a Paradoxon between Energy and Exergy in Process Integration

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Abstract: In the public and scientific debate on biofuels, ethanol from lignocellulosic biomass is generally the most popular alternative that may allow for a sustainable production. Compared to thermochemical processing of biomass which assures a complete conversion of the feedstock, it yet suffers from an inherently lower fuel yield due to the resistance of lignin to biological degradation. Based on a recently developed process model for fuel ethanol production from lignocellulosic biomass, this paper discussed the cogeneration alternatives for the conversion of the residual lignin. Whereas an integrated gasification combined cycle (IGCC) increase the power cogeneration efficiency compared to the conventional combustion and power generation in a steam Rankine cycle, it is shown that alternative gasification and methanation to Synthetic Natural Gas (SNG) allows for roughly doubling the fuel yield from biomass.

The paper further demonstrates the paradox situation that conventional energy recovery is limited by the available energy, and not, as usually, the available exergy from the waste heat. In order to overcome this limitation, a more general energy integration approach that allows for increasing the cogeneration efficiency in this kind of situations is proposed.

Keywords: biofuels, energy integration, ethanol, exergy, process integration, SNG

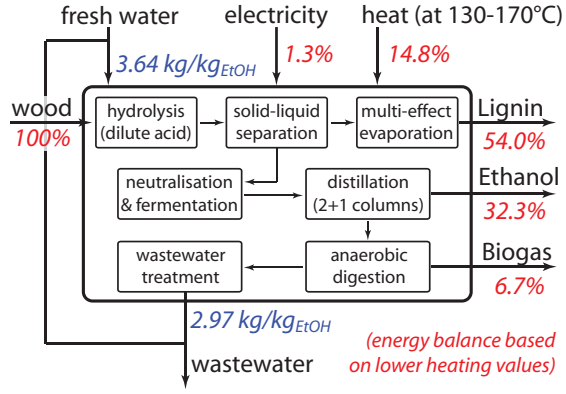
1. Introduction

In the public and scientific debate on biofuels, ethanol from lignocellulosic biomass is one of the most popular alternatives that may allow for a sustainable production. Since lignin resists to biological degradation and hemicellulose can only be partially hydrolysed, ethanol fermentation yet suffers from a relatively low fuel yield. The process efficiency is therefore essentially dependent on the valorisation of the residues and the quality of the process integration. Compared to the conventional intention of drying and burning the residual lignin slurry to provide heat for ethanol distillation and power cogeneration [1], thermochemical processing is a promising alternative for substantially increase the fuel yield since it assures a complete conversion of the feedstock.

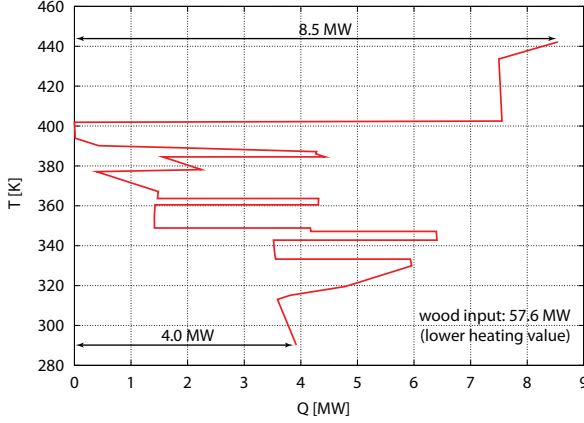
This paper discusses the prospects for increasing the efficiency of biomass-to-fuel conversion by polygeneration and demonstrates shortcomings of a conventional energy integration approach for a complete recovery of the process' exergy potential.

