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Thermo-chemical H$_2$ production:
Thermo-economic modeling and process integration

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Abstract

Within the global challenge of climate change and energy security, hydrogen is considered as a promising decarbonized energy vector to be used in electricity production and transportation. In this paper, the thermo-chemical production of hydrogen by natural gas reforming and by lignocellulosic biomass gasification are analyzed, compared and optimized by developing thermo-economic models. Combining flowsheeting with process integration techniques, thermo-economic analysis and life cycle assessment (LCA), a systematic comparison of different process options with regard to energy, economic and environmental considerations is made. The choice of the technologies is optimized together with the operating conditions using multi-objective optimization.

In both natural gas and biomass based H$_2$ pathways, a CO$_2$ removal step is included during the H$_2$ purification which allows for CO$_2$ capture and further sequestration. The potential for greenhouse gas mitigation is assessed and compared with conventional plants without capture based on the CO$_2$ avoidance cost and the overall CO$_2$ equivalent emissions computed from the life cycle chain. The system's performance is improved by introducing process integration valorizing the waste heat by the combined production of heat and power. The H$_2$ application purpose and the corresponding required purity are key factors defining the process performance. The trade-offs between competing thermoenvironomic (i.e. energy, economic and environmental) objectives are finally assessed using a multi-objective optimization.

For natural gas based H$_2$ production overall energy efficiencies up to 80% and production cost of 22-110\$/MW$_{H2}$ are computed compared to around 60% efficiency and 75-263\$/MWh$_{H2}$ for biomass based processes having the advantage of using renewable resources. The CO$_{2eq}$ emissions are reduced by more than 6.4kg$_{CO2eq}$/kg$_{H2}$ for NG and 20kg$_{CO2eq}$/kg$_{H2}$ for BM processes compared to the cases without CO$_2$ capture. The competitiveness on the energy market depends strongly on the resource price and on the imposed CO$_2$ taxes. Our study shows that the thermo-chemical hydrogen production has to be analyzed as a polygeneration unit producing not only hydrogen but also captured CO$_2$ and electricity.

Introduction

Within the worldwide challenge of global warming mitigation and energy security renewable resources and carbon capture and storage (CCS) have received considerable attention, especially for hydrogen and electricity production from fossil resources [1]. Biomass-based technologies being renewable and emitting no CO_2 if carefully managed have also a high potential [2]. H_2 is regarded as a clean, reliable and affordable energy vector that can substitute fossil fuels by the combustion in an internal combustion engine or by electrochemical conversion to electricity in a fuel cell system with high efficiency and without on site CO_2 emissions. In this perspective, the pre-combustion, hydrogen routes are investigated here with regard to different resources (i.e. wood and natural gas) and competing outputs such as captured CO_2, H_2 and/or electricity, and their interactions in polygeneration. Several studies have already been performed in order to identify promising fuel decarbonization and biomass conversion processes. Reported efficiencies range from 69 to 80% for fossil fuel hydrogen production [3-6] and from 51 to 60% for biomass based processes [7,8]. The differences are explained by different assumptions made in the calculation and by the variety of technologies that are assessed. In [9] the economics of producing H_2 from fossil and renewable resources are compared; for natural gas fed processes costs of 59-80$/MWh$_{H2}$ with a NG price of 34$/MWh$_{NG}$ are reported, while for renewable processes using biomass, solar or wind costs in the range of 70-253$/MWh$_{H2}$ are assessed. The studies in [4,9] comparing H_2 processes using different resources and technologies are based only on a literature survey with regard to the production cost and the comparison in [6] takes into consideration performance estimates and thermodynamics without economic analysis and no detailed energy integration is performed. To overcome the difficulties of comparing processes with different assumptions, our goal is here to propose a comprehensive comparison framework based on thermo-economic models to compare different hydrogen production processes in a consistent way.

The objective is to compare and optimize different configurations with regard to energy, economic and environmental considerations by applying a consistent methodology and to assess their competitiveness. Special interest is given to the effect of polygeneration of H_2 fuel, captured CO_2, heat and electricity, in order to identify its advantages and constraints, and to better understand trade-offs between efficiency, investment and emissions.

1. Methodology
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The methodology described in [10] for the conceptual process design combining energy integration techniques and multi-objective optimization is applied to assess systematically the energetic, economic and environmental cost of carbon capture and H_2 generation. Figure 1 illustrates the applied design methodology. The energy-flow model computes the chemical and physical transformations and the associated heat transfer requirements. The energy-integration model optimizes the heat recovery and the combined fuel, heat and power production using heat cascade constraints and a linear programming model minimizing the operating cost [11]. Based on the pinch analysis the optimal process integration is computed and the process needs are satisfied by different utilities including waste and process gas combustion, Rankine cycle, gas turbine and cogeneration. The economic performance is evaluated based on equipment rating and cost correlations from literature [12,13]. Life cycle assessment (LCA) is included according to the approach described in [14] in order to evaluate the overall life cycle environmental impact of the process. The method developed by the Intergovernmental Panel on Climate Change

