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CO₂ mitigation in thermo-chemical hydrogen processes: Thermo-environomic comparison and optimization

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Abstract

A systematic comparison and optimization of thermo-chemical hydrogen production processes with CO₂ capture is performed. The process options include the resource type, the syngas production method and the hydrogen purification technology, including CO₂ separation by ab- or adsorption or membrane processes. With regard to climate change mitigation, the removed CO₂ can be compressed for storage. To analyze the competitiveness of different CO₂ capture options and H₂ process alternatives a consistent multi-objective optimization methodology combining energy-flow models with process integration techniques and economic and environmental evaluation is applied. The potential of efficient decarbonization in fossil and renewable H₂ processes is highlighted.

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Keywords: Hydrogen; CO₂ capture; Thermo-environomic modeling; Multi-objective optimization; Process integration

1. Introduction

Today, concerns about fossil fuel resources depletion, energy supply security and greenhouse gas emissions are growing. In this context, hydrogen is considered as one promising clean, reliable and affordable energy vector allowing CO₂ capture and/or penetration of renewable energy resources. Many technologies are available for hydrogen production from fossil and renewable resources. In order to reduce the CO₂ emissions, CO₂ can be captured in the H₂ production process for subsequent storage and sequestration. Common technologies for CO₂ capture and H₂ purification are chemical absorption with amines, physical absorption, adsorption and membrane processes.

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The economic performance of H₂ production from conventional and alternative resources has been assessed in [1]. In addition to the costs, the thermodynamic performance is reported in [4], while in [2, 3] the life cycle impacts are investigated. In most of the H₂ production studies, thermodynamic and engineering, energy integration, economical, and environmental aspects are investigated separately. Here a systematic framework for the comparison and optimization of different H₂ process configurations taking into account simultaneously energetic, economical and environmental considerations is developed. Since CO₂ capture affects the process performance through the thermal and mechanical energy required for CO₂ separation and the related investment, such a methodical platform appears to be useful to analyze and compare such processes whose efficiency and competitiveness highly depends on the quality of the energy integration. In addition, the use of a multi-objective optimization strategy allows studying the influence of the operating and design conditions of the process configurations.

Nomenclature

ATR	Autothermal reforming
BBA	Black box model
BM	Biomass
CC	Carbon capture
E _{imp}	Electricity import
LCA	Life cycle assessment
Self	Self sufficient configuration that do not import or export electricity
SMR	Steam methane reforming
TEA	Triethanolamine
PSA	Pressure swing absorption
POX	Partial oxidation
WGS	Water gas shift
C	Production cost [\$/GJ]
\dot{E}	Mechanical/electrical power [kW] (\dot{E}^+ entering the system, \dot{E}^- leaving the system)
ϵ_{tot}	Energy efficiency [%]
Δh°	Lower heating value [kJ/kg]
\dot{m}	Mass flowrate [kg/s] or [t/y]
\dot{n}	Molar flowrate [mol/s]
η_{CO_2}	CO ₂ capture rate [%]

2. Process Description

In this study, the H_2 production processes that are considered use either natural gas or biomass (BM) as a resource. The main process steps are syngas production, gas cleaning and purification. For each step, different technological options are investigated following the superstructure in Fig. 1. For the natural gas processes, steam methane reforming (SMR) and autothermal reforming (ATR) satisfying the energy demand of the endothermic reforming by partial oxidation are considered. Indirectly heated fluidized bed gasification of wood is considered in the biomass processes. The generated syngas is reacted with water in two subsequent water-gas shift (WGS) reactors, one operating at high (HTS) and one at low (LTS) temperature, in order to increase the H_2 and CO_2 content. During the purification, a CO_2 removal step is designed for CO_2 capture and storage. It is realized by chemical absorption with amines, physical absorption with Rectisol or Selexol, or by membrane processes. The resulting CO_2 is then compressed to 110 bars and dehydrated to feed a CO_2 transportation grid for sequestration. The H_2 is purified further by pressure swing adsorption (PSA). The process electricity demand is satisfied either by importing electricity from the grid (E_{imp}) or by burning part of the H_2 -rich fuel in a gas turbine to close the electricity balance by combined heat and power production (self).