2. Process description

Following the systematic process design methodology outlined in [2], Zhang et al. [3] recently developed a process model for fuel ethanol production from lignocellulosic biomass based on double acid hydrolysis, whose principal process steps are depicted in the block flow diagram of Figure 1(a). In this model, the biomass is first hydrolysed in two stages at 155-165°C with 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 to ethanol and CO₂ at conversion yields of 95% and 60%, respectively. The distillation is carried out in three columns, where ethanol is subsequently concentrated from 2.7%wt to 40% and further to the azeotrope at 95% wt, from which it is rectified with cyclohexane as entrainer to 99.5% wt. 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 Fig-



(a) Block flow diagram.



(b) Composite curve of the process streams.

Figure 1: Principal mass and energy balances of ethanol production according to the model of [3].

ure 1(b) assesses a minimum energy requirement (MER) at 130-170°C of roughly 15% of the biomass input, which also includes the multi-effect 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 modest yields assumed in hydrolysis and fermentation.

3. Process integration

3.1. Methodology

As detailed in the applied methodology [2], the energy integration of the process is formulated as a mixed integer linear programming problem in which the mass balances between the subsystems and the heat cascade of the corrected temperature-enthalpy profiles act as constraints. Once the MER of the conversion process determined, appropriate technologies for the heat supply and energy re-

covery can be chosen. By considering the depleted residuals and, if required, intermediate product streams as fuels for this purpose, the optimal process integration that minimises the exergy depletion – or maximises the combined production of fuel, heat and power – is then determined.

3.2. Performance indicators

In order to characterise the relative outputs of a polygeneration plant, it is convenient to normalise the net yields of useful products as partial efficiencies of the biomass input. Accordingly, partial fuel and electric efficiencies ϵ_{fi} and ϵ_{el} are defined as:

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

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

in which Δh^0 represents the lower heating value of a fuel f_i or biomass, \dot{m} its mass flow and \dot{E} electrical power. The superscripts $-$ and $+$ refer to net output and input flows, and one of the terms \dot{E}^- and \dot{E}^+ thus cancels out since only the net balance is of interest.

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

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

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

in which Δk^0 refers to the exergy value of a material stream. Although providing a strictly physical measure of the energy conversion and its quality degradation, ϵ and η do yet not satisfactorily assess the value of the fuel products with respect to the technical feasibility of their further conversion into final energy services. For this purpose, it is 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%:

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

3.3. Results and discussion

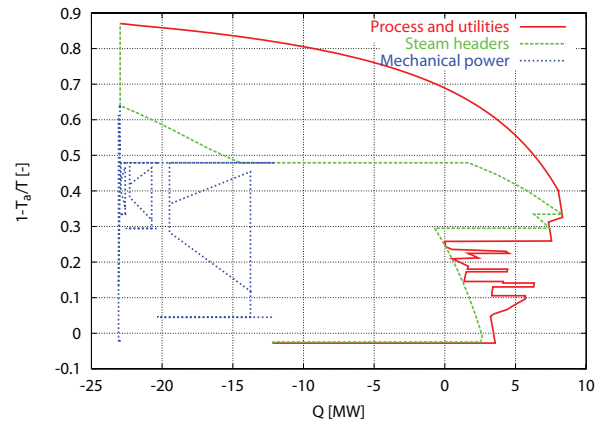
3.3.1. Combustion and power cogeneration

The most straightforward use of the residual lignin slurry and biogas is to supply the process MER by combustion and cogenerate power from the excess heat in a steam Rankine cycle, which is the solution proposed in NREL's reference design [1]. Despite the considerable heat demand of distillation, the exergy composite curve of Figure 2(a) highlights that combustion of the residues generates a lot of excess heat which is recovered at a very modest efficiency. Assuming a single steam production level at 80 bar (295°C), superheating to 550°C, steam utilisation at 14.9 bar (198°C) and 3.6 bar (140°C) and condensation at 0.02 bar (20°C), the energy balance of Table 1 assesses a net partial electric efficiency of 17.1% based on the overall plant input, which corresponds to an electricity yield of roughly 34% from the residuals. In this configuration, the Rankine cycle operates largely independent of the ethanol plant and an important amount of energy is lost in the cooling water due the exergy losses in the heat recovery. Benefits from process integration are small.

