

Hydrogen production from biogas: Process optimization using ASPEN Plus®

Thanh Son Phan, Doan Pham Minh^{}, Fabienne Espitalier, Ange Nzihou, Didier Grouset*

Université de Toulouse, IMT Mines Albi, UMR CNRS 5302, Centre RAPSODEE, Campus Jarlard, F-81013 Albi Cedex 09, France

A B S T R A C T

This work is part of the VABHYOGAZ (valorization of biogas into hydrogen) program, which targeted the industrial deployment of hydrogen production from biogas in France. To-date, different processes of methane reforming, such as steam reforming of methane (SRM), dry reforming of methane (DRM) and tri-reforming of methane (TRM), have been studied in the literature, but only SRM is applied at industrial scale. Since SRM is an energy-intensive process, a critical analysis of these routes for hydrogen production from biogas is indispensable for process optimization. This has been addressed in this work, by using ASPEN Plus® simulation. Different global processes of hydrogen production from biogas, via DRM, SRM, or TRM, with or without tail gas recycling, have been studied. Among them, hydrogen production using TRM technique (H₂-TRM0.3C process) with a partial recycling of tail gas (30%) was found to be the best option, leading to the highest hydrogen production rate and the best energy yield. H₂-TRM0.3C process was also found to be more efficient than the actual industrial process (H₂-REF), which is based on SRM technique. Under the same conditions, H₂-TRM0.3C process led to a higher H₂ production (8.7% more), a lower total energy consumption (18.6% less), and a lower waste heat generation (15.4% less), in comparison with the actual industrial process (H₂-REF).

Keywords:

Biogas
Hydrogen production
ASPEN Plus®
Catalytic reforming
Process optimization

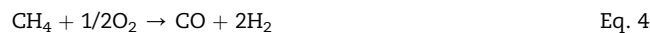
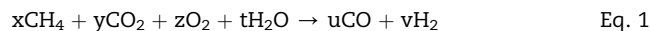
Introduction

To-date, more than 96% of hydrogen are produced from fossil resources such as coal, natural gas, petroleum [1]. To reduce the environmental impact, new alternative solutions, such as water electrolysis, using electricity from renewable resources (e.g. wind energy, solar energy, geothermic energy, biomass etc.), should be developed [2–6]. Nowadays, these routes of hydrogen production have been adapted, in particular in Europe [7], and are deployed at industrial scale [8,9]. Another alternative to produce renewable hydrogen calls for the use of biogas as feedstock instead of natural gas, since both of them mainly contain methane (>80 vol% for natural gas, and up to ca. 70 vol% for biogas) [1,10–12]. This is significant because the global capacity of biogas production continuously increases during the last decades, according to the World Biogas Association [13]. However, research and development are still needed to deploy hydrogen production from biogas at large scale. This was the intent and focus of the VABHYOGAZ (valorization of biogas into hydrogen) program, which was supported by the French “Programme d’Investissements d’Avenir” under supervision of ADEME, the French Energy and Environment Agency [14]. This program included three stages of research and development. The first stage was the study on the technico-economic feasibility (2008–2009). The second stage was the conception (2011–2012) and realization (2012–2014) of a pilot of liquid hydrogen production of 10 kg per day capacity. This pilot is in operation since 2014 [14]. The third stage, called VABHYOGAZ3 project, targeted the development of two units of liquid hydrogen production (at least 100 kg H₂ per day per unit) and three distribution units for hydrogen vehicles, as well as an option for carbon dioxide valorization, using biogas as feedstock [15]. This biogas is produced from a landfill site of one industrial partner of the VABHYOGAZ3 project (also called landfill gas), and contains around 60 vol% CH₄, 40 vol% CO₂ and traces of N₂ and O₂. Our research team (RAPSOEE research center, UMR CNRS 5302, IMT Mines Albi) participated to this VABHYOGAZ program as an academic partner, together with several industrial partners.

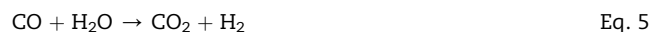
The main units of the pilot of hydrogen production built in 2014 are summarized as below:

- Landfill gas purification. This allows removing impurities present in landfill gas such as H₂S, NH₃, siloxanes etc. This step is crucial before the next catalytic transformations.
- Catalytic reforming of methane at high temperature (909 °C), high pressure (16 bar), and high molar ratio of steam-to-carbon (S/C) equal to 3/1. Taking into account the composition of the biogas used, which contains not only methane and carbon dioxide, but also oxygen, this process is commonly called tri-reforming of methane (TRM, Eq. (1)), which allows converting methane, carbon dioxide, water vapor and oxygen into syngas (mixture of carbon dioxide and hydrogen). In fact, TRM combines steam reforming of

methane (SRM, Eq. (2)), dry reforming of methane (DRM, Eq. (3)), and partial oxidation of methane (POM, Eq. (4)) in one step.



- Catalytic water-gas-shift (WGS) to convert carbon monoxide and water vapor to hydrogen and carbon dioxide. This step is achieved by two reactors: i) high-temperature WGS reactor (HTWGS) using iron and chromium oxides catalyst at 350 °C and 16 bar; and ii) low-temperature WGS reactor (LTWGS) using a copper oxide catalyst at 210 °C and 16 bar.



- Separation of hydrogen from the mixtures recovered from LTWGS reactor, using as pressure-swing adsorption (PSA) process. This gaseous hydrogen, with a high purity of at least 99.9%, is then compressed into liquid hydrogen to feed hydrogen vehicles.
- Burning residual gas (tail gas) from PSA unit to recover heat before releasing flue gas to atmosphere.

These steps also represent current technology of hydrogen production from natural gas via steam reforming (SRM, Eq. (2)). However, SRM is an energy-intensive process because of the large excess of steam (S/C ratio equal to 3/1) used for the reforming step, compared to steam amount really consumed in the steam reforming reaction (Eq. (2)). Syngas from reforming reactor must be cooled down to feed the next exothermic step of WGS. Important heat loss generally takes place during this heat recovery step and makes increasing the final cost of hydrogen as the final product as well as its environmental impact. So, in parallel with the industrial deployment of this technology, a major objective of research and development in the framework of the VABHYOGAZ3 project was to optimize energy yield and hydrogen production from biogas. For this purpose, different methane reforming routes, e.g. DRM and TRM, were investigated using ASPEN Plus® simulation. The impact of the tail gas recycling rate was also studied. These two factors were identified by the partners of the VABHYOGAZ consortium, which can be potentially

modified for the existing industrial technology. For this study, the operation conditions of the industrial pilot were considered as reference. To the best of our knowledge, this approach has never been reported in the literature for hydrogen production from biogas reforming.