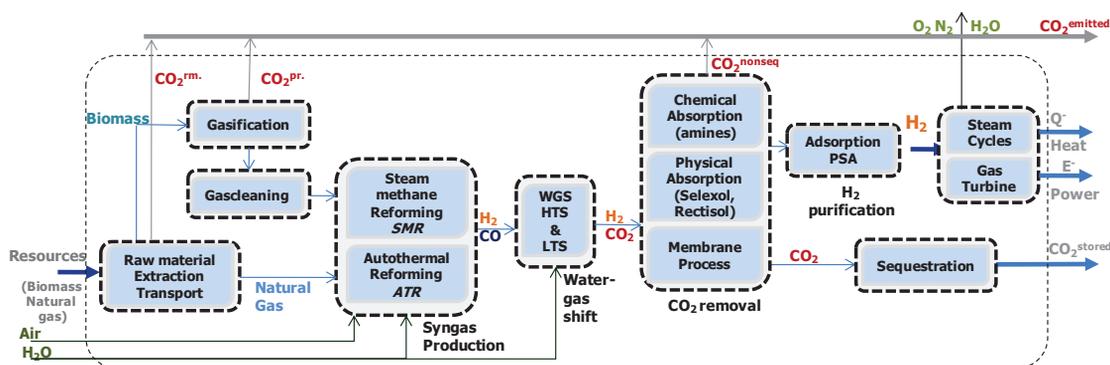


Fig. 1 Process superstructure of H_2 production

3. Methodology: Thermo-environomic modeling and optimization

Following the methodology described in [5] and [6], H_2 processes with CO_2 capture are studied by combining flow sheeting, energy integration techniques, economic evaluation and life cycle assessment (LCA) in a multi-objective optimization framework. The chemical and physical transformations and the associated heat transfer requirements are computed for each process unit of the superstructure (Fig. 1) using commercial flow sheeting software (Belsim-Vali and Aspen Plus). Pinch analysis is applied in the energy integration model to maximize the heat recovery in the process and to maximize the combined H_2 , heat and power production. The optimal process integration is computed by solving the heat cascade model of the process. The process heat transfer requirement is satisfied by taking into account different utilities, including waste and H_2 -rich fuel combustion, steam cycle and gas turbine cogeneration. Based on the flows and operating conditions each equipment is then sized and the costs are estimated according to the approach described in [5]. The environmental impacts are evaluated following the methodology presented in [6]. The trade-off between competing thermo-environomic objectives is assessed by solving

a multi-objective optimization problem that aims at defining the optimal process design and operating conditions and revealing competitive configurations. The optimization applies an evolutionary algorithm which has the advantage of making the approach less sensitive to convergence problems.

3.1 Process modeling

The modeling of the H₂/CO₂ gas mixture production from natural gas or woody biomass resources is based on the models developed in [7] and [8] respectively. For CO₂ capture during the H₂ purification, different technologies options models are developed. In a first study [8] a black box model (*BBA*) has been developed taking into account the thermal and mechanical energy demand and the cost based on average data for the chemical absorption with amines. Detailed models for CO₂ separation by chemical absorption with triethanolamine (TEA) and by physical absorption with Rectisol (i.e. Methanol) and Selexol (i.e. DEPG, mixture of dimethyl ethers and polyethylene glycol) are developed in this study by adapting the models available from AspenTech. The solvent recycling is modeled by imposing design specs. Fig. 2 (left) illustrates the schematic flowdiagram of the absorption processes. The main decision variables are the gas and solvent inlet temperature and pressure, the stripper pressure and temperature, and the solvent mass flowrate and for TEA the amine concentration, the process integration and the column design (number of stages, diameter,...). The membrane process is modeled considering two successive membranes (Fig. 2 right) following the approach of [9] with the data of [10] for a CO₂ selective Pebax membrane. The decision variables are the pressure and the stage cuts.

