

THERMO-ECONOMIC OPTIMISATION OF THE INTEGRATION OF ELECTROLYSIS IN A WOOD TO METHANE PROCESS

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ABSTRACT

Converting wood to grid quality methane allows to distribute a CO₂ free, renewable energy resource in a conventional energy distribution system and use it in transportation applications. Using a previously developed thermo-economic process model for thermochemical production of synthetic natural gas from wood and applying a multi-objective optimisation algorithm, the present paper assesses the prospect of integrating an electrolyser in the system. Due to an inherent lack of hydrogen for complete conversion of wood into methane, it is shown that electrolysis is a viable option for increasing the gas output, storage of electricity and production of fuel that further mitigates national CO₂-emissions.

Keywords: biofuels, bioenergy, gasification, methanation, electrolysis, optimisation.

NOMENCLATURE

Roman letters

C_{GR}	grass roots costs	[k€]
C_{OP}	operating costs	[€/MWh]
C_P	total production costs	[€/MWh]
c	concentration	[% vol]
H_r^0	standard heat of reaction	[kJ/mol]
$e_{a,i}$	specific avoided CO ₂ emissions assigned to substance i	[kg/MWh _i]
$e_{p,i}$	specific CO ₂ emissions assigned to the production of substance i	[kg/MWh _i]
$e_{u,i}$	specific CO ₂ emissions assigned to the usage of substance i	[kg/MWh _i]
\dot{m}	mass flow	[kg/s]
p_g	gasification pressure	[bar]
p_m	methanation pressure	[bar]
$p_{s,bi}$	pressure of bleeding level i	[bar]
r_{H_2}	additional H ₂ (methanation)	[% wt]
r_{H_2O}	additional steam (methanation)	[% wt]
SN	stoichiometric number	[-]
SNG	synthetic natural gas	
s_i	stoichiometric coefficients	[-]
T_d	drying temperature	[°C]

T_g	gasification temperature	[°C]
T_m	methanation temperature	[°C]
$T_{s,s}$	steam superheat temperature	[°C]
w^-	produced electrical power	[kW]
w^+	consumed electrical power	[kW]

Greek letters

Δh_{vap}	latent heat of vaporisation	[MJ/kg]
Δh_i^0	lower heating value of i	[MJ/kg]
Δk_i^0	exergetic value of i	[MJ/kg]
ΔT_{min}	minimum approach temperature	[°C]
ε	energetic efficiency	[%]
η	exergetic efficiency	[%]
μ	mean value	
ρ	correlation coefficient	[-]
σ	standard deviation	
Φ_w	wood humidity	[% wt]

1 INTRODUCTION

Thermochemical production of synthetic natural gas (SNG) from wood by means of wood gasification, methane synthesis and CO₂-removal from the product gas offers several interesting features. A widely available and renewable energy source which is not in competition with food production is used in a process that might be operated as an overall CO₂ sink. Clean gaseous fuel is produced and distributed

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into existing networks. Its use in transport applications would allow to cut greenhouse gas emissions in a domain where few solutions for mitigating CO₂ emissions and using biomass resources exist.

Currently, different process designs are under investigation [1, 2]. They all have in common that the gas produced by gasification lacks of hydrogen for completely reforming the carbon into methane, which results in a by-production of CO₂. Furthermore, the overall process is exothermic and cogeneration of electricity is therefore possible. For this reason, integrating an electrolyser in the system would allow to increase the methane yield by adding hydrogen to the carbon flow and to produce pure oxygen that is needed for the gasification process while using the cogenerated power. Alternatively, by importing renewable electricity, the process is a way of storing green electrical power in the form of SNG.

Based on a process model described in [1], this paper aims to analyse the integration of electrolysis and its impact on process design and performances.