Methodology

Simulation method

The thermodynamic equilibrium in a given reactor is generally calculated by using either the equilibrium constant, or the minimization of Gibbs free energy [16–21]. For methane reforming, solid carbon is generally a by-product, which can be an obstacle for the calculation by the equilibrium constant approach [22]. Therefore, the method of Gibbs free energy minimization was applied to this study, using ASPEN Plus® (version 8.6) [23], which allows calculating the temperature and the composition at the equilibrium under well-defined thermodynamic conditions. Taking into account the reforming reactions of methane and the main products, the following components were considered for ASPEN Plus® simulation: Hydrogen (H_2), nitrogen (N_2), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO), water (H_2O), solid carbon and coke (C_s), oxygen (O_2), air (molar ratio $N_2/O_2 = 79/21$). The composition of the purified biogas produced by our industrial partner was used for this simulation study, which is as follows: 59.97 vol% CH_4 , 40.06 vol% CO_2 , 0.2% N_2 and 0.04% O_2 . For these components, the PRMVH2 property method was used as recommended by Carlson [24]. PRMVH2 is based on Peng Robinson – MHV2 equation of state model, which is an extension of Peng – Robinson equation of state [25,26]. In fact, this property method can be used for both non-polar and polar compounds, which is the case of the mixture considered in this work. Moreover, this method can be used for processes working at high temperature and pressure [26]. Other hypotheses used in this study includes:

- For each global hydrogen production process, the same inlet biogas mass flowrate of 38.51 kg h^{-1} was used. The total pressure of 16 bar was kept unchanged during three steps of reforming, WGS and PSA while the combustion was performed at 1 bar. The temperature was also fixed unchanged for reforming (909°C), HTWGS (350°C), LTWGS (210°C) and PSA (38°C) steps. These conditions are provided by our industrial partner, which are applied to their pilot.
- Heat loss is negligible during methane reforming, WGS and combustion of purge gas.
- Reaction time is long enough to reach reaction conversions imposed for each step, which are detailed thereafter.
- Pumps' yield is imposed at 75%.
- Compressors' isentropic efficiency is imposed at 75%.

Hydrogen production processes

To perform ASPEN Plus® simulation, different global hydrogen production processes were defined and considered

in this work. Firstly, we remind that a pilot of hydrogen production of 10 kg day^{-1} capacity was built and experimentally validated during the second stage of the VABHYOGAZ program. On the basis of this pilot, an industrial unit of hydrogen production of 100 kg day^{-1} was dimensioned in the framework of the VABHYOGAZ3 project. This industrial unit is considered as the industrial reference, named thereafter H_2 -REF, which need to be improved. Fig. 1 shows the principal steps of this reference process including:

- Biogas reforming: The reforming reactor is fed by 38.5 kg h^{-1} purified biogas and 46 kg h^{-1} water vapor. Both of them are kept at 909°C and 16 bar. Methane conversion is imposed at 80% which is the value obtained by our industrial partner.
- HTWGS and LTWGS: Syngas from the reforming reactor outlet is cooled down to 350°C (at 16 bar) to feed HTWGS (HTS_WGS unit in Fig. 1). Carbon monoxide conversion is imposed at 75%, which is also the value obtained by our industrial partner. Because of the exothermicity of WGS reaction, the temperature of the mixture at the outlet of HTWGS reaches 457°C at 15.75 bar. This mixture still contains non-negligible amounts of carbon monoxide. It is cooled down to 210°C at 15.70 bar to feed LTWGS (LTS_WGS unit in Fig. 1). Carbon monoxide conversion in this reactor is also imposed at 75%. The temperature of the mixture at the LTWGS reactor outlet reaches 238°C . This mixture is cooled down to 38°C at 15.65 bar to separate water from the gas. The latter is sent to the PSA unit (component splitter).
- PSA separation: This unit allows obtaining hydrogen of high quality (99.99% purity) from the gas mixture. Hydrogen separation yield is imposed at 79%, which is the value obtained by our industrial partner. This hydrogen is compressed to 350–700 bar for injection to hydrogen vehicles. The tail gas (fraction rejected by the PSA unit) contains unreacted CH_4 , CO_2 , residual CO , and H_2 .
- Combustion: The tails gas is mixed with air and preheated to 250°C at 1 bar before being burned. This preheating allows increasing the temperature of the combustion (1651.6°C in the case of this pilot) to improve the combustion efficiency and to valorize any waste heat at moderate and low temperatures [27]. Heat from this combustion is mainly recovered and flue gas is released to the atmosphere at 200°C to avoid any condensation, which is generally applied at the industrial scale.

In this study, the reforming reactor was modeled by using RGibbs module. The reactors of HTWGS, LTWGS and combustion were modeled using RSTOIC module, knowing the stoichiometry of the inlet and outlet mixtures. The PSA is approximately isothermal and does not require any significant heat load. Thus, it was simulated by using a component splitter. Table 1 lists the units and their specification used in this study. Table 2 shows the stream parameters of the H_2 -REF process.

From this reference process (H_2 -REF), other global hydrogen production processes have been considered in this study, as described below. The objective is to optimize hydrogen production by changing methane reforming process

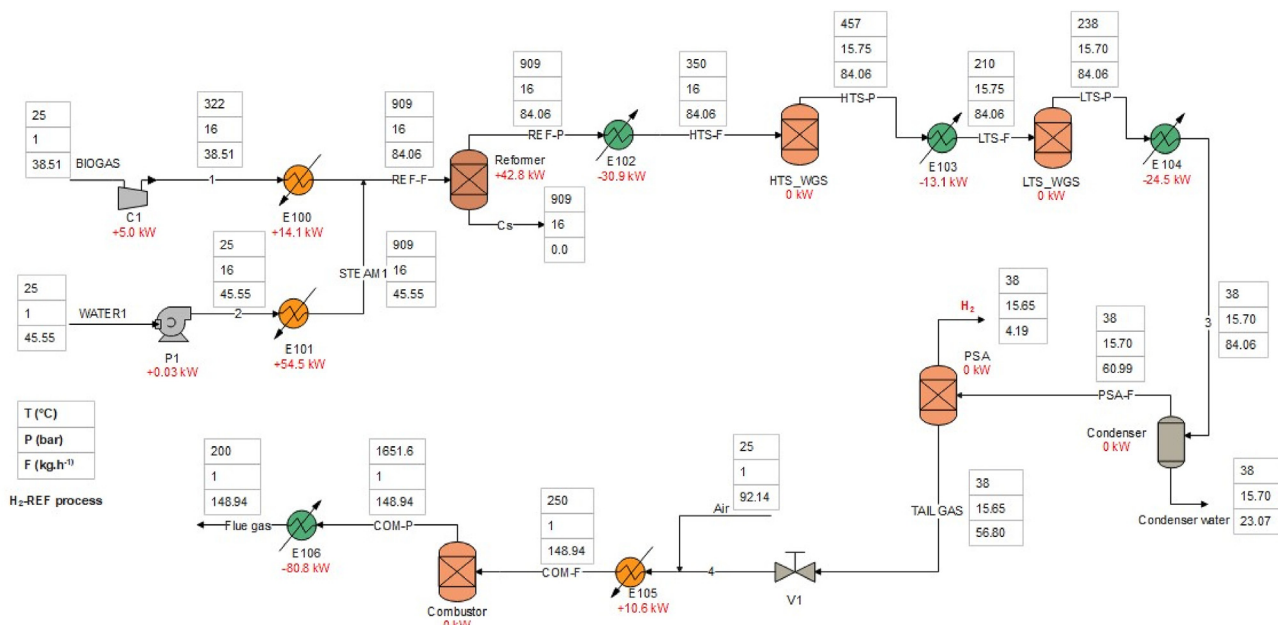


Fig. 1 – Flowsheet of the global hydrogen production process dimensioned by our industrial partner of the VABHYOGAZ3 project with a capacity of 100 kg of H₂ day⁻¹.