(IPCC) is applied to assess the equivalent CO_2 emissions based on a time horizon of 100 years for the global warming potential (GWP). The functional unit is 1MJ of H_2 produced. In this study, the amount of CO_2 that is captured and sequestrated is accounted as negative contribution of fossil CO_2 and for the electricity impact contribution the Swiss mix for medium voltage electricity production at grid is considered. For comparison, the produced H_2 is substituting H_2 produced by cracking (95%) and electrolysis (5%) using data from the ecoinvent database [15]. Finally, multi-objective optimization is performed to identify the trade-off between competing objectives with regard to environomic criteria and to reveal competitive configurations yielding a good compromise between the different targets.
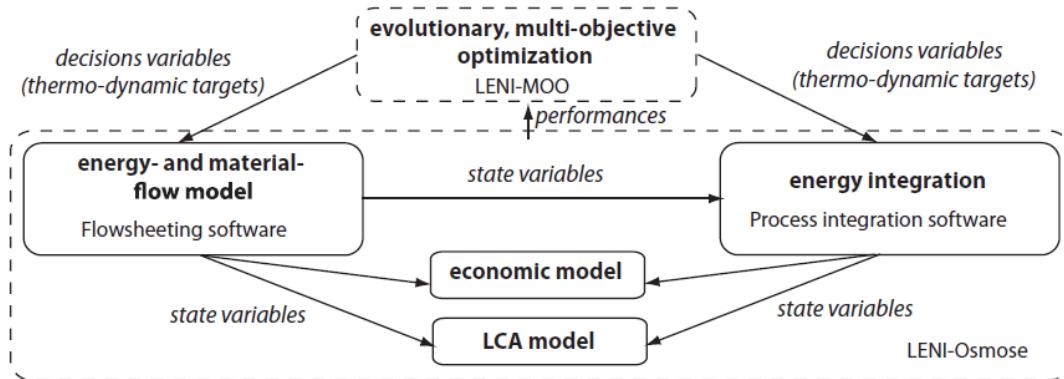

Figure 1: Design methodology overview [14]

2. Process description

The main process steps are resource extraction and treatment, syngas (i.e. H_2 and CO) generation by natural gas (NG) reforming or lignocellulosic biomass (BM) gasification, gas cleaning and treatment, CO_2 removal and finally H_2 purification and/or H_2 burning for electricity generation. Depending on the production purpose, the process produces either H_2 with and without captured CO_2 or is self-sufficient in terms of power, or exports electricity if H_2 is combusted. The process layout in Figure 2 shows the biomass conversion unit operations and the natural gas fed process is represented in Figure 3.
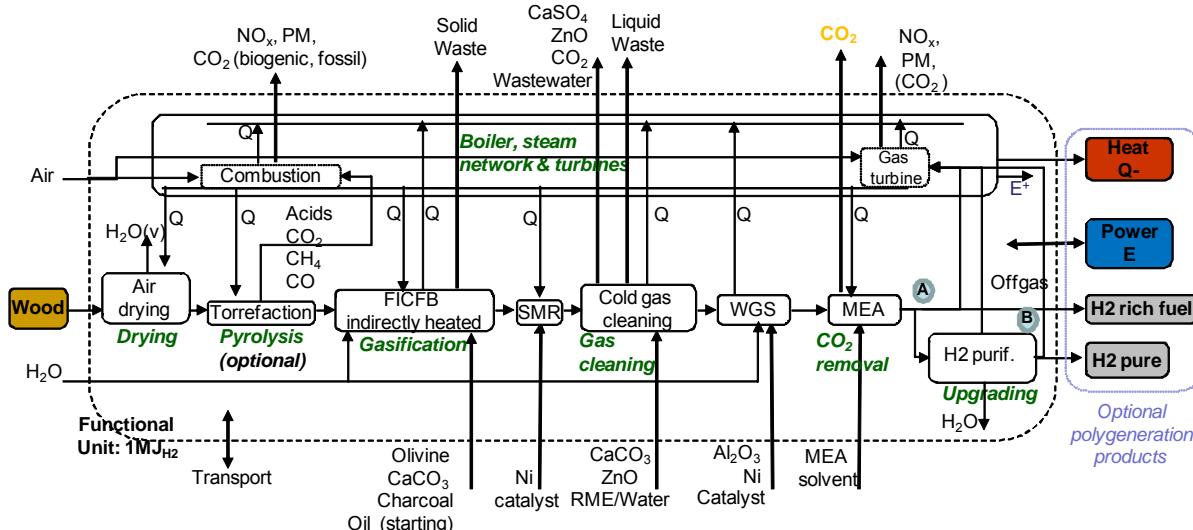