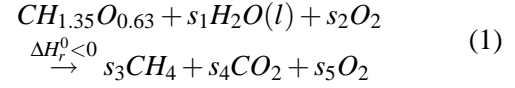
2 PROCESS DESCRIPTION

A general block flow diagram of the process showing the superstructure with the investigated technological alternatives is given in figure 1. In a first process step, chipped wood with an initial moisture content of 50%wt and a corresponding lower heating value¹ of 16.2 MJ/kg_{dry} is dried to avoid severe exergetic losses and enhance the formation of CH₄ during gasification. Indirectly heated, steam blown gasification in a internally circulating fluidised bed usually operating at around 850°C and atmospheric pressure [3] and directly heated, oxygen blown, pressurised fluidised bed gasification operating at around 800°C [4] are considered as gasification technologies. The oxygen necessary for the latter might be supplied externally or produced on-site using either ion transfer membranes [5] or electrolysis. After gasification, the obtained gas needs to be cleaned from impurities to prevent methanation catalyst damage. Being rich in H₂, CO and CO₂, the gas is reformed at around 300-400°C in an internally cooled, pressurised fluidised bed reactor [6] where a sufficient amount of steam is added to avoid carbon deposition. The synthesis gas is dried and CO₂ is

¹ Δh_{wood}^0 is calculated considering the latent heat of vaporisation for moisture and referred to the dry mass of wood, i.e. $\Delta h_{\text{wood}}^0 = \Delta h_{\text{wood,dry}}^0 - \Delta h_{\text{vap}} \Phi_w / (1 - \Phi_w)$.

removed in order to increase its calorific value and meet the condition of a Wobbe index between 13.3 and 15.7 kWh/Nm³ needed for injection into the gas grid. The integration of a Rankine cycle allows to produce electrical power from excess heat available below the pinch.

Representing wood as a typical molecule with the carbon atom as reference, the overall conversion can be expressed as:



The stoichiometric coefficients s_i are dependent on the considered technological production route. For processes without oxygen imports or exports (i.e. $s_2 = s_5 = 0$), s_1 , s_3 and s_4 amount to 0.3475, 0.51125 and 0.48875 respectively, having an enthalpy of reaction H_r^0 of -10.5 kJ/mol_{wood}. If it is aimed to completely reform the carbon contained in wood into CH₄ (i.e. $s_2 = s_4 = 0$), the values of s_1 , s_3 and s_5 are 1.325, 1 and 0.9775 respectively. In this case, the enthalpy of reaction H_r^0 is of 425 kJ/mol_{wood} and indicates an important gap of energy due to water evaporation and separation.

The thermodynamic process performances are determined in terms of energetic (ϵ) and exergetic (η) efficiency, defined as respectively:

$$\epsilon = \frac{\Delta h_{\text{SNG}}^0 \dot{m}_{\text{SNG}} + w^-}{\Delta h_{\text{wood}}^0 \dot{m}_{\text{wood}} + w^+} \quad (2)$$

$$\eta = \frac{\Delta k_{\text{SNG}}^0 \dot{m}_{\text{SNG}} + \Delta k_{\text{O}_2}^0 \dot{m}_{\text{O}_2} + w^-}{\Delta k_{\text{wood}}^0 \dot{m}_{\text{wood}} + w^+} \quad (3)$$

In these equations, Δh^0 and Δk^0 designate the lower heating and exergetic value per unit mass respectively, w^- refers to overall produced power and w^+ to overall consumed power. The economic performances of the process are determined as outlined in [1] using the assumptions of table 1. The capital costs of the plant are denominated gross roots costs (C_{GR}) and correspond to the initial investment without land. Operating costs (C_{OP}) include estimated expenses for raw materials, utilities, labour and maintenance. Total production costs (C_{P}) designate the expected cost of manufacturing including the investment's depreciation. The environmental impact of the process is assessed with a CO₂ emission inventory. The emissions assigned to SNG as well as the effects on the national CO₂ balance are determined.