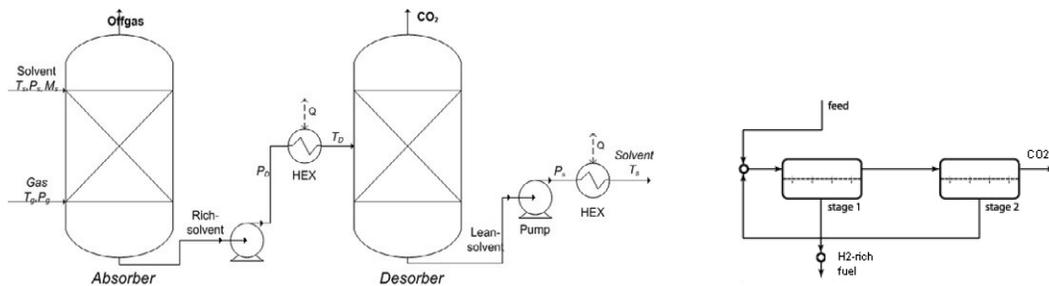


Fig. 2 Schematic absorption process layout (left).

Two-stage countercurrent recycling membrane (right).

4. Process Performance

4.1 Performance Indicators

The different process configurations are compared based on the following performance indicators:

- Energy efficiency:
$$\epsilon_{\text{tot}} = \frac{\Delta h_{\text{H2,out}}^{\circ} \dot{m}_{\text{H2,out}} + \dot{E}^-}{\Delta h_{\text{feed,in}}^{\circ} \dot{m}_{\text{feed,in}} + \dot{E}^+} \quad (1)$$

- CO₂ capture rate:
$$\eta_{\text{CO2}} = \frac{\dot{n}_{\text{CO2,captured}}}{\dot{n}_{\text{C,in}}} 100 \quad (2)$$

$$\bullet \text{ CO}_2 \text{ avoidance cost: } \frac{\$/\text{t}_{\text{CO}_2, \text{avoided}}}{\text{t}_{\text{CO}_2, \text{avoided}}} = \frac{C_{\text{cc}} - C_{\text{ref}}}{\dot{m}_{\text{CO}_2, \text{emit, ref}} - \dot{m}_{\text{CO}_2, \text{emit, cc}}} \quad (3)$$

The first law energy efficiency (Eq.1) is expressed on the lower heating value basis and considers thermal and mechanical energy as being equivalent. The CO₂ mitigation potential is assessed by the CO₂ capture rate (Eq.2) and the CO₂ avoidance cost (Eq.3). No carbon emissions have been accounted for electricity import since green electricity is considered. As a reference H₂ plant without CO₂ capture, the natural gas autothermal reforming process with PSA is considered with the same assumptions and operating conditions as the corresponding configuration with CO₂ capture. Based on the developed models, the results yield an efficiency of 79.4%, CO₂ emissions of 69kg_{CO2}/GJ_{H2}, and production cost of 14.7\$/GJ_{H2}(with 9.7\$/GJ_{NG}), 8.7\$/GJ_{H2} (with 5\$/GJ_{NG}) or 6.2\$/GJ_{H2} (with 3\$/GJ_{NG}) respectively, depending on the natural gas purchase price. The assessed performance is in the range of the one reported in [4] and [11] giving production costs of 6.5-10\$/GJ_{H2} (with 5\$/GJ_{NG}) and 5.2\$/GJ_{H2} (with 3\$/GJ_{NG}) respectively. Small differences with regard to the CO₂ emissions are related to how the electricity import, export or autonomy is accounted for. The electricity cost affects the operating cost, and consequently also the production cost.