Figure 2: Layout of the biomass conversion process including thermo-economic and LCA model flows. The process products are defined by the decisions made at the cross points A and B.
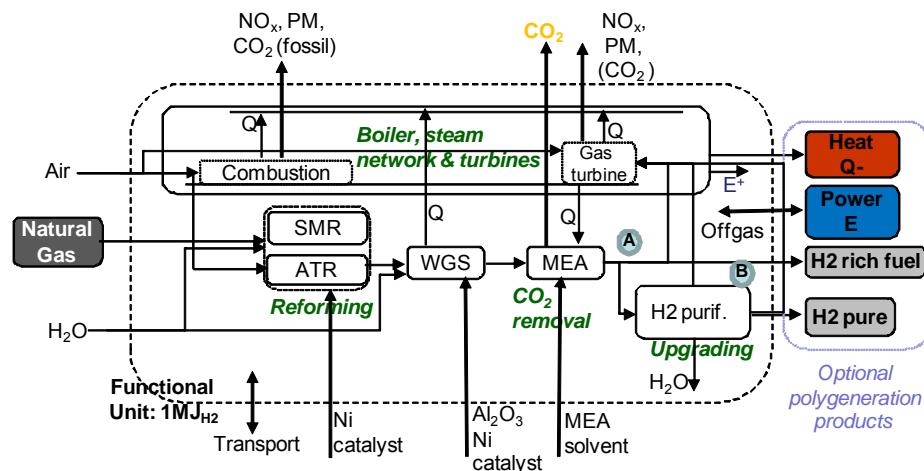
Figure 3: Superstructure of the natural gas reforming processes including thermo-economic and LCA model flows. The process products are defined by the decisions made at the cross points A and B.

The biomass process modeling is described in detail in [16,17]. For NG reforming, steam methane reforming (SMR Eq.1) requiring heat supply and autothermal reforming (ATR) satisfying the SMR heat demand by partial oxidation with air (POX Eq.2) are compared. The syngas is reacted with H_2O in two sequential water-gas shift (WGS Eq.3) reactors one operating at high (HTS) and one at lower temperature (LTS) to increase the H_2 and CO_2 content. Table 1 summarizes the main operating conditions.

Steam methane reforming (SMR): $CH_4 + H_2O \xleftrightarrow{\Delta \tilde{h}_r^o = 206 kJ/mol} CO + 3H_2$ Eq. 1

Partial oxidation (POX): $CH_4 + \frac{1}{2}O_2 \xleftrightarrow{\Delta \tilde{h}_r^o = -36 kJ/mol} CO + 2H_2$ Eq. 2

Water gas shift (WGS): $CO + H_2O \xleftrightarrow{\Delta \tilde{h}_r^o = -41 kJ/mol} CO_2 + H_2$ Eq. 3
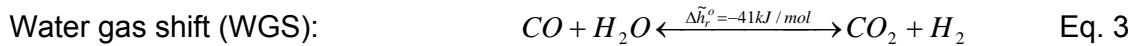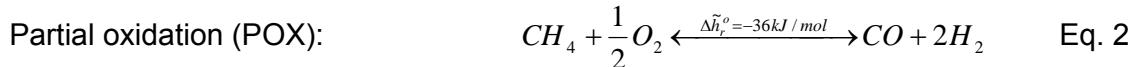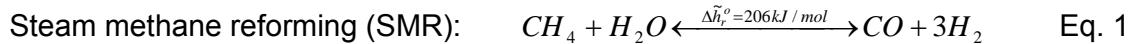
Table 1: Operating conditions of the process and feasible range for optimization

Operating Parameters	Nominal	Range
T_{HTS} [K]	633	[523-683]
T_{LTS} [K]	473	[423-523]
S/C $_{ATR/SMR}$ [-]	2.5/ 3	[0.5-6]
$T_{ATR/SMR}$ [K]	1173/1073	[780-1400]
$P_{ATR/SMR}$ [bar]	15 / 5	[1-30]

The CO_2 removal and H_2 purification models are identical for the BM and NG fed processes. Chemical absorption with amines (MEA) is followed by a pressure swing absorption step (PSA) to generate high purity H_2 and CO_2. The chemical absorption is modeled as a blackbox using the data in Table 2. The PSA modeling approach outlined in [16] is adapted for H_2/CO_2 separation using data from [18]. After the MEA unit the H_2-rich gas exits at the process pressure and after PSA at atmospheric conditions. No H_2 compression for storage and transportation has been included in this study. Standard H_2 purity levels over 99%mol are targeted. If CO_2 sequestration is considered, compression up to 110bar is included. It has to be noted that the CO_2 purification step eventually required before the CO_2 compression to reach the purity characteristics for transportation and storage (min 95%v) has been neglected.

Table 2: Parameters for the H₂ purification unit model

Process	Specification	Value
MEA (chem. absorption)	Thermal Q @150°C	3.7MJ/kgCO₂
	Electric Power	1.0MJ/kgCO₂
PSA	Adsorption P	10bar
	Purging P	0.01bar
	H2 recovery	90%

3. Process performance

The energy efficiency is calculated using Eq.4 where the electricity is accounted as pure energy.

Energy efficiency [%]
$$\varepsilon_{tot} = \frac{\Delta h^0_{H2,out} \cdot \dot{m}_{H2,out} + \dot{E}^-}{\Delta h^0_{feed,in} \cdot \dot{m}_{feed,in} + \dot{E}^+}$$
Eq. 4

In the natural gas equivalent efficiency defined by Eq.5 the net electricity that is consumed is substituted by an equivalent amount of NG required for generating the same quantity of electricity in a combined cycle with an exergy efficiency of 55%.