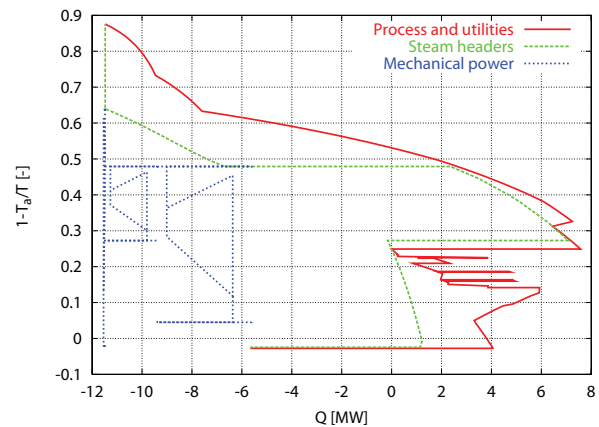
3.3.2. Gasification alternatives

Compared to the chemical energy potential of the residuals, the process heat demand is relative small and cogeneration technologies with a low heat share are thus preferable. For this purpose, the use of an integrated gasification combined cycle (IGCC) has been investigated by Hamelinck et al. [4] and later also Laser et al. [5]. By generating power from the producer gas in a gas turbine, the exergy losses at high temperature are reduced and the total power output thus increased (cf. Fig. 2(b)). With a topping cycle design similar to the one proposed by Brown et al. [6], IGCC based on pressurised, oxygen blown gasification allows for increasing the power cogeneration from 17.1% to 21.5% of the total biomass input compared to a simple steam Rankine cycle.

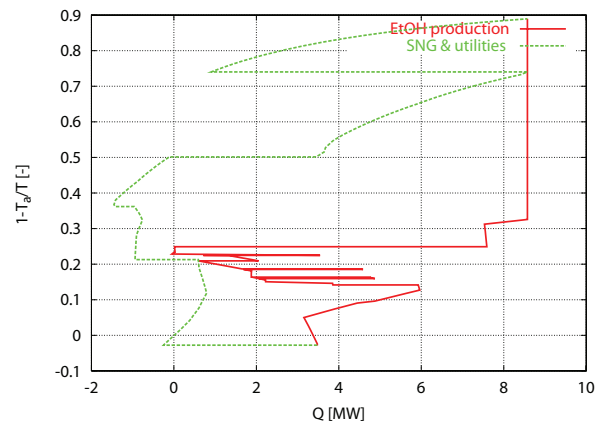
In order to increase the overall fuel yield, a second alternative would be to thermochemically convert the residual lignin slurry to other liquid or gaseous products. Compared to the power generation options discussed in the previous sections, the share of excess heat of this processes is generally lower, and less exergy losses are thus expected in the conversion. While Laser et al. [7] discuss scenarios for the coproduction of Fischer-Tropsch fuels, dimethyl ether or hydrogen, we explored the suitability of



(a) Combustion and steam cycle.



(b) IGCC (gasification, gas turbine and steam cycle).



(c) SNG production (gasification and methanation).

Figure 2: Balanced exergy composite curves for different alternatives of lignin valorisation in the production of ethanol from wood (biogas is combusted in all cases).

SNG production at a case based on conventional indirectly heated gasification with the model of [8]. As illustrated by the balance exergy composite curve of Figure 2(c), the excess heat available from the conversion of the residual lignin slurry into SNG matches well with the requirement for ethanol

| Lignin conversion | combustion | gasification | SNG (gasification and methanation) | | |
|--------------------|-------------|--------------|------------------------------------|-------------|--------------|
| Power cogeneration | steam cycle | IGCC | - | steam cycle | & heat pumps |
| Composite curve | 2(a) | 2(b) | 2(c) | 3(b) | 3(c) |
| ϵ_{EtOH} | 32.3% | 32.3% | 32.3% | 32.3% | 32.3% |
| ϵ_{SNG} | - | - | 40.3% | 35.2% | 41.9% |
| ϵ_{el} | 17.1% | 21.5% | -3.0% | 1.9% | -0.5% |
| ϵ | 49.4% | 53.8% | 70.5% | 69.4% | 73.6% |
| ϵ_{chem} | 62.3% | 70.0% | 67.3% | 70.8% | 73.2% |
| η | 52.5% | 56.9% | 74.9% | 73.8% | 78.5% |