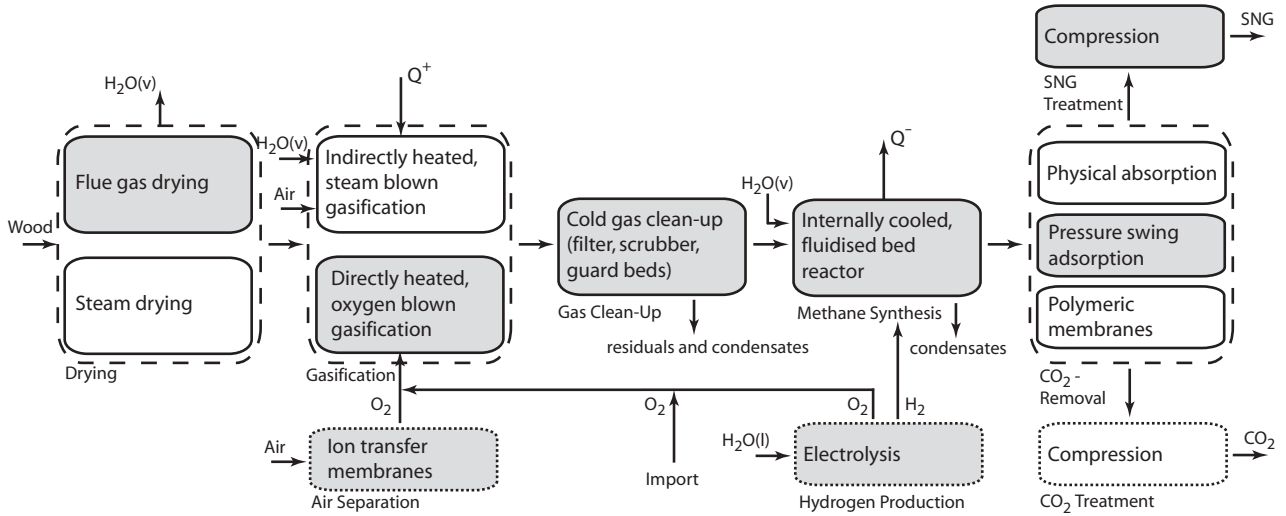


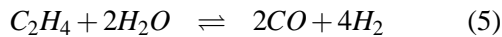
Figure 1: Process superstructure. Dashed boxes assemble competing technologies and dotted ones are used for optional equipment. The process configuration examined in this paper is shown shaded.

Parameter	Value
Marshall&Swift index (2004)	1197
Dollar exchange rate	0.99 €/US\$
Interest rate	6%
Expected lifetime	15 years
Plant availability	90%
Operators	4 p./shift
Operator salary	60 k€/year
Maintenance costs	5%/year of C_{GR}
Wood costs ($\Phi_w=50\%$ wt)	13.2 €/MWh
Electricity costs (import)	88.9 €/MWh
Electricity costs (export)	26.4 €/MWh

Table 1: Assumptions for the economic analysis.

3 INTEGRATION OF ELECTROLYSIS IN THE PROCESS

The prospect of integrating electrolysis in the process rests upon the lack of hydrogen to completely reform the wood's carbon into methane. Hydrogen might be conveniently added to the methanation, where the following reactions take place:



The stoichiometric coefficients of these reactions allow to determine the amount of hydrogen that is needed to prevent the formation of CO_2 . Considering ethene to represent the higher hydrocarbons, it

is possible to define the stoichiometric number SN of the reactant mixture in order to characterise the achievable methane yield:

$$SN = \frac{c_{CH_4}}{3c_{CO} + 4c_{CO_2} + 2c_{C_2H_4}} \quad (7)$$

To obtain a pure methane stream from the stoichiometry, this ratio must be close to unity, whereas it is generally lower for gas produced from biomass.

In this paper, it is assumed that hydrogen might be added using an electrolyser at an efficiency of 85% based on the electricity input and the lower heating value of H_2 . The by-production of oxygen is used to supply the gasifier. According to the US/DOE target by 2010, capital costs of electrolysers are assumed to 297 €/kW_{el,installed} [7].