NG eq. efficiency [%]
$$\varepsilon_{eq,NG} = \frac{\Delta h^0_{H2,out} \cdot \dot{m}_{H2,out} + \frac{1}{0.55}\frac{\Delta h^o_{NG}}{\Delta k^o_{NG}}\dot{E}^-}{\Delta h^0_{feed,in} \cdot \dot{m}_{feed,in}}$$
Eq. 5

The CO₂ capture cost is expressed based on the CO₂ avoidance cost (Eq.6) with regard to the H₂ production cost ($C_{H2,ref}$) and the CO₂ emissions ($CO_{2,emit,ref}$) of a reference plant without CO₂ capture[1].

CO₂ avoidance cost
$$\$/t_{CO2,avoided} = \frac{C_{H2,CC} - C_{H2,ref}\left[\$/MWh_{H2}\right]}{CO_{2,emit,ref} - CO_{2,emitCC}\left[t_{CO2}/MWh_{H2}\right]}$$
Eq. 6

The CO₂ capture rate is defined in Eq.7 by the ratio of the carbon that is captured and the carbon delivered by the natural gas or the biomass respectively. For electricity import no carbon emissions a have been accounted for, however in the LCA they have been included.

CO₂ capture rate
$$CO2\ capture\ [\%] = \frac{mol\ C_{captured}}{mol\ C_{in}} \cdot 100$$
Eq. 7

Table 3 summarizes the assumptions made for calculating the capital cost and the H₂ production cost.
The climate change impact is expressed by the equivalent CO₂ emissions computed from the LCA model.

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[1] As a reference the data for a H₂ plant without carbon capture from [1] (28$/MWh_{H2} and 493kg/MWh_{H2}) or the data computed from the respective scenario without CO₂ compression (no stor.) are considered.

The different scenarios that are investigated are; biomass gasification (BM), natural gas reforming by SMR and ATR with/without CO_2 capture and compression[2]. The possibility to import electricity ($\dot{E}$ imp) or to burn part of the H_2-rich gas to satisfy the process power demands (self-sufficient) is considered.

Table 3: Economic assumptions

Parameter	Value
Marshall & Swift Index	1473.3
Expected life time	15 years
Interest rate	6 %
Yearly operation NG	7500 h/year
Yearly operation BM	8000 h/year
NG / BM price	50 \$/MWh$_{NG}$
Electricity import price	270 \$/MWh$_e$
MEA price	0.970\$/kg$_{MEA}$

3.1. Multi-objective optimization

The trade-off of competing factors defining the process performance is assessed by multi-objective optimization applying an evolutionary algorithm. The key process operating conditions given in Table 1 are chosen as decision variables. The objectives are the maximization of the overall energy efficiency ε_{tot} (Eq.4) and of the carbon capture rate (Eq.7). The optimal Pareto frontiers presented in Figure 4 for the different scenarios show that CO_2 capture reduces the efficiency. For each scenario one configuration yielding a good compromise between efficiency and CO_2 capture is chosen in order to compare more in detail the performance of the different process configurations. For biomass conversion processes, a lower capture rate is accepted in order to reach a higher efficiency ε_{tot} because the emissions from the renewable resource are anyway biogenic and so less harmful.
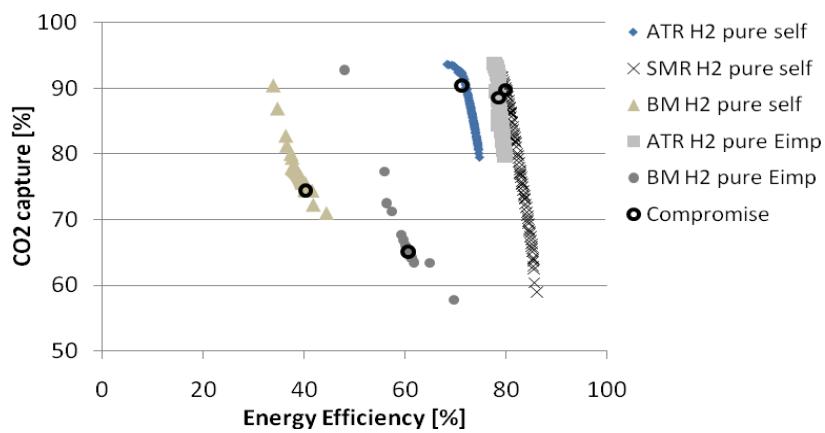
Figure 4: Pareto optimal frontier for H_2 production processes maximizing the energy efficiency and the CO_2 capture rate. Selected scenarios yielding a good compromise with regard to the objectives are highlighted.

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[2] Base cases consider CO_2 capture and compression to 110bar regardless of the CO_2 concentration. No stor means no storage/ no CO_2 compression is included. No CCS means there is no CO_2 separation by chemical absorption and no CO_2 compression.