Table 1: Screening of partial and total efficiencies defined by (1) to (5) for different lignin valorisation and process integration options (without any optimisation).

distillation. Together with the sensible heat of the producer gas and fumes, the excess heat from the exothermal methane synthesis just balances with the demand for ethanol production, and the total cooling requirement equals the strict MER assessed in Figure 1(a). In this setup, SNG production allows for increasing the combined fuel yield to over 70%. However, no excess excess heat is available for power cogeneration and an equivalent net amount of 3% of the biomass input is consumed by the process (Table 1).

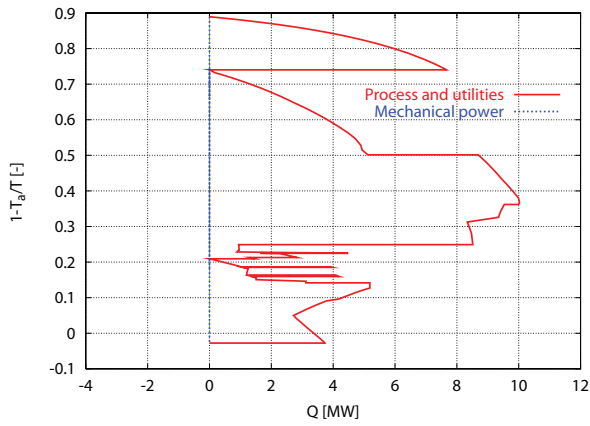
4. A paradox of energy and exergy

Transforming the section composite curves of Figure 2(c) into a single grand composite curve of Figure 3(a) reveals a paradoxical situation in waste heat recovery: Although valuable exergy is potentially available below the high temperature process pinch at 875°C, there is no heat excess in the system for its extraction as mechanical power. The exergy loss in the heat transfer – represented by the surface area between the hot and cold streams – cannot be prevented without supplying additional energy. Electricity cogeneration is thus limited by the first law of thermodynamics and not, as in the usual waste heat recovery problem, by the second. In order to overcome this limitation and valorise the exergy potential at high temperature, energy must be supplied to the system above the low temperature process pinch at 104°C.

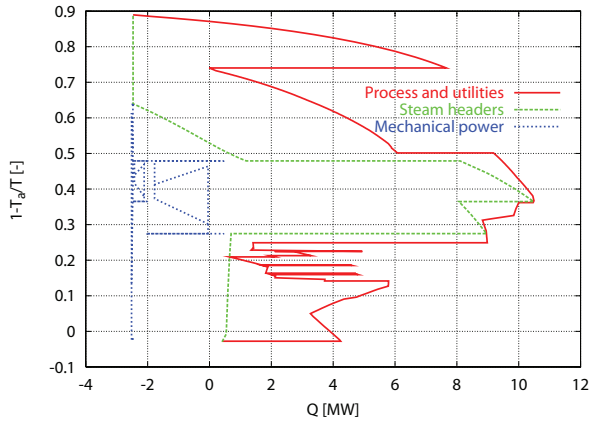
One alternative is the combustion of additional producer gas to not only satisfy the pinch at gasification temperature, but also provide supplementary energy for power cogeneration from the available exergy. Such a solution is illustrated in Figure 3(b). As just as much energy to extract the exergy potential of the high-temperature streams is supplied, a marginal

electric efficiency $\Delta\epsilon_{el}/\Delta\epsilon_{SNG}$ of 96% is obtained since no thermodynamic, but only thermal and mechanical losses in the boiler and turbomachinery occur. The according energy balances of Table 1 highlight that this allows for a gross power generation of roughly 5% of the total biomass input and results in an overall positive balance of the integrated plant.