4 IMPACT OF ELECTROLYSIS

4.1 Process optimisation strategy

In previous work [1, 8, 9], a thermo-economic process model including different technological options has been developed. Its thermodynamic part consists of an energy-flow and an energy-integration model. The energy-flow model computes the transformation of species and the associated heat requirements. These data are implemented in the energy-integration model which determines the optimal thermal process integration and optimises the combined heat and power production. Considering the thermodynamic conditions as decision variables,

Section	Variable	Variation domain	
Drying	$T_{d,in}$	[160; 240]	°C
	$\Phi_{w,out}$	[2; 30]	% wt
Gasification	p_g	[1; 20]	bar
	T_g	[750; 900]	°C
Methane synthesis	p_m	[1; 50]	bar
	$T_{m,in}$	[300; 400]	°C
	$T_{m,out}$	[300; 400]	°C
	r_{H_2O}	[5; 35]	% wt
Steam network	$r_{H_2}^1$	[0; 12]	% wt
	ΔT_{min}	[30; 100]	°C
	$T_{s,s}$	[380; 580]	°C
	$p_{s,b2}$	[0.35; 58.9]	bar

¹ r_{H_2} is the amount of hydrogen produced by electrolysis that is added to the methanation (in $\text{kg}_{H_2,added}/\text{kg}_{g,out}$).

Table 2: Decision variables for optimisation.

the economic model then calculates the capital costs of the plant by sizing the major equipment necessary to reach the process requirements.

The impact of electrolysis on the process design and performances has been investigated by applying an evolutionary, multi-objective optimisation algorithm to an exemplary process layout based on flue gas drying, directly heated gasification and pressure swing adsorption, as depicted in gray on figure 1. Total production costs and exergetic efficiency have been regarded as objective functions. The list of decision variables and their variation domain is given in table 2. Nominal power based on wood input has been fixed to 20 MW_{th} . In order to demonstrate the interest of using electrolysis, an optimisation of the process without electrolysis considering the same decision variables has been performed for comparison.

4.2 Analysis of optimisation results

The computed pareto curves representing the optimal trade-off between total production costs and exergetic efficiency for the process with and without electrolysis are depicted in figure 2. The plot shows that the process clearly benefits from electrolysis with regard to both objectives. While the range of exergetic efficiencies varies from 65.8 to 67.2% for a plant without electrolyser, it is extended up to 78.6%, with minimal production costs for SNG decreasing from 46.0 to 42.2 €/MWh. Break-

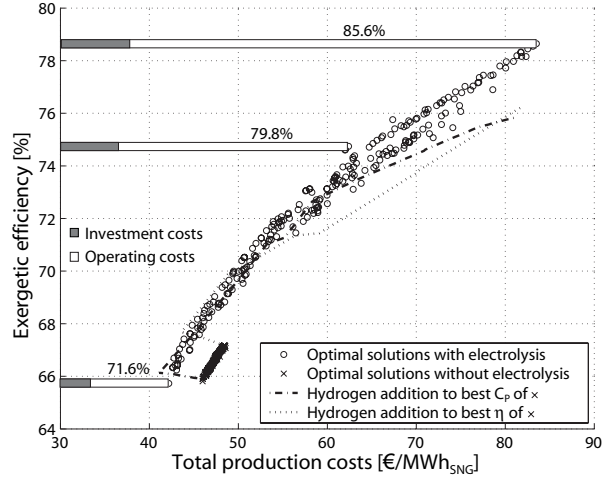


Figure 2: Optimal trade-off of efficiency vs. cost.

downs of the costs between investment and operating expenses for solutions that consider electrolysis show that efficiency improvement associates with increases in operating costs. As it will be shown in the subsequent sections (cf. figures 5 and 6), both exergetic efficiency and operating costs increase with the additional production of hydrogen from electricity. However, due to the price of 88.9 €/MWh_{el} for the imported electricity, this leads to an increase of the SNG production costs.

4.3 Impact of electrolysis on process design

Dashed lines on figure 2 show the evolution of efficiency and total production costs if hydrogen from electrolysis is continuously added to the process. Due to the limited amount of iterations and numeric noise, the solutions calculated in this way equal or even exceed the performances of the evolutionary procedure results when small amounts of hydrogen are added (cf. figure 7). However, they become sub-optimal for the addition of large quantities, which demonstrates that the integration of the electrolyser modifies the process design. In order to get an idea of this impact, the correlation coefficient ρ between the decision variables and the amount of additional hydrogen r_{H_2} have been computed according to:

$$\rho_{i,r_{H_2}} = \frac{\mu(x_i - \mu(x_i))\mu(r_{H_2} - \mu(r_{H_2}))}{\sigma(x_i)\sigma(r_{H_2})} \quad (8)$$

where x_i designates the observations of the sets i , μ the corresponding mean values and σ their standard