Table 1 – Module, function and specification of different units used in ASPEN Plus simulation.			
Unit in ASPEN Plus	Module	Function	Specification
Reformer	RGibbs	To simulate biogas reforming process	Operating temperature: 909 °C Operating pressure: 16 bar
HTS_WGS	RSTOIC	To simulate water-gas shift process	Operating temperature: 350–570 °C Operating pressure: 15.75 bar
LTS_WGS	RSTOIC	To simulate water-gas shift process	Operating temperature: 210–270 °C Operating pressure: 15.70 bar
Condenser	Flash2	To simulate liquid-vapor separation	Operating temperature: 38 °C Operating pressure: 15.65 bar
PSA	Flash2	To simulate H ₂ separation	Operating temperature: 38 °C Operating pressure: 15.65 bar
Combustor	RSTOIC	To simulate combustion process	Operating temperature: 1327–1743 °C Operating pressure: 1 bar
C1 (compressor)	Compr	To simulate stream compression	
P1, P2 (Pump)	Pump	To simulate water pump	
E100 to E108	Heater	To simulate temperature change of stream	
V1	Valve	To simulate pressure change	

Table 2 – Main stream parameters of the H ₂ -REF process.											
Stream	T (°C)	P (bar)	Mass flowrate (kg.h ⁻¹)	Molar flowrate (kmol.h ⁻¹)	Molar composition						
					CH ₄	CO ₂	H ₂ O	N ₂	CO	H ₂	O ₂
BIOGAS	25	1.01	38.51	1.41	59.7	40.06		0.2			0.04
WATER1	25	1.01	45.55	2.53			100				
REF-F	909	16	84.06	3.94	21.39	14.35	64.17	0.07			0.01
REF-P	909	16	84.06	5.29	3.19	9.73	36.05	0.05	13.72	37.26	
HTS-F	350	15.75	84.06	5.29	3.19	9.73	36.05	0.05	13.72	37.26	0
HTS-P	457	15.75	84.06	5.29	3.19	20.01	25.76	0.05	3.43	47.55	
LTS-P	238	15.70	84.06	5.29	3.19	22.59	23.19	0.05	0.86	50.13	
PSA-F	38	15.65	60.99	4.03	4.17	28.88	0.52	0.07	1.11	65.25	
TAIL GAS	38	15.65	56.8	1.95	8.6	59.59	1.08	0.14	2.29	28.28	
H ₂	38	15.65	4.19	2.08						100	
COM-F	250	1.18	148.94	5.13	3.28	22.7	0.41	46.48	0.87	10.78	15.48
FLUE GAS	200	1.16	148.94	4.83		28.52	18.84	49.35			3.29

(DRM or TRM instead of SRM) and by recycling the tail gas generated from PSA unit:

- Global hydrogen production using DRM process, named thereafter H₂-DRM: For that, the reforming reactor is only fed with biogas flux. A new water vapor flux (STEAM2 in Fig. SI 1, supplementary information) is then created to feed HTWGS and LTWGS reactors for WGS reaction. In this case, the purge gas from the PSA unit is also completely burned to recover heat. Details on this process are available in SI. 1 (supplementary information).
- Global hydrogen production using DRM process, with the recycling of 30 wt% of the purge gas recovered from the PSA unit. This process is named thereafter H₂-DRM0.3C. The choice of 30 wt/% of the tail gas to be recycled will be later justified in Section 3.3. The only difference of this process compared to H₂-DRM is the return of 30 wt% of the tail gas to the reforming reactor. The objective is to increase H₂ production since heat recovered from the burning of tail gas could not be totally consumed by the same production process. Details on this process are available in SI. 2 (supplementary information).
- Global hydrogen production using TRM process, named thereafter H₂-TRM. Biogas flux is firstly mixed with oxygen flux before feeding the reforming reactor, together with water vapor flux. Details on this process are available in SI. 3 (supplementary information).
- Global hydrogen production using TRM process, with the recycling of 30 wt% of the tail gas recovered from the PSA unit. This process is named thereafter H₂-TRM0.3C. The choice of 30 wt/% of the tail gas to be recycled will be later justified in Section 3.3. The only difference of this process compared to H₂-TRM is the return of 30 wt% of the tail gas to the reforming reactor. The objective is also to increase H₂ production. Details on this process are available in SI. 4 (supplementary information).

PINCH analysis

PINCH analysis provides a systematic methodology for process energy saving. The methodology is based on thermodynamic principles. An industrial chemical process is generally composed of different units working at different temperatures. Energy saving of each process can be done by recovering heat from hot flux which need to be cooled down to heat cold flux. In PINCH analysis, plotting accumulative enthalpy of cold and hot streams as functions of temperature allows obtaining composite curves of a given process, as illustrated in Fig. 2. Thus, PINCH analysis allows determining the maximum recoverable heat of a process, which is the overlap between its cold and hot streams (Fig. 2) at a given ΔT_{min} [28]. The latter (ΔT_{min} , or Pinch point) is minimum difference of temperature between cold and hot streams (Fig. 2) [29]. The value of ΔT_{min} has to be determined for each process. In the present study, ΔT_{min} was set at 20 °C, according to Peng for the hydrogen production process [30]. PINCH analysis also allows calculating the remaining hot and cold duties, which are

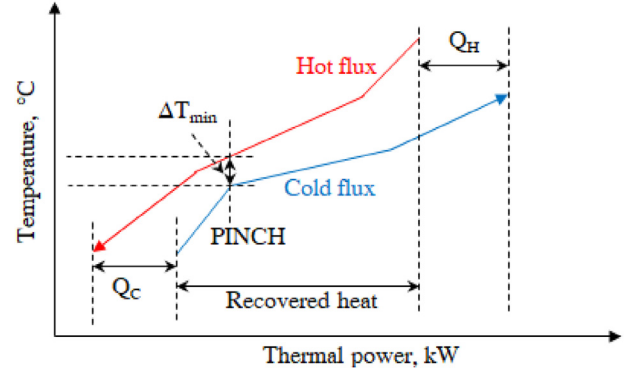


Fig. 2 – PINCH analysis: Illustration of composite curves of a given process.

handled by utility system (Fig. 2) [29]. The hot utility (hot duty, Q_H , kW) represents the external thermal energy required by the process, while the cold utility (cold duty, Q_C , kW) represents the internal thermal energy generated by the process, but cannot be reused by this process itself.