In this study, the economic performance is evaluated by the capital investment and the production cost with the economic assumptions given in [7]: Operation: 7500h/y, lifetime 25y, interest rate 6%, resource price: 9.7\$/GJ_{NG}, 13.9\$/GJ_{BM}, 75\$/GJ_e.

4.2 Multi-objective optimization

The objectives are the maximization of the energy efficiency (Eq.1) and the maximization of the CO₂ capture rate (Eq.2). As decision variables, the operating conditions given in [7] are considered together with the ones described for the CO₂ capture technologies. The Pareto optimal frontiers given in Fig. 3 for some process configurations show the trade-off between CO₂ capture, efficiency and cost. CO₂ capture reduces the efficiency and increases the cost due to the energy demand for CO₂ separation and compression to 110bar and the associated cost. To compare the different processes, configurations with around 90% CO₂ capture are selected for the natural gas scenarios and around 65% for the biomass scenarios. Biomass scenarios yield over 20% lower efficiencies due to the presence of oxygen in the fuel which induces a higher energy penalty for the CO₂ separation. By importing electricity from the grid, the efficiency is increased up to 6% compared to self-sufficient configurations due to the larger H₂ yield. The production cost are however increased by 3-6\$/GJ_{H2} due to the electricity purchase at the price of green electricity (75\$/GJ_e). Membrane processes yield lower efficiencies due to the lower H₂ purity. However, these configurations remain to be further optimized following the design approach reported in [9].

With regard to the CO₂ capture technologies, the difference in the overall efficiencies can be explained by the change in the energy integration. The available excess heat is different due to the difference in the energy demand for the CO₂ separation, consequently the cogeneration potential changes. The power balance shown in Fig. 4 (left) illustrates the difference for several process configurations.

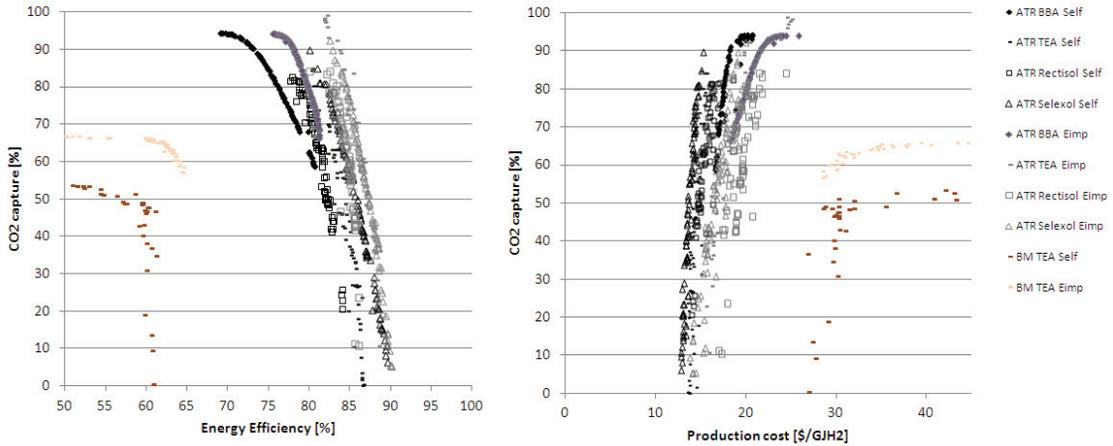


Fig. 3 Trade-off between CO2 capture, energy efficiency and production cost for different H2 process configurations.

For the self-sufficient scenarios, the change of the cogeneration potential translates in differences in the H₂ productivity, since some H₂-rich fuel has to be burnt in order to generate electricity in addition to the steam network to satisfy the process demand as shown in Fig. 4 (left). Due to the lower energy demand for solvent regeneration, the Selexol physical absorption processes yield slightly higher efficiencies for the self-sufficient natural gas scenario.