3.2. Performance comparison

3.2.1. Resource and technology comparison

Different technologies generating H_2 without electricity import (self) are compared in Figure 5 (left). SMR yields a higher efficiency than ATR and biomass gasification has the lowest efficiency.
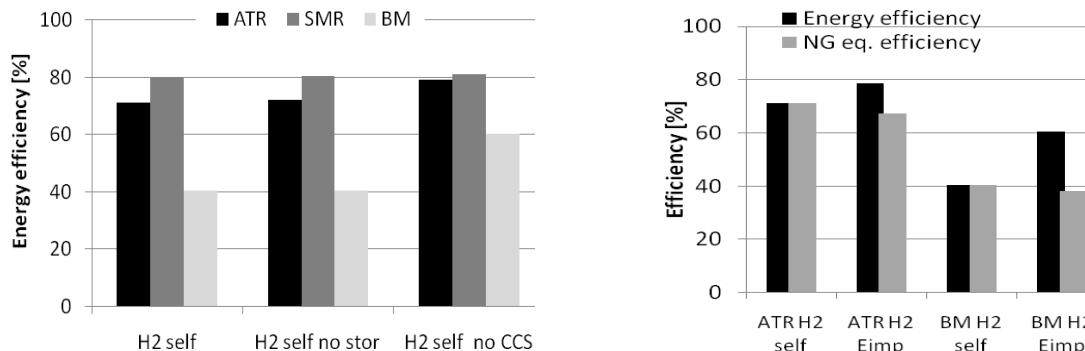

Figure 5: (Left) Energy efficiency for different scenarios producing high purity H_2 without $\dot{E}$ import with and without CO_2 capture. (Right) Energy efficiency and natural gas equivalent efficiency of ATR and BM scenarios with and without $\dot{E}$ import.

Energy integration

The comparison of the integrated composite curves in Figure 6 highlights the difference in the energy demands of the different processes. The endothermic gasification and SMR processes require heat supply, while in the ATR process the heat is delivered internally by a POX reaction. As a consequence, the ATR process requires the lowest hot utility. Above the pinch point the heat demands are satisfied by the combustion of offgases and part of the H_2-rich gas produced. The chemical absorption with MEA requires a large amount of energy for the solvent regeneration. By introducing a heat pump, the energy efficiency of the CO_2 capture unit has been improved by making higher temperature heat available for combined heat and power production. The heat excess below the pinch point is valorized in a steam network for electricity generation.
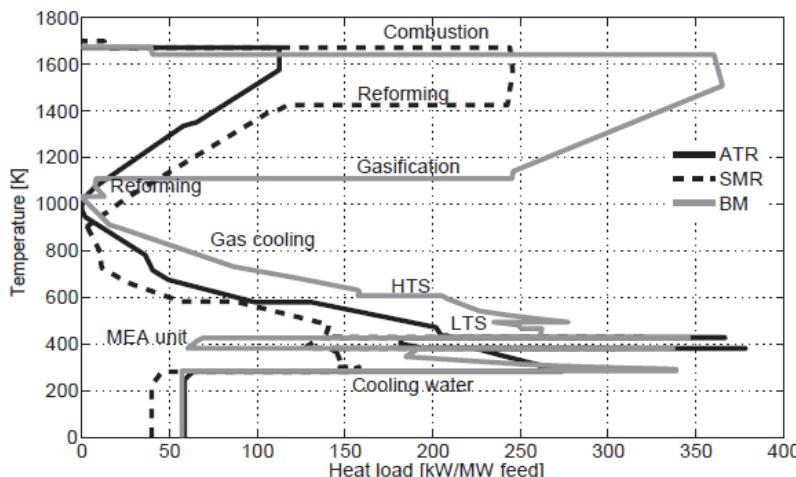

Figure 6: Integrated composite curves for H_2 production (self-sufficient) from different resources and reforming technologies. The steam network integration is omitted on the figure for clarity.

Electricity balance

The power balance reported in Figure 7 shows that the largest power demand of all processes is due to the gas treatment including CO_2 separation, product purification and CO_2 compression, when needed. Moreover, the heat pumping improving the capture unit integration requires power for the compression. The power demand is satisfied by the power generated by the steam network and by the gas turbine. For self-sufficient configurations without electricity import, part of the H_2 product is burnt in a gas turbine, while for the other scenarios the balance is closed by importing electricity from the grid. For the ATR processes, using air as oxidant, some N_2 remains in the products yielding a H_2 purity of 96%mol compared to around 99.9%mol for SMR and BM processes. The purification is demanding more power and is more expensive due to larger volume flows to be treated. In addition, air has to be compressed to the operating pressure. Even if air separation requires also power and adds cost, feeding the ATR with pure O_2 might become an alternative lowering the purification penalty and allowing to reach the standard purity level of over 99%mol H_2.