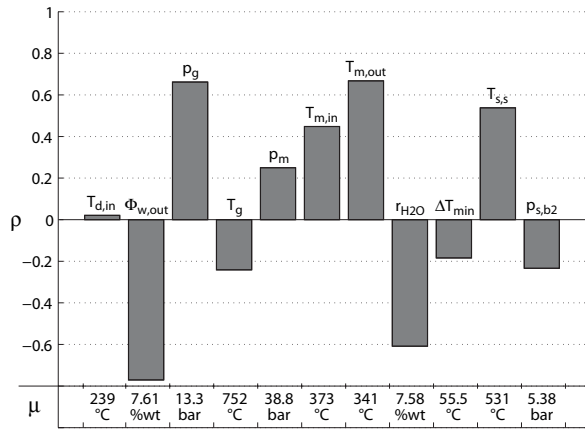


Figure 3: Correlation of decision variables and η_{H_2} .

deviations. Positive values of these coefficients indicate that an increase of the value is expected when the hydrogen flowrate increases.

According to figure 3, it is observed that optimal designs with increasing additional hydrogen are characterised by higher drying rates, gasification pressure, methanation temperature as well as maximal steam cycle temperature, whereas they require less additional steam for methanation and a lower approach temperature for the steam production. Most of these trends match a more efficient steam cycle design, which is of increasing importance since more heat is available from the process streams, in particular from methane synthesis.

The influence of electrolysis on the process sections gets apparent by investigating their associated investment costs (figure 4). Due to the increased amount of reformed methane, larger equipment for its synthesis, the associated power production and the overall heat exchange is needed, while the presence of less CO_2 after methanation decreases the expenses for its removal. The process sections upstream of the methane synthesis are indirectly affected by the need to dry wood more extensively and due to the higher gasification pressure, which causes itself increasing expenses for the gasifier and decreasing costs for gas cleaning.

4.4 Impact of electrolysis on process efficiency

Figure 5 shows the evolution of the energetic and exergetic efficiency as a function of the electrolyser

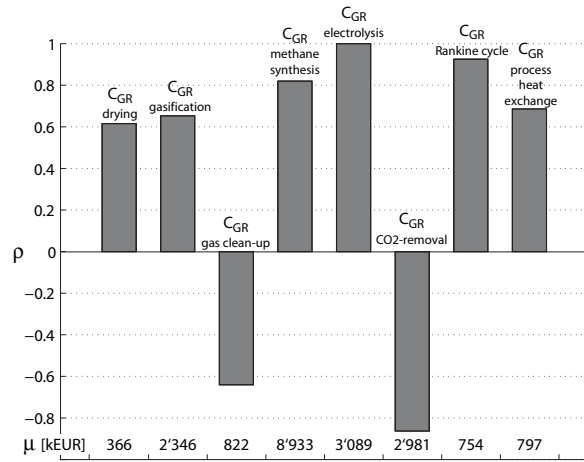


Figure 4: Correlation of equipment costs and η_{H_2} .

input power. The efficiency of the electrolyser is higher than the plant efficiency. Therefore, the total efficiency increases with the rate of electrolysis and proves an efficient use of hydrogen in the process. The maximal energetic efficiency of the process is reached at 85.7% and occurs at a relative electrolyser power of 0.36 MW_{el}/MW_{wood} . The maximal exergetic efficiency is of 78.6% and corresponds to a relative power consumption of 1.12 MW_{el}/MW_{wood} . The difference between the optimal values for the electrolyser power is thereby caused by an important difference between the lower heating and exergetic value of wood of $\Delta k_{wood}^0/\Delta h_{wood}^0 = 1.29$, which is explained by the value of the wood moisture content of 50% wt.