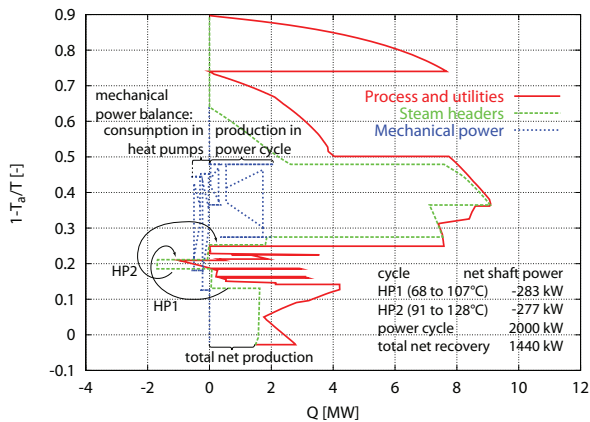
Another, thermodynamically more promising alternative is to supply the required energy not by combustion of producer gas, but by heat pumping across the low temperature pinch. While combustion only transforms the chemical energy of an intermediate product without second-law losses into power, heat pumping adds more energy from below the process pinch – or the environment – above the process pinch. As illustrated in Figures 3(b) and (c), the exergy available below the pinch at 104°C is valorised and losses at high temperature are prevented. This allows for generating a net supplement of useful energy in the form of power, and not just the conversion of chemical into mechanical energy. The prevailing temperature profiles enable water as working fluid of two heat pump cycles from 68 to 107°C (0.28 to 1.29 bar) and 91 to 128°C (0.72 to 2.53 bar). With a combined shaft power of only 560 kW_{el}, these cycles provide 3.9 MW_{th} above the pinch, which allows the power cycle to extract 2.0 MW_{el} of the available high-temperature exergy. In this situation, heat pumping thus paradoxically allows for generating a net supplement of 1.4 MW_{el} of power that almost balances the overall electricity demand of the biomass conversion plant. At the same time, the SNG yield is not only constant but even increased, since the heat pumps also substitute heat that has previously been transferred across the high temperature pinch by only partially preheating the combustion air.



(a) Without exergy recovery (identical to Fig. 2(c)).



(b) Steam cycle with partial producer gas combustion.



(c) Steam cycle with heat pumping.

Figure 3: Exergy recovery alternatives in combined ethanol and SNG production.

5. Conclusions

Table 1 summarises the benefit of designing site-scale integrated processes. Starting from an overall energy efficiency of 49.4% for the conventional process design, the combined production of SNG and ethanol from lignocellulosic resources allows for increasing the efficiency to up to 73.6%.

This brief outlook thus detects substantial potential in the polygeneration of fuels by exploiting the synergies between complementary conversion processes. The proper, overall-site integration of mass and energy is thereby a necessary condition to fully exploit the resource, which can only be realised by a systematic approach. In this regard, the findings with respect to thermal exergy recovery are not restricted to applications in the biofuel sector. Instead of addressing a waste heat recovery problem from the process streams' energy excess, it should be formulated as a problem of exergy minimisation, in which energy and exergy conversion technologies symmetrically allow for exchanges between all process streams and the environment.

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Nomenclature

Abbreviations

HP Heat pump

IGCC Integrated gasification combined cycle

MER Minimum energy requirements

NGCC Natural gas combined cycle

SNG Synthetic natural gas

Roman Letters

\dot{E} Electricity, MW

\dot{m} Mass flow, kg s^{-1}

T Temperature, K

Greek Letters

Δh^0 Lower heating value, MJ kg^{-1}

Δk^0 Exergy value, MJ kg^{-1}

ϵ Energy efficiency, %

η Exergy efficiency, %

Subscripts and superscripts

a atmosphere

el electric

th thermal

$+$ net input

$-$ net output

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