Comparing the processes without electricity import, the SMR process has the lowest power consumption (Figure 7) which explains the higher efficiency in Figure 5 even if the thermal energy demand is larger (Figure 6). The power demand is reduced by 29% and 35% when compared with the ATR and the BM process respectively. Since less process gas has to be burnt in a gas turbine for power generation more H_2 is produced. The H_2 productivity is decreased by 10% for the ATR and by 50% for the BM process. These trends are also reflected by the production costs reported in Figure 8.
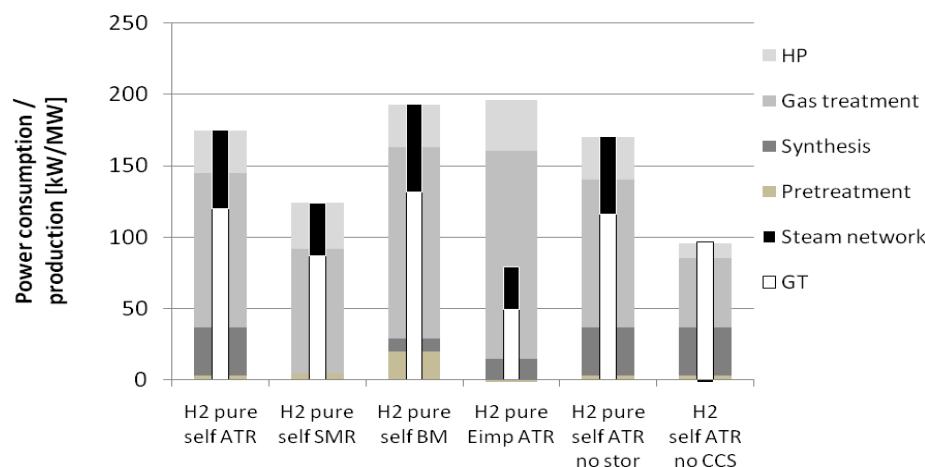

**Figure 7: Power balance comparison for different scenarios**

With electricity import the energy efficiency (ε_{tot}) of the ATR process is increased by more than 7%-points because more H_2 is produced as none has to be burnt for power generation (Figure 5 right). However, expressed in terms of NG equivalent efficiency (Eq.5) the efficiency of the self-sufficient scenario is nearly 4%-points higher. This shows that the internal electricity generation is more efficient than the separate production of electricity by natural gas. The marginal electricity production yield calculated with regard to Eq.5 is in the order of 67% for the ATR process compared to 59% for the BM process. Even if, 18% more H_2 is produced, Figure 8 shows that the production costs are over 10% higher due to the electricity purchase at the price of green electricity (270$/MWh$_e$). With an electricity purchase price around 95$/MWh$_e$ the production cost would be identical. By

importing electricity, electricity can be stored in the form of H_2 for future conversion into electricity with an efficiency of over 1.4kWh$_{H2}$/kWh$_e$.

Economic performance

The SMR process has the lowest production costs due to the highest H_2 yield. The production costs of the biomass gasification processes are high because of the large capital investment required especially for the gasifier purchase which corresponds to 40% of the capital cost. It is to note that the equipment sizing and costing method might overestimate the equipment costs; nevertheless biomass gasification being an emerging technology is more expensive than the well established reforming technologies. The production costs are composed mainly of the resource purchase (50-80%) and of the annual investment (7-25%).
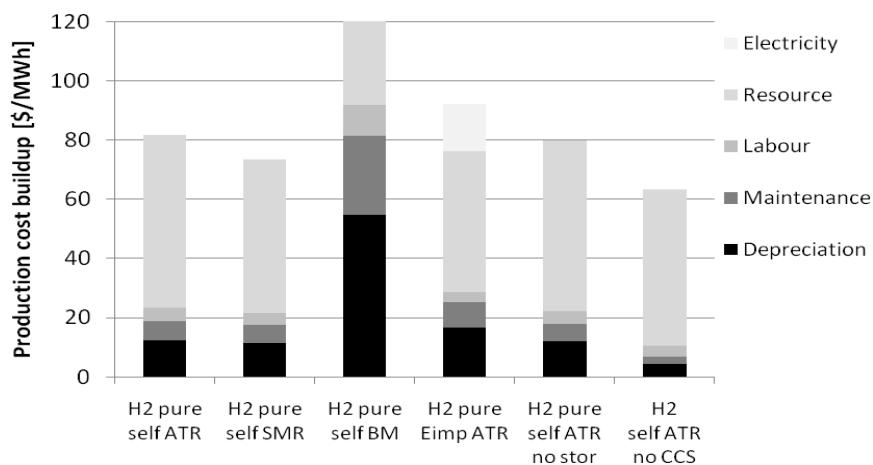
Figure 8: Production cost build-up for different scenarios. (Resource price 50$/MWh)

Without CO_2 compression, the production costs are slightly reduced since the capital investment is reduced and less power is required. Consequently slightly more product is generated and the efficiency is slightly increased. Without CO_2 capture by chemical absorption these effects are more pronounced (Figure 5), however the product purity is lower and does not reach the standard level over 99%mol. This product having a H_2 content between 75 and 95%mol could however be considered for electricity generation by burning in a gas turbine.

Environmental performance

Figure 9 shows the life cycle CO_2 emissions expressed in kgCO$_2$eq per MJ of H_2 produced for different configurations. The impact is constituted by the contribution of the process from which the substituted emissions from the H_2 production by other means (using emissions reported by the ecoinvent database) and the CO_2 emissions that are sequestrated are deduced. CO_2 capture for storage has therefore a substitution benefit on the climate change impact which outweighs the impact of the plant itself.

By comparing the biomass and the natural gas fed processes, the impact of non captured fossil CO_2 can be seen for the NG process, while for the BM process, the emissions are considered as biogenic and therefore not accounted for. It is also seen that the natural gas extraction has a larger impact than the biomass based processes. Electricity import contributes to the impact and reduces the benefit of the CO_2 capture. Since more H_2 is

produced and the CO_2 capture rate is reduced, the specific environmental impact per H_2 produced is more important (i.e. less beneficial).