Other definitions

In order to facilitate the comparison of different global hydrogen production processes, the following terms are defined:

- The total energy consumption which corresponds to the energy required for heating and for pumps and compressors: E_{total} , kW
- Thermal power calculated from low heating value, composition and mass flowrate of biogas fed to each process: P_{PCI_biogas} , kW.
- Thermal power calculated from low heating value and mass flowrate of hydrogen produced by each process: $P_{PCI_H_2}$, kW.
- The production of hydrogen of each process: Q_{H_2} , kg h⁻¹.
- The total energy consumption per kg h⁻¹ of hydrogen (E_{H_2}):

$$E_{H_2} = \frac{E_{total}}{Q_{H_2}} \left(\frac{\text{kW} \times \text{h}}{\text{kg}} \right) \quad \text{Eq. 6}$$

- The energetic yield of the global hydrogen production process (η), which is the ratio of the thermal power calculated from produced hydrogen ($P_{PCI_H_2}$) to the sum of the thermal power calculated from biogas fed to the reformer (P_{PCI_biogas}) and the hot duty (Q_{Hot_min}):

$$\eta = \frac{P_{PCI_H_2}/Q_{H_2}}{(P_{PCI_biogas} + Q_{Hot_min})/Q_{H_2}} \times 100 \quad \text{Eq. 7}$$

Results

Determination of water flowrate for WGS step

For the global hydrogen production using DRM or TRM processes, HTWGS and LTWGS reactors need a supplementary water feed (STEAM2 in SI. 1 to SI. 4). It is necessary to calculate the minimum flowrate of STEAM2 for each case. The composition of the syngas at the outlet of the reforming reactor is well known because the conversion of the reforming step is imposed at 80%. Consequently, the relationship between the STEAM2 flowrate and the theoretical conversion in HTWGS and LTWGS reactors could be established. Fig. 3 shows the example in the case of the H₂-DRM process. When STEAM2 flowrate is below 5.9 kg h⁻¹, water vapor is not enough to react with CO, thus, this water vapor is completely consumed by the HTWGS reactor. Consequently, CO conversion in the HTWGS reactor linearly increases with STEAM2 flowrate, while CO conversion in the LTWGS reactor is null. When the STEAM2 flowrate is set at 5.9 kg h⁻¹, CO conversion in the HTWGS reaches 75% which is the value imposed for this reactor in this study. When STEAM2 flowrate is above 5.9 kg h⁻¹, CO conversion in the LTWGS linearly increases, and reaches 75% at the STEAM2 flowrate of 8.4 kg h⁻¹. The latter is the minimum value of STEAM2 flowrate, which allows obtaining 75% of CO conversion in both HTWGS and LTWGS reactors for the H₂-DRM process. By the same method, the minimum STEAM2 flowrate required to reach 75% of CO conversion in LTWGS reactor is 15.5, 13 and 15 kg h⁻¹, for H₂-DRM0.3C, H₂-TRM and H₂-TRM0.3C processes, respectively.

Determination of the molar ratio of steam to carbon (S/C) and oxygen to carbon (O/C) for the global hydrogen production using TRM

In the global hydrogen production via TRM of biogas (having the CH₄/CO₂ molar ratio equal to 59.97/40.06 in this study), the feeding composition of the reforming reactor can be

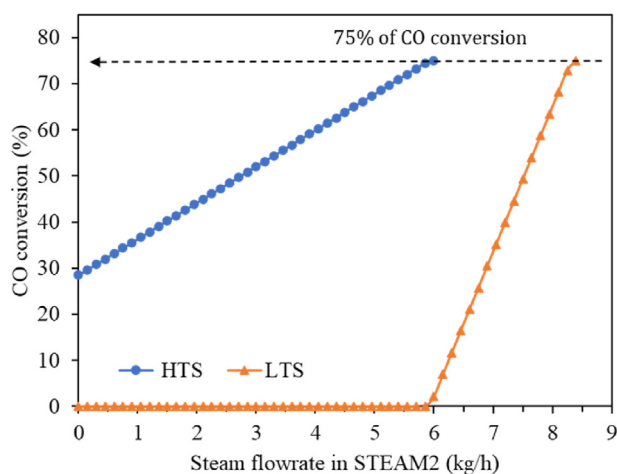


Fig. 3 – CO conversion of the HTWGS (15.75 bar) and LTWGS (15.7 bar) reactors as a function of the STEAM2 flowrate for the H₂-DRM process.

controlled by varying the S/C and O/C molar ratios. This generally affect both Q_{H_2} (kg h⁻¹) and E_{H_2} (kW × h kg⁻¹) and it is necessary to determine the appropriate values of S/C and O/C to maximize Q_{H_2} , and to minimize E_{H_2} . Fig. 4 shows the impact of S/C and O/C molar ratios on Q_{H_2} and E_{H_2} for H₂-TRM process by fixing other parameters (reforming temperature of 909 °C, reforming pressure of 16 bar, STEAM2 flowrate of 13 kg h⁻¹). When the O/C molar ratio increases, both Q_{H_2} and E_{H_2} decreases at the S/C molar ratio of 0.7 and 0.9, but Q_{H_2} increases at the S/C molar ratio of 0.4 and 0.5. At the O/C molar ratio of 0.08, Q_{H_2} is nearly unchanged at the S/C molar ratio of 0.5, 0.7 and 0.9, while E_{H_2} get the lowest value at the S/C molar ratio of 0.4 and 0.5. Consequently, the molar ratios of O/C = 0.08 and S/C = 0.5 have been selected for H₂-TRM process, which are a good compromise between a high Q_{H_2} and low E_{H_2} . Those molar ratios are also selected for H₂-TRM0.3C process for comparison.

Determination of the tail gas recycling rate

The tail gas from the PSA separation unit still contains energetic molecules such as CH₄, CO, H₂. This tail gas can be either burned to produce heat or recycled to produce more H₂. For the latter, it is necessary to determine the tail gas recycling rate (ratio of recycled tail gas flowrate to total tail gas flowrate). Fig. 5 presents the variation of E_{total} and Q_{H_2} as functions of the recycling rate. The increase of the recycling rate leads to an increase in Q_{H_2} . In parallel, E_{total} also increases with the recycling rate, but with a higher slope in comparison with that of Q_{H_2} . The recycling rate at 10 and 50% is not interesting because Q_{H_2} at 10% of recycling rate is much lower than that of the H₂-REF process, while E_{total} at 50% of recycling rate is too high (Fig. 5). The increase of the tail gas recycling rate from 20 to 30%, and from 20 to 40% allows increasing Q_{H_2} by 4.9 and 9.9%, respectively; but in parallel, E_{total} also increases by 1.2 and 3.7%, respectively. In addition, the recycling rate of 40% requires a much higher Q_{Hot_min} (27.7 kW) in comparison with that of the recycling rate of 30% (18.3 kW) (see Table SI 5). Consequently, the recycling rate of 30% appears as a good compromise between Q_{H_2} and E_{total} (and also Q_{Hot_min}). This recycling rate of 30% is also chosen for the H₂-DRM0.3C process, to facilitate the comparison.

Comparison of hydrogen production by different global processes

As mentioned in the Section: Methodology, the operation conditions (e.g. reaction temperature and pressure) of each step of the global processes of hydrogen production are based on the values applied to the industrial pilot described in the Section: Introduction. Also, for ASPEN Plus® simulation, the conversion of reformer, HTWGS and LTWGS reactors as well as the yield of PSA unit are imposed to be equal to the values obtained with the industrial pilot. All these values are the same for different global processes of hydrogen production as shown in Table 3.