The changes in the H₂ productivity explain also the difference in the production cost. The production cost build-up in Fig. 4 (right) shows that, the resource purchase contributes to more than two thirds of the production cost. Decreasing the resource price to 5.5\$/GJ_{res} (low) will reduce the cost by 30%, while an increase of the resource price to 20\$/GJ_{res} (high) will lead to up to 60% higher production costs.

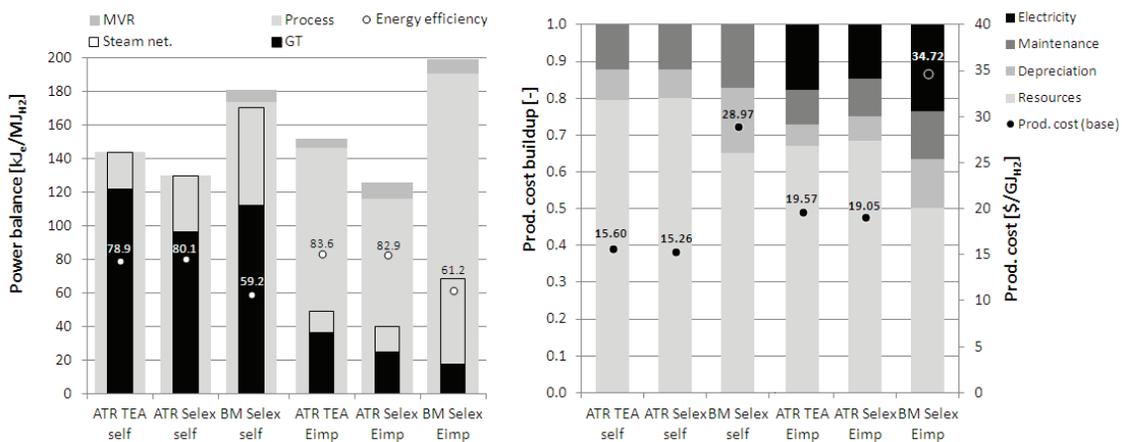


Fig. 4 Power balance (left) and production cost buildup (right) for different H2 process configurations.

The CO₂ mitigation cost is calculated by comparing the optimized processes with the conventional process without CO₂ capture using the same economical conditions and including a carbon tax. Fig. 5 illustrates the competitiveness compared to the process without CO₂ capture (no CC) for two different economic scenarios. Assuming a natural gas price of 9.7\$/GJ_{res} (Fig. 5 left), the electricity importing ATR process with 85% CO₂ capture becomes competitive with a carbon tax of 40\$/t_{CO2} and the self-sufficient one even with a tax around 8\$/t_{CO2}. Due to the increased advantage of capturing biogenic CO₂ emissions, the biomass process becomes also competitive at a carbon tax 40\$/t_{CO2}, even if the capital investment is higher and the efficiency lower compared to the natural gas process. With 45% lower resource prices (5.5\$/GJ_{res}) (Fig. 5 right), the break even carbon tax is 27\$/t_{CO2} for the electricity importing ATR process. Consequently, the carbon tax highly influences the competitiveness. By capturing about 85% of the CO₂, the CO₂ emissions can be reduced up to 8kg_{CO2}/kg_{H2} for the natural gas processes and up to 17kg_{CO2}/kg_{H2} for the biomass scenarios with 65% capture. Considering the biomass emissions as being biogenic, this reveals the environmental advantage of renewable resources fed processes compared to natural gas fed ones.