The ATR process with CO_2 capture allows reducing the climate change impact around 20% compared to the SMR process. For the BM process the impact reduction is between 40 and 80% compared to NG fed processes with CO_2 capture. By replacing a process without CO_2 capture with the selfsufficient BM process capturing CO_2 the benefit in terms of CO_2 emissions reduction is around $20kg_{CO2eq}/kg_{H2}$ (0.17 kg_{CO2eq}/MJ_{H2}).

Without CO_2 capture the reference H_2 production (95% cracking 5% electrolysis) from the ecoinvent database gives for some scenario a lower impact. The cumulated data used for the ecoinvent process do not give transparency on the processes used and the allocations made; therefore one cannot be sure that exactly the same system boundaries are considered. Moreover, the processes analyzed in our study are optimized for maximal H_2 production with CO_2 capture and consequently the energy requirement for CO_2 capture increases the impact.

For the self-sufficient BM process the RME (rape methyl ester) for scrubbing in the gas cleaning worsens the impact due to the contribution from the colza cultivation. The usage of conventional Diesel instead of RME would increase the impact by around 4%. Considering the importance of the contribution of the RME impact on the impact of the biomass processes, it can be concluded that alternative gas cleaning technologies, such as hot gas cleaning have to be investigated.
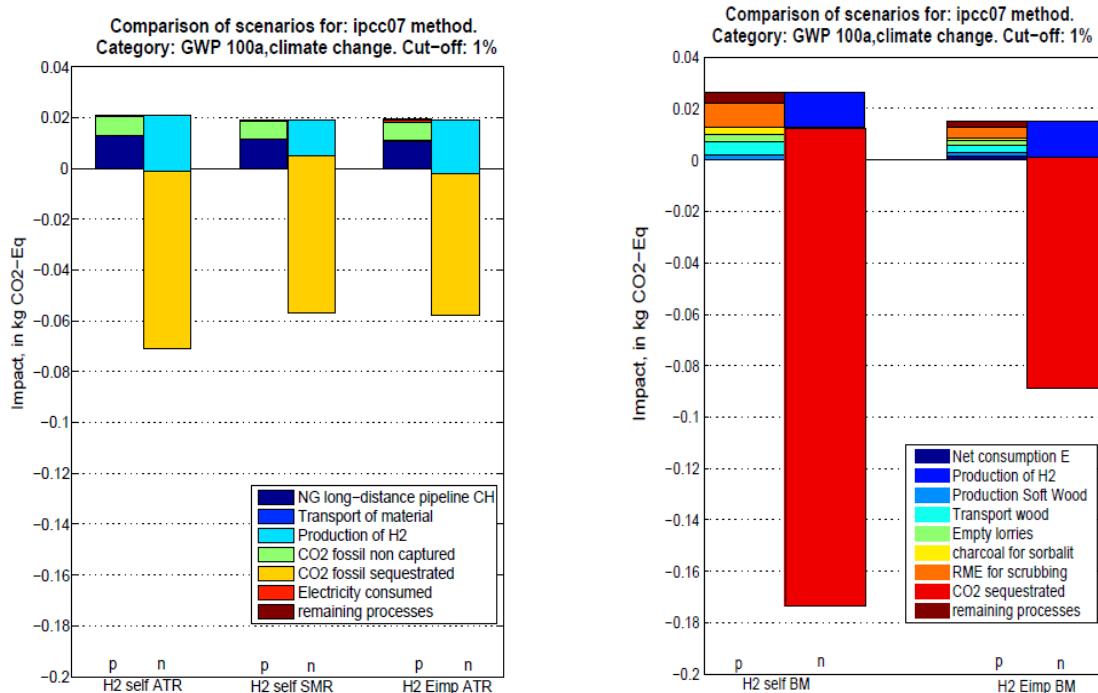
Figure 9: Comparison of the climate change impact of the processes generating H_2 by NG reforming (left) or BM gasification (right) based on the impact method IPCC07 for 1MJ of H_2 produced.

3.2.2. Economic evaluation: resource price sensitivity analysis

The production cost build-up in Figure 8 has shown that the economic performance is highly sensitive to the resource market price.