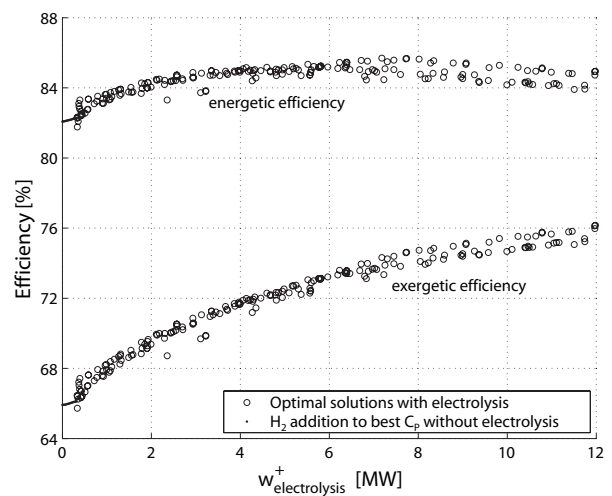


Figure 5: Impact of electrolysis on efficiency.

4.5 Impact of electrolysis on process economics

4.5.1 Specific production costs

The impact of electrolysis on the specific production costs of synthetic natural gas is shown in figures 6 and 7. In order to highlight the influence of the capital costs for electrolysers, production costs considering investment costs of 297 and 989 €/kW_{el,installed} are shown. While the former represents a targeted cost by 2010, the latter is seen as a lower bound for current investments [7].

According to the plots, the addition of small amounts of hydrogen allows to decrease the production costs, while larger quantities cause a significant increase. Minimum specific costs of 41.1 €/MWh_{SNG} occur at an electrolyser power of 320 kW_{el}, which corresponds to the configuration where the oxygen demand from gasification exactly matches the amount of oxygen available from the electrolysis. The benefit of electrolysis with regard to specific production costs is thus based on its by-production of oxygen which eliminates the need for an additional air separation unit. With the assumed electricity costs, larger rates of electrolysis might however get profitable if the oxygen in excess is commercialised, and prices in the range of 60 to 70 €/ton_{O₂} at 200 bar have been assessed² to break even the minimum specific production costs.

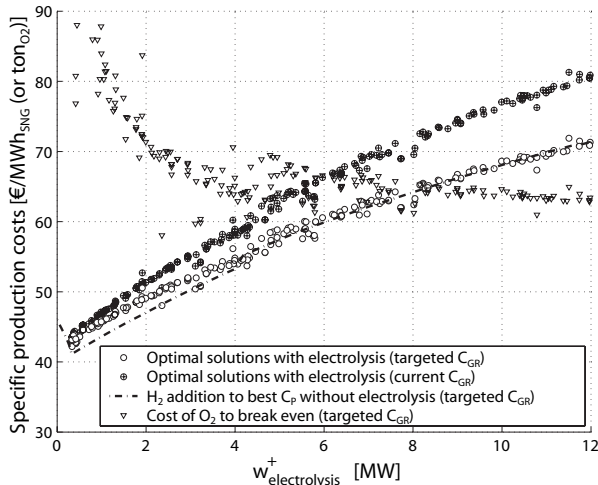


Figure 6: Impact of electrolysis on production costs.

²This value obviously depends on the cost of electricity.

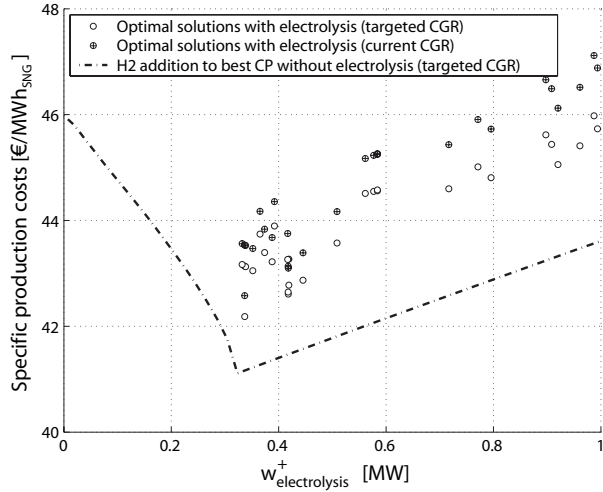


Figure 7: Impact of electrolysis on production costs (detail).