For each global process of hydrogen production, the composition of the inlet gas mixture fed to the reforming reactor is calculated from the composition and the flowrate of each fluid. Since the conversion of the reforming reactor is

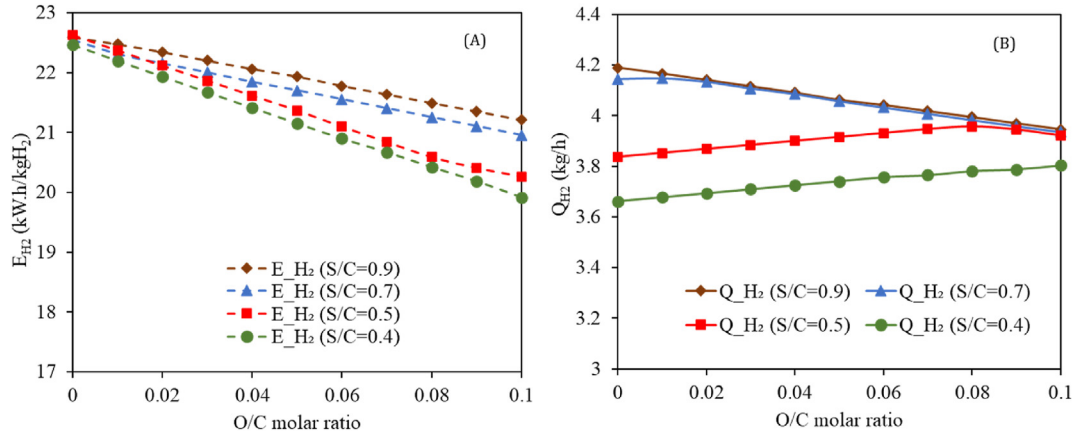


Fig. 4 – Relationship between (A) – the energy consumption to produce 1 kg h⁻¹ of H₂ (E_{H_2}), and (B) – the hydrogen production (Q_{H_2}) as functions of the initial molar ratios of O/C and S/C at 909 °C and 16 bar in H₂-TRM process.

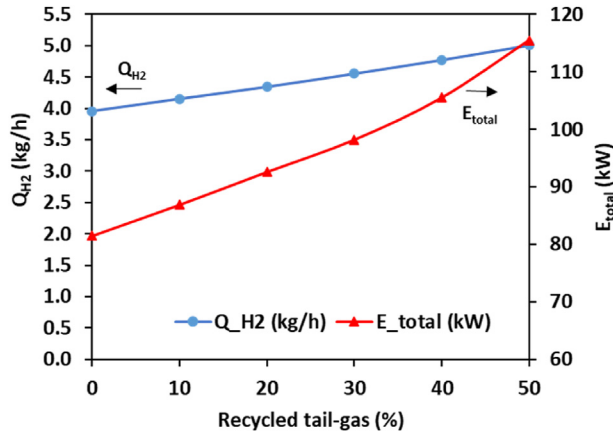


Fig. 5 – Hydrogen production (Q_{H_2}) and total energy consumption (E_{total}) as functions of tail-gas recycling rate.

Table 3 – Summary of operation conditions for each step of the global processes of hydrogen production, as well as the conversion and the yield imposed to these steps.

Unit	Temperature, °C	Pression, bar	Imposed conversion yield, %
Reforming	909	16	80 ^a
HTWGS	350	15.75	75 ^b
LTWGS	210	15.70	75 ^b
PSA	38	15.65	79 ^c

^a CH₄ conversion in the reformer.
^b CO conversion in HTWGS and LTWGS.
^c PSA separation yield.

imposed at 80%, the composition of the gas mixture at the outlet of this reactor could be calculated. By the same way, the composition of the gas mixture at the inlet of the HTWGS, LTWGS and PSA units could also be calculated and is reported in Table 4. First, despite the fact that all the reforming reactors are fed by the same mass flowrate of biogas (38.51 kg h⁻¹, Table 5), the molar composition of methane at the inlet of these reactors is not the same because the biogas is diluted

differently with other gas for each global process. This also impacts the molar composition of other components. Consequently, the molar composition of the gas mixture at the inlet of the next units (e.g. HTWGS, LTWGS and PSA) varies for each global process. For example, the CO concentration at the outlet of HTWGS reactor (or the inlet of the LTWGS reactor) changes from 3.43% for H₂-REF to 7.35% for H₂-DRM0.3C, and reaches less than 2% after LTWGS step. In reality, the CO concentration at the outlet of LTWGS reactor could fall to 0.1–0.3% by using a copper-based catalyst [31]. In all cases, the gas mixture at the outlet of LTWGS is rich in H₂ (58–65%) and CO₂ (28–36%), which is favorable for the PSA separation step.

Table 5 shows the mass flowrate (kg h⁻¹) of each component at the inlet of each unit of the global processes of hydrogen production. The molar flowrate (kmol h⁻¹) of each component at the inlet of each unit of the global processes of hydrogen production is available in SI 6 (supplementary information). When the component is a gas mixture (e.g. biogas, syngas), it counts for the total flowrate taking into account all the molecules present in this gas mixture. We remind that H₂-REF is considered as the reference process because it considers all the conditions applied to the industrial pilot of the VABHYOGAZ3 project. By this process and under the considered conditions, the hydrogen production (Q_{H_2}) reaches 4.19 kg h⁻¹. The hydrogen production obtained by H₂-DRM, H₂-TRM, H₂-DRM0.3C, and H₂-TRM0.3C reaches 2.88, 3.88, 3.90, and 4.56 kg h⁻¹, respectively, or 68.8, 94.4, 92.5, and 108.7% in comparison with the value of the reference process (4.19 kg h⁻¹). Thus, only H₂-TRM0.3C leads to a higher hydrogen production (Q_{H_2}) than that of the reference process.

Fig. 6 compares the formation rate of solid carbon (stream S5 of reforming units) by each global process of hydrogen production. As expected, H₂-REF, with a large steam excess, allows theoretically avoiding solid carbon formation. This is similar for H₂-TRM and H₂-TRM0.3C processes since steam, oxygen and carbon dioxide are used to convert methane into syngas. On the other hand, H₂-DRM and H₂-DRM0.3C are not thermodynamically favorable for limiting solid carbon formation, as already reported in the literature by several authors for DRM [32–36]. This means the global process of hydrogen production integrating DRM step can potentially

Table 4 – Molar composition of the mixtures at the inlet of each unit of the global processes of hydrogen production; all the molecules are considered at the gaseous state.

Unit	Compound	Molar composition (%) at the inlet of the units				
		H ₂ -REF	H ₂ -DRM	H ₂ -TRM	H ₂ -DRM0.3C	H ₂ -TRM0.3C
Reforming	CH ₄	21.39	59.70	44.35	43.50	33.31
	CO ₂	14.35	40.06	29.76	47.47	40.47
	H ₂ O	64.17	0.00	22.17	0.27	15.79
	O ₂	0.01	0.04	3.58	0.03	2.59
HTWGS	CH ₄	3.19	6.01	4.38	4.38	3.65
	CO ₂	9.73	3.99	4.16	6.10	8.64
	H ₂ O	36.05	23.80	25.92	28.01	27.26
	CO	13.72	25.21	27.59	29.40	28.81
LTWGS	H ₂	37.26	40.90	37.88	32.00	31.44
	CH ₄	3.19	6.01	4.38	4.38	3.65
	CO ₂	20.01	22.89	24.85	28.15	30.25
	H ₂ O	25.76	4.89	5.22	5.96	5.65
PSA	CO	3.43	6.30	6.90	7.35	7.20
	H ₂	47.55	59.80	58.58	54.05	53.05
	CH ₄	4.17	6.01	4.38	4.38	3.65
	CO ₂	28.88	27.62	30.02	33.66	35.65
Combustion	H ₂ O	0.52	0.16	0.05	0.45	0.24
	CO	1.11	1.58	1.72	1.84	1.80
	H ₂	65.25	64.53	63.75	59.57	58.45
	CH ₄	3.28	4.09	3.34	2.63	2.34
Recycling part of the tail-gas	CO ₂	22.70	18.80	22.88	20.18	22.80
	H ₂ O	0.41	0.11	0.04	0.27	0.16
	O ₂ (air)	15.48	18.52	15.52	17.07	16.49
	N ₂ (air)	46.48	48.70	46.37	51.26	49.14
Recycling part of the tail-gas	CO	0.87	1.07	1.31	1.10	1.15
	H ₂	10.78	9.23	10.21	7.50	7.86
	CH ₄	0	0	0	8.28	6.79
	CO ₂	0	0	0	63.58	66.23
Recycling part of the tail-gas	H ₂ O	0	0	0	0.85	0.45
	CO	0	0	0	3.47	3.35
	H ₂	0	0	0	23.63	22.81

Table 5 – Mass flowrate of components at the inlet of each unit of the global processes of hydrogen production.