Figure 10 illustrating the variation of the resource price between 10 and 70$/MWh shows a potential production cost reduction with regard to the price evolution. Compared to the performance stated in the IPCC report [1] for a H_2 plant with CO_2 capture, the different scenarios reveal to be competitive. The computed efficiency is higher than the one reported in [1] but in the range of the ones given in [3-6]. Through good process integration higher efficiencies are reached in this study. Biomass gasification technology development could lead to a capital cost reduction and consequently to more competitive biomass processes in the future.
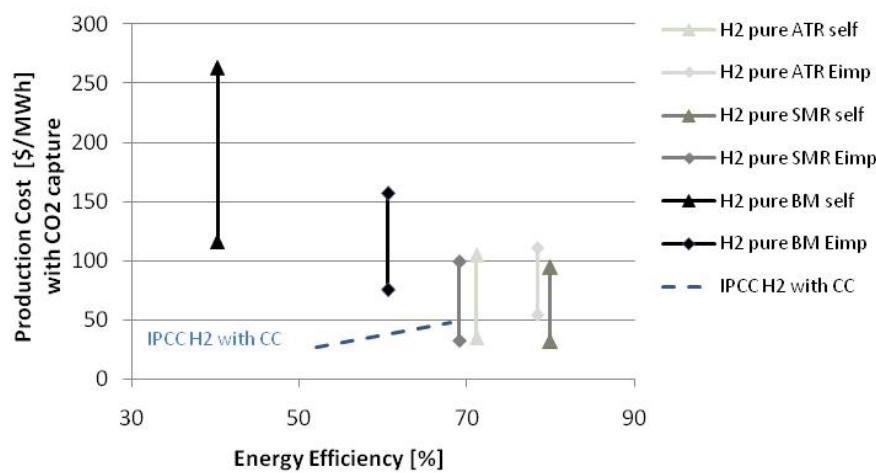

Figure 10: Process performance comparison: production cost variation with regard to the resource price [10-70$/MWh] versus energy efficiency.

3.2.3. CO_2 avoidance cost

As shown previously by the LCA results (Figure 9), CO_2 capture is beneficial for the environment. Regarding the economic competitiveness of CO_2 capture, it depends on the CO_2 taxes that are imposed in the future. In Figure 11 the CO_2 avoidance cost ranges are presented considering the lowest and highest production cost estimates taking into account the resource price variation from 10 to 70$/MWh. Two different reference plants are considered first the reference plant without CO_2 capture from [1] and second the computed scenarios without CO_2 compression (no stor). The later one yield lower avoidance cost which can be due to the underestimation of the CO_2 compression cost. The assessed costs are in the range of the one reported in [1].

These results reveal that processes with CO_2 capture are not only competitive with regard to environmental considerations but also with regard to the economic performance. Compared to the cases without CO_2 capture, the CO_2 emissions are reduced by 221kg/MWh$_{H2}$ for the SMR, 248kg/MWh$_{H2}$ for the ATR and 669kg/MWh$_{H2}$ for the BM process.
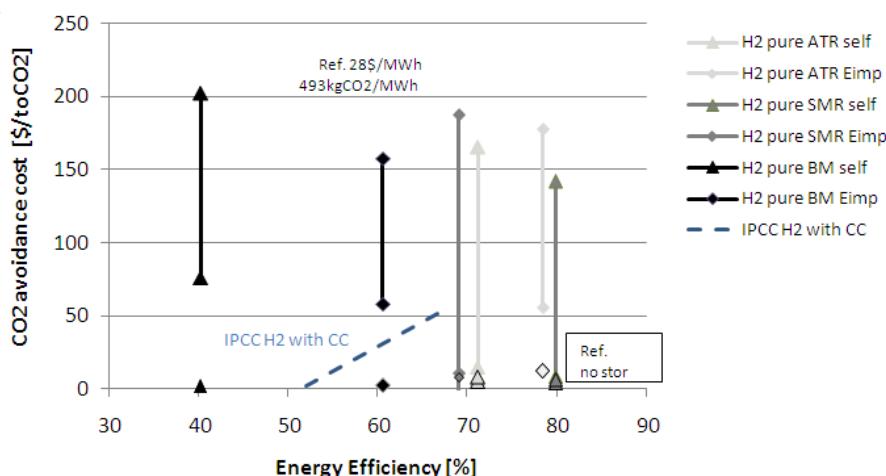
Figure 11: CO₂ avoidance cost with regard to efficiency for different scenarios. The variation of the CO₂ avoidance cost is related to the variation of the resource price [10-70$/MWh]. The reference plant without CO₂ capture is: a) from IPCC [1] b) computed from the corresponding scenarios without CO₂ compression (no stor).

4. Conclusions

The competiveness of the H_2 production from natural gas and biomass resources with and without CO_2 capture is compared with regard to energy efficiency, cost and environmental impacts based on thermo-economic models. Process integration techniques, life cycle assessment and multi-objective optimizations allow to assess the trade-offs and to reveal the potential of polygeneration of H_2, heat and power and captured CO_2. LCA analysis underlines the benefit of using renewable resources and capturing CO_2. The CO_2 capture costs depend strongly on the production process in question. Maximal CO_2 emissions reduction in the order of $20 kg_{CO2eq}/kg_{H2}$ (0.17 kg_{CO2eq}/MJ_{H2}) is reached for the biomass process capturing CO_2 without electricity import. Depending on the resources market price evolution, production costs in the range of 22-110 $/MWh are assessed for natural gas fed processes and 75-263$/MWh for biomass conversion processes with efficiencies in the range of 69-83% and 40-60% respectively. For the NG reforming SMR performs better in terms of thermo-economic performance than ATR using air as an oxidant, while the environmental performance is comparable. A future study will compare the performance with ATR using O_2 instead of air. The market price of resources, fuel and CO_2 taxes defines the competitiveness of H_2 production from fossil and renewable resources with and without CO_2 capture. This analysis shows the potential of efficient decarbonization in fossil and renewable based production of H_2 which can be used as a future energy vector for various applications.

Acknowledgements

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