4.5.2 Process profitability

Although the specific production costs of SNG tend to increase with the production of H₂ by electrolysis, the profit from treating a fixed amount of wood might increase due to the generation of additional gas. This effect is analysed on figure 8, where the most profitable process operation depending on electricity cost and gas price is shown, when sales of oxygen are not considered. By comparison with typical costs of generating electricity [10] and swiss gas prices [11], the plot indicates that electrolysis might effectively allow to increase the revenue from wood, if not the market price of electricity, but its real production costs are considered. While the most profitable process configurations for electricity costs corresponding to the market price consider electrolysis only for oxygen production, electricity generated by nuclear power allows profitable base load operation of electrolysis for gas prices higher than 45.0 to 54.5 €/MWh_{SNG}, while wind power requires gas prices higher than 59.3 to 87.3 €/MWh_{SNG}, which corresponds to the range of transportation applications.

4.5.3 Marginal production costs

As outlined in section 3, the stoichiometric number of the gas from wood gasification is lower than unity and the methane production is only limited by the available hydrogen. The marginal efficiency of electrolysis can be estimated by rearranging equation (2)

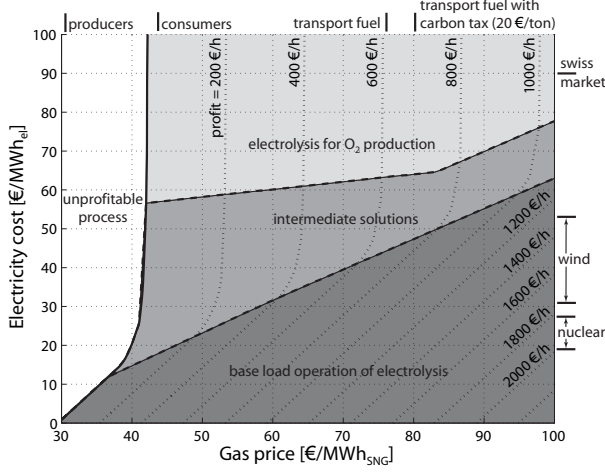


Figure 8: Optimal size for maximum profit.

and assuming a constant process efficiency ε as well as a fixed flow of wood ($\partial \dot{m}_{\text{wood}} / \partial w^+ = 0$):

$$\Delta h_{\text{SNG}}^0 \frac{\partial \dot{m}_{\text{SNG}}}{\partial w^+} = \varepsilon \left(\Delta h_{\text{wood}}^0 \frac{\partial \dot{m}_{\text{wood}}}{\partial w^+} + 1 \right) \quad (9)$$

from which follows:

$$\Delta h_{\text{SNG}}^0 \frac{\partial \dot{m}_{\text{SNG}}}{\partial w^+} = \varepsilon \quad (10)$$

It is thus possible to store electricity with an efficiency equal to the overall process efficiency of 81.8% to 85.7% and additional SNG can be produced at the marginal cost of electricity factored by $1/\varepsilon$. In this way, the installation of an electrolyser allows to absorb seasonal overproduction of electrical power and efficiently produce fuel for transport applications.

4.6 Impact of electrolysis on CO₂ balance

Based on the data for an emission inventory given in table 3, figure 9 shows the specific avoided emissions of CO₂ due to the substitution of fossil natural gas by synthetic natural gas produced from wood. Values for both the Swiss and UCTE electricity mix as well as electricity generated from renewable sources are given. In addition to the avoided emissions for a process without CO₂ sequestration, values corresponding to an optional carbon dioxide sequestration are further shown.