Unit	Component	Mass flowrate at the inlet of the units (kg h ⁻¹)				
		H ₂ -REF	H ₂ -DRM	H ₂ -TRM	H ₂ -DRM0.3C	H ₂ -TRM0.3C
Reforming	Biogas	38.51	38.51	38.51	38.51	38.51
	H ₂ O, (STEAM1)	45.55	0.00	7.59	0.00	7.59
	H ₂ O from recycling of tail gas	0.00	0.00	0.00	0.10	0.06
	O ₂	0.02	0.02	2.18	0.00	2.23
	Tail gas	0.00	0.00	0.00	20.11	25.16
HTWGS	Syngas	84.06	33.46	48.26	55.42	73.42
	H ₂ O, (STEAM2)	0.00	8.40	13.00	15.50	15.00
	H ₂ O from reforming and STEAM2	34.35	12.03	18.20	20.63	24.04
LTWGS	Syngas	84.06	41.86	61.26	70.92	88.42
PSA	Products of LTWGS	84.06	41.86	61.26	61.26	88.42
Q _{H2}	kg h ⁻¹	4.19	2.88	3.96	3.88	4.56
	In comparison with Q _{H2} obtained by H ₂ -REF (%)	100.0	68.8	94.4	92.5	108.7

quickly be clogged by solid carbon accumulation in the catalyst bed of the reforming reactor. The recycling of 30% of the tail gas in the case of H₂-RDM0.3C process only allows reducing, but not avoiding, the formation rate of solid carbon.

Analysis of energy consumption

Hydrogen production from biogas includes different steps as described in the introduction section. For each global

process, the energy needs under the form of both heat and electricity for different units were determined and presented in Table 6. As expected, methane reforming is strongly endothermic, leading to a high thermal consumption inside the reforming reactor (component ⑤, Table 6). Biogas heating (component ②, Table 6), tail gas and air heating (component ⑧, Table 6), and steam generation (components ④ and ⑦, Table 6) also need high thermal energy consumption. Particularly, for H₂-REF process working at high S/C ratio of 3/

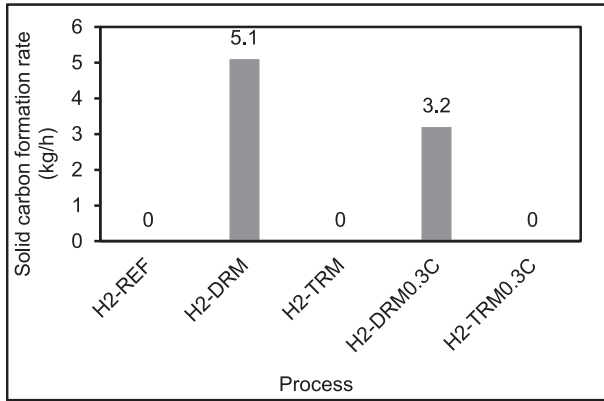


Fig. 6 – Solid carbon formation rate calculated for different processes of hydrogen production.

1, large thermal energy amount is needed to generate steam for the reforming step. Thus, this process has the highest E_{total} amount, followed by H₂-TRM0.3C, H₂-DRM0.3C, H₂-TRM, and H₂-DRM.

Since the global processes of hydrogen production are composed of different steps, operating at different temperatures, it is possible to recover heat when fluids are cooled down to desired temperatures. Table 7 summarizes the recoverable energy from different steps of these processes. The reference process (H₂-REF) requiring a high S/C ratio of 3/1, this causes a much higher value of heat released by cooling the syngas from reformer outlet, in comparison with that of other processes. The reference process also presents the highest recoverable heat from the HTWGS reactor outlet and from the combustion of tail gas. Thus, the total recoverable heat is highest for the reference process (149.4 kW), followed by H₂-TRM0.3C (115.7 kW), H₂-TRM (120.7 kW), H₂-DRM0.3C (100.9 kW), and H₂-DRM (96.9 kW). The flue gas released to the atmosphere at 200 °C (conventional temperature applied in the industrial sector to avoid eventual condensation in chimney) also represents a non-negligible waste heat amount, accounting for 13.3–17.5 kW.

Table 7 – Recoverable energy in the global processes of hydrogen production studied.

Entry	H ₂ -REF	H ₂ -DRM	H ₂ -TRM	H ₂ -DRM0.3C	H ₂ -TRM0.3C
① Cooling of the syngas from the reformer outlet, kW	30.9	12.9	17.3	17.9	22.9
② Cooling of the syngas from the HTWGS outlet, kW	13.1	9.4	13.9	15.2	18.1
③ Cooling of the syngas from the LTWGS outlet, kW	24.5	6.0	8.5	9.2	11.0
④ Heat from tail gas combustion, kW	80.8	68.6	81.0	58.5	63.7
⑤ Total recoverable heat, kW	149.4	96.9	120.7	100.9	115.7
⑤ = ① + ② + ③ + ④					
Waste heat under the form of flue gas, kW	17.5	13.9	16.9	13.3	14.8

Results of PINCH analysis

From the data in Tables 6 and 7, cold and hot composite curves could be established for each global process of hydrogen production, using PINCH analysis according to the hypotheses mentioned in Section 2.3. It is worth to note that the electrical energy required for pumps, compressors and for process control did not be considered in PINCH analysis. Fig. 7 and Table 8 shows the results obtained. For H₂-REF process (Fig. 7 A), the thermal energy consumption (cold composite curve) is mostly covered by the hot flux (heat recovery = 121.8 kW, see Table 8). The heating duty (Q_H), which is the minimum amount of external heating, is negligible (0.3 kW, Table 8), while the cooling duty (Q_C), which is the minimum amount of external cooling, represents a large amount of 27.6 kW. Even this thermal energy can be recovered by cooling, it cannot be reused by the same process. This large amount of Q_C is explained by the fact that H₂-REF process consumes large amount of thermal energy to heat the feed mixture with the S/C ratio equal to 3/1

Table 6 – Energy needs of different units of the global processes of hydrogen production studied. For E_{total} , electricity consumption of the PSA unit and for process control were not considered (which are supposed to be similar for all these processes).