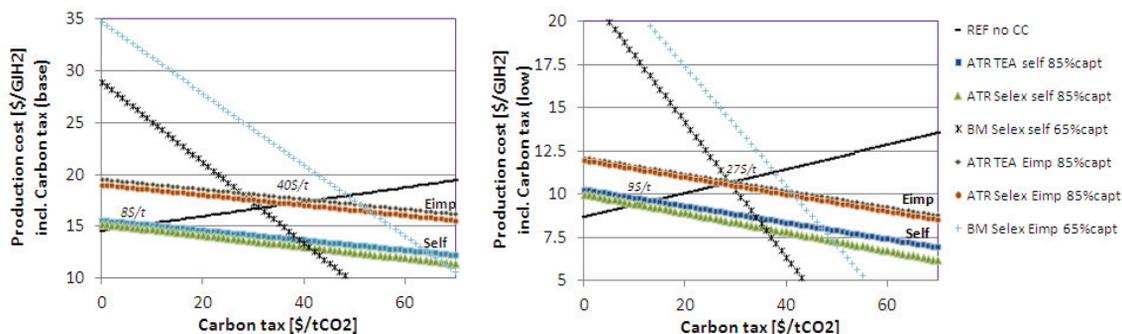


Fig. 5 Influence of the carbon tax and economic assumptions the process performance. Economic scenarios: base (left) 9.7\$/GJ_{NG} /13.9\$/GJ_{BM}, 75\$/GJ_e and low (right) 5.5\$/GJ_{res}, 42\$/GJ_e.

Considering different CO₂ capture rates the influence on the production cost including a carbon tax is illustrated in Fig. 6 for different configurations. Due to the energy demand for CO₂ capture and compression, higher CO₂ capture rates lead to lower efficiencies and higher production cost (Fig. 3). However when a carbon tax is introduced, the additional cost for capturing the CO₂ are compensated by the lower expenses related to the carbon tax due to the lower CO₂ emissions. Depending on the economic assumptions the production cost including a carbon tax might even decrease at high capture rates as shown in Fig. 5. Consequently, the carbon tax and the resource price highly influence the CO₂ capture rate and the technology choice.

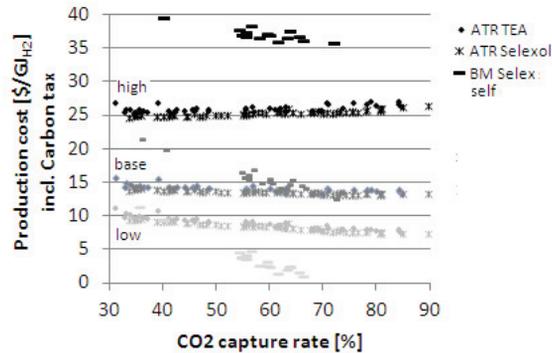


Fig. 6 Influence of the economic assumptions and the CO₂ capture rate on the process performance. Economic scenarios (low/base/high): 5.5/9.7(13.9)/19.5\$/GJ_{res}, 42/75/84\$/GJ_e, 50/35/20\$/t_{CO₂}.

5. Conclusions

The development of a platform for comparing and optimizing H₂ processes with CO₂ capture using fossil and renewable resources is presented. Using a multi-objective optimization, the competitiveness of different H₂ process configurations with CO₂ capture is evaluated with regard to thermodynamic, economic and environmental aspects. It is highlighted how the performance are influenced by the resource price and the carbon tax, and how the efficiency can be increased by optimal process integration. Depending on the resource price, H₂ production costs in the range of 10-43\$/GJ_{H2} are assessed for natural gas processes and of 23-62\$/GJ_{H2} for biomass processes yielding CO₂ avoidance cost in order of 17-270\$/t_{CO₂avoided} and 63-290\$/t_{CO₂avoided} respectively and CO₂ emissions reductions up to 8kg_{CO₂}/kg_{H₂} and 17kg_{CO₂}/kg_{H₂} respectively. Due to the lower energy demand for solvent regeneration, physical absorption processes yield slightly lower efficiency losses for CO₂ separation, however the overall performance is comparable. It is revealed that H₂ production from fossil and renewable resources with CO₂ capture is a competitive alternative. However, no clear decision in favor of one or the other CO₂ capture technology can be made.

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