The impact of adding hydrogen from electrolysis to the process is influenced by different effects. Firstly, the SNG production and hence the amount

Type	Associated emissions	
Wood growth	-418	kgCO ₂ /MWh _{wood}
Wood chopping ¹	5.38	kgCO ₂ /MWh _{wood}
Wood transport ²	0.87	kgCO ₂ /MWh _{wood}
Swiss electricity ($e_{p,el}$)	110	kgCO ₂ /MWh _{el}
UCTE electricity ($e_{p,el}$)	450	kgCO ₂ /MWh _{el}
NG production ($e_{p,NG}$)	26.7	kgCO ₂ /MWh _{NG}
(S)NG combustion	203	kgCO ₂ /MWh _{(S)NG}

¹ data for $\Phi_w=55\%$ wt

² average distance of 40 km with lorry (16t)

Table 3: Data for CO₂-emission inventory [12].

of substituted natural gas as well as the avoided CO₂ emissions are increased. If the electricity needed for this purpose is generated from fossil sources, this is counterbalanced by additional emissions of carbon dioxide associated with the power demand. Furthermore, adding hydrogen to the carbon flow decreases the ratio of CO₂ emitted on-site to CO₂ emitted during combustion of SNG. If carbon dioxide is not captured at the process outlet, this does however not change the total emissions of carbon originating from wood. The only effect on the overall CO₂ balance is that the emissions of fossil natural gas are substituted by the ones for electricity production. Reminding equation (10), it is possible to produce SNG from electrical power at an efficiency equal to the process efficiency. Accordingly, the overall greenhouse gas emissions decrease if

$$e_{p,el} < \varepsilon \cdot e_{u,NG} \approx 188 \text{ kgCO}_2/\text{MWh}_{el} \quad (11)$$

and specific avoided emissions of

$$e_{a,el} = \varepsilon \cdot e_{u,NG} - e_{p,el} \quad (12)$$

are assigned to the electricity used in the process. If carbon dioxide is captured at the process outlet, adding hydrogen results in a smaller amount of CO₂ that is sequestered, but emitted during combustion of the additionally produced SNG. Only the emissions related with the production and transportation of natural gas are mitigated and a decrease of the total emissions is obtained if

$$e_{p,el} < \varepsilon \cdot e_{p,NG} \approx 21.8 \text{ kgCO}_2/\text{MWh}_{el} \quad (13)$$

resulting in specific avoided emissions of

$$e_{a,el} = \varepsilon \cdot e_{p,NG} - e_{p,el} \quad (14)$$

CO₂ sequestration will therefore require an electricity production based on renewable resources.

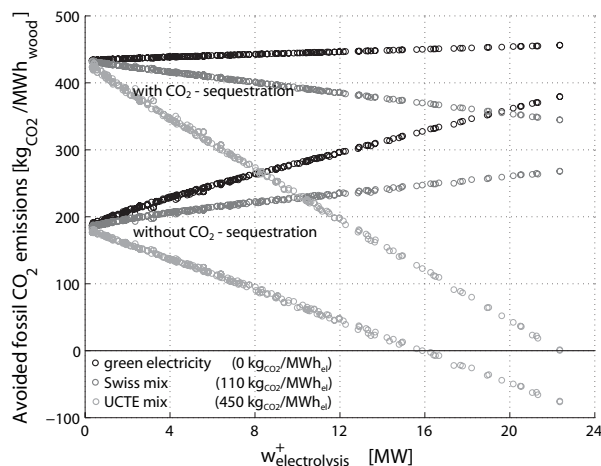


Figure 9: Avoided fossil CO₂ emissions.

5 CONCLUSION

Exploring a detailed process model of thermochemical production of SNG from wood and using a multi-objective optimisation framework, the impact of electrolysis on process design and its thermodynamic, economic and environmental performances has been investigated. It has been shown that due to an appropriate use of hydrogen in the methanation, the integration of an electrolyser allows to increase both the energetic and exergetic efficiency of the plant. However, for an electrolyser size whose by-production of oxygen exceeds the amount required by the gasification, the actual market price of electricity causes specific productions costs to rise until the oxygen is commercialised. Nevertheless, if electricity is available at the cost of its generation or if it is seasonally cheap, electrolysis increases the profit of the conversion and allows to convert and store electricity in the form of transportation fuel with an efficiency of 82 to 86%. Furthermore considering the possible CO₂ sequestration and the substitution of fossil natural gas, CO₂ emission are mitigated and negative specific emissions are allocated to the electricity used in the process, especially when renewable electricity is available.

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