Component	H ₂ -REF	H ₂ -DRM	H ₂ -TRM	H ₂ -DRM0.3C	H ₂ -TRM0.3C
① Biogas compressor (electricity), kW	5.0	5.0	5.3	5.0	5.3
② Biogas heating for reforming reaction, kW	14.1	14.1	14.4	14.1	14.4
③ WATER1 pump (electricity), kW	0.03	0.00	0.005	0.000	0.005
④ Heating and evaporation of water to produce STEAM1, kW	54.5	0.0	9.1	0.0	9.1
⑤ Endothermal reaction of methane reforming, kW	42.8	31.1	36.6	42.0	42.4
⑥ WATER2 pump (electricity), kW	0.0	0.005	0.009	0.010	0.011
⑦ Heating and evaporation of water to produce STEAM2, kW	0	7.1	11.0	13.1	12.7
⑧ Heating of tail gas and air to feed combustion unit, kW	10.6	8.3	10.4	9.7	10.9
⑨ Heating of tail gas for recycling, kW	0	0	0	7.1	8.7
⑩ Total thermal energy consumption, kW	122.1	60.6	81.5	86.0	98.2
⑩ = ② + ④ + ⑤ + ⑦ + ⑧ + ⑨					
⑪ Total energy consumption (E_{total}), kW	127.1	65.7	86.8	91.1	103.4
⑪ = ① + ③ + ⑥ + ⑩					

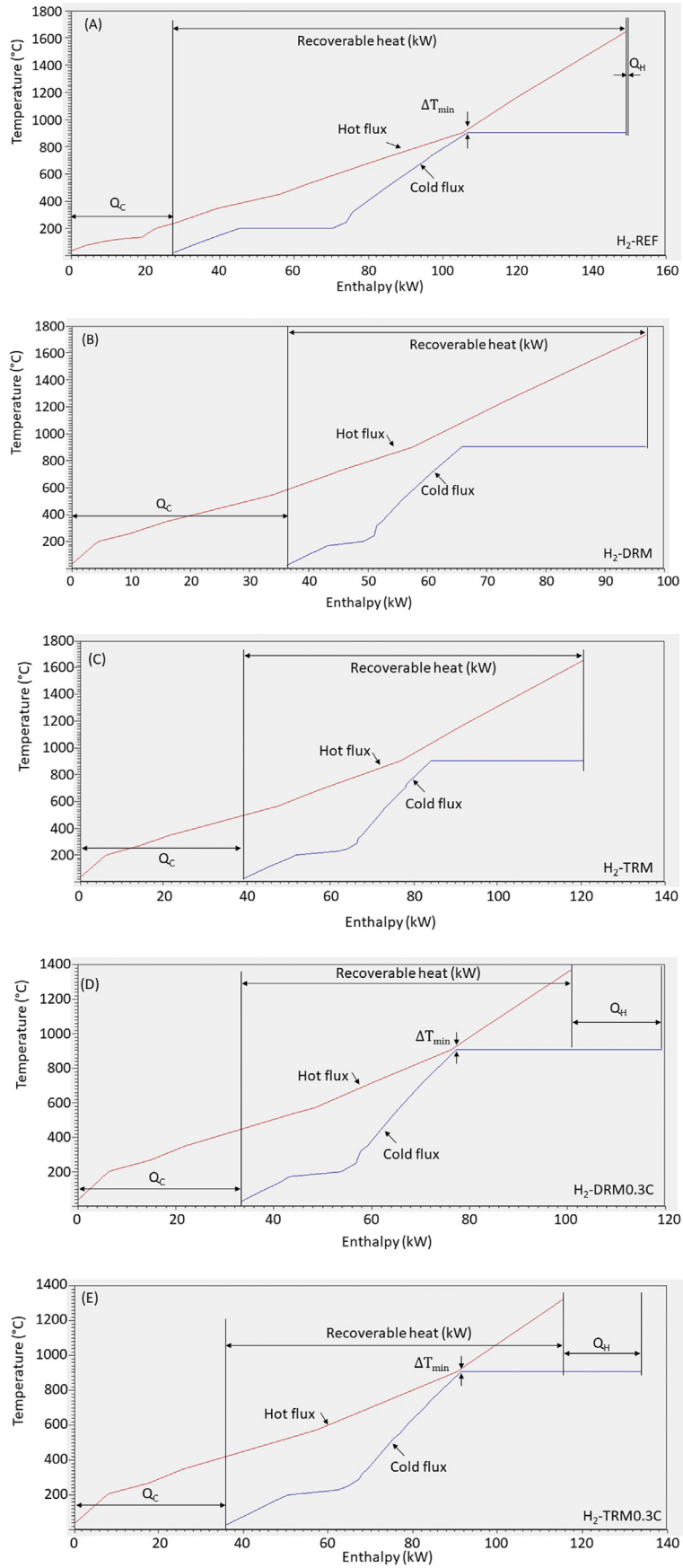


Fig. 7 – Composite curves of the studied processes: (A) H₂-REF; (B) H₂-DRM; (C) H₂-TRM; (D) H₂-DRM0.3C; (E) H₂-TRM0.3C; Q_h : Heating duty; Q_c : Cooling duty.

Table 8 – Synthesis of PINCH analysis and energetic yield of the global hydrogen production processes.

Entry	H ₂ -REF	H ₂ -DRM	H ₂ -TRM	H ₂ -DRM0.3C	H ₂ -TRM0.3C
① Total cold flux, kW	122.1	60.6	81.5	86.0	98.2
② Total hot flux, kW	149.4	96.9	120.7	100.9	115.7
③ Total recoverable heat by PINCH analysis, kW	121.8	60.6	81.5	67.6	79.8
④ Q _H , kW (④ = ①–③)	0.3	0	0	18.5	18.4
⑤ Q _C , kW	27.6	36.3	39.2	33.3	35.8
⑥ P _{PCI_biogas} , kW	187.9	187.9	187.9	187.9	187.9
⑦ P _{PCI_H₂} , kW	139.6	96.0	131.8	129.2	151.8
⑧ η (energy yield of the global hydrogen production process, %)	74.2	51.1	70.1	62.6	73.6
⑧ = ⑦ \times 100/(⑥ + ④)					

up to 909 °C for the reforming step. Then, this steam is only partially consumed by the reforming reaction, and generates heat when the unconsumed part is cooled down to lower temperature (350 °C) of downstream process (HTWGS).

For H₂-DRM process, which does not need steam for the reforming step, and for H₂-TRM process, which consumes much less steam for the reforming step than that for H₂-REF process, the consumption of the thermal energy is much lower than that of H₂-REF. Also, both H₂-DRM and H₂-TRM processes represent the case of a threshold, which only requires a hot or cold utility. For each of these processes, the recovered heat is enough for the need of the process itself. Thus, there is no PINCH point and these processes do not need hot utility (Q_H null). However, the cooling duty of these processes is relatively high: 36.3 kW for H₂-DRM and 39.2 kW for H₂-TRM (see Table 8).

For H₂-DRM0.3C and H₂-TRM0.3C processes, because 30% of tail gas are reinjected in the reforming unit for recycling, the flowrate of the tail gas, which is sent to the combustion unit, decreases. Thus, the recovered heat from the combustion unit decreases. Moreover, the tail gas recycled to the reforming unit must be preheated (see Table 6), and the reforming reaction of this tail gas also consumes heat because of the endothermicity of this reaction. Thus, the heating duty of these processes are relatively high, which reaches 18.5 and 18.4 kW for H₂-DRM0.3C and H₂-TRM0.3C, respectively. Despite those needs in thermal energy, these processes also generate high amounts of cooling duty (33.3 kW for H₂-DRM0.3C and 35.8 kW H₂-TRM0.3C). In fact, the temperature of the thermal energy corresponding to the cold unit is not enough high to be used in hot unit.

Table 8 summarizes the main parameters of the PINCH analysis (entry ① to ⑧), the thermal power (P_{PCI_biogas}) calculated from low heating value, composition and mass flowrate of biogas fed to each process, the thermal power (P_{PCI-H₂}) calculated from low heating value and mass flowrate of hydrogen produced by each process, and the energy yield (η) of the global hydrogen production process. By considering the values of the energy yield, we can see that three process H₂-DRM, H₂-TRM, and H₂-DRM0.3C, are not competitive in comparison with the reference process (H₂-REF). Particularly, both H₂-DRM and H₂-DRM0.3C processes had much lower energy

yield in comparison to the reference one. This must be a serious challenge of DRM-based processes in view of eventual industrial deployment. About H₂-TRM process, its energy yield is not so far from that of the reference process (Table 8), but its hydrogen mass flowrate produced (Q_{H₂}, Table 5) is smaller than that of the reference process. So, H₂-TRM process is also less competitive than the reference one. On the other hand, H₂-TRM0.3C process has the similar energy yield (Table 8), but a higher Q_{H₂} (Table 5), in comparison with those of H₂-REF process. Thus, in view of hydrogen production and energy efficiency, H₂-TRM0.3C is the best process among the investigated systems. This process allows producing more H₂ (8.7%) than the industrial process, by keeping the same energy yield.

Conclusions

Hydrogen is gaining momentum in the energy mix of the near future society. However, hydrogen is still principally produced from fossil resources such as natural gas. To contribute to the effort against the global warming, it is crucial to increase the share of hydrogen produced from renewable resources. However, in order to be economically viable, global process of hydrogen production from renewable resources, such as biogas, must be optimized. To-date, some first industrial demonstration operations, such as the case of the VABHYOGAZ3 project, have been launched, but they are still based on the conventional SRM process, which is energetically not optimized.

On the basis of the experimental data obtained with the pilot unit in the framework of the VABHYOGAZ3 project, and using ASPEN Plus® simulation, a comparative study has been done for global processes of hydrogen production from biogas via different methane reforming routes, e.g. DRM and TRM, with and without recycling of tail gas. The main conclusions are as follows:

- The recycling of the tail gas to the reforming unit allows increasing hydrogen production. In the range of the tail gas recycling rate of 10–50%, the optimal recycling rate is found at 30%, taking into consideration the hydrogen production rate and the energy yield of the global process.
- The hydrogen production via DRM, with or without tail gas recycling, is not competitive in comparison with the actual industrial process using SRM.
- The hydrogen production via TRM is only more efficient than the actual industrial process if the tail gas is partially recycled (30% in this study).

Future work should be conducted with the industrial pilot under the optimized conditions to validate the results of this simulation study. The design of an active, selective, and stable catalyst should also be performed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Declaration of permission

Permission from ASPEN Technology, Inc. for the use of the data obtained by using ASPEN Plus® software is available. AspenTech is ownership of intellectual property rights.

Acknowledgement

This work is a part of the VABHYOGAZ3 project supported by the French “Programme d’Investissements d’Avenir” under supervision of ADEME, the French Energy and Environment Agency. The authors are grateful towards the ADEME for their support to this project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2022.01.100>.

REFERENCES

- [1] Pham Minh D, Siang TS, N. Vo DV, Phan TS, Ridart C, Nzihou A, Grouset D. Hydrogen production from biogas reforming: an overview of steam reforming, dry reforming, dual reforming, and tri-reforming of methane. In: Azzaro-Pantel C, editor. Hydrogen supply chains. Academic Press; 2018. p. 111–66.
- [2] Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. *Int J Hydrogen Energy* 2015;40:11094–111.
- [3] Tanksale A, Beltrami JN, Lu GQM. A review of catalytic hydrogen production processes from biomass. *Renew Sustain Energy Rev* 2010;14:166–82.
- [4] Wang M, Wang G, Sun Z, Zhang Y, Xu D. Review of renewable energy-based hydrogen production processes for sustainable energy innovation. *Glob Ener Interconnect* 2019;2:43–4.
- [5] Dincer I. Green methods for hydrogen production. *Int J Hydrogen Energy* 2012;37:1954–71.
- [6] El-Emam RS, Ozcan H. Comprehensive review on the techno-economics of sustainable large-scale clean hydrogen production. *J Clean Prod* 2019;220:593–609.
- [7] European Commission. A hydrogen strategy for a climate-neutral Europe. Brussels, 8.7.2020 COM(2020) 301 final. 2021. https://ec.europa.eu/energy/sites/ener/files/hydrogen_strategy.pdf. [Accessed 19 August 2021].
- [8] LeRoy RL. Industrial water electrolysis: present and future. *Int J Hydrogen Energy* 1983;8(6):401–7.
- [9] Grigoriev SA, Fateev VN, Bessarabov DG, Millet P. Current status, research trends, and challenges in water electrolysis science and technology. *Int J Hydrogen Energy* 2020;45(49):26036–58.
- [10] IEA bioenergy, Task 37 - energy from biogas and landfill gas. 2009.
- [11] Mameri A, Tabet F. Numerical investigation of counter-flow diffusion flame of biogas–hydrogen blends: effects of biogas composition, hydrogen enrichment and scalar dissipation rate on flame structure and emissions. *Int J Hydrogen Energy* 2016;41:2011–22.
- [12] Ahmed S, Lee SHD, Ferrandon MS. Catalytic steam reforming of biogas – effects of feed composition and operating conditions. *Int J Hydrogen Energy* 2015;40(2):1005–15.
- [13] Jain S, Newman D, Nzihou A, Dekker H, Le Feuvre P, Richter H, Gobe F, Morton C, Thompson R. Global potential of biogas. World Biogas Association; 2019.
- [14] ADEME: VABHYOGAZ. <https://www.ademe.fr/sites/default/files/assets/documents/hydrogene-piles-atelier3.pdf>. [Accessed 1 February 2022].
- [15] ADEME. VABHYOGAZ3 - valorisation du Biogaz en Hydrogène. <https://bibliothèque.ademe.fr/recherche-et-innovation/1895-vabhyogaz3.html>. [Accessed 19 August 2021].
- [16] Jarunthammachote S, Dutta A. Thermodynamic equilibrium model and second law analysis of a downdraft waste gasifier. *Energy* 2007;32:1660–9.
- [17] Nikoo MK, Amin NAS. Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation. *Fuel Process Technol* 2011;92(3):678–91.
- [18] Chen WH, Lin MR, Lu JJ, Chao Y, Leu TS. Thermodynamic analysis of hydrogen production from methane via autothermal reforming and partial oxidation followed by water gas shift reaction. *Int J Hydrogen Energy* 2010;35(21):11787–97.
- [19] Rahbari A, Ramdin M, van den Broeke, Jlp Vlugt, Jth. Combined steam reforming of methane and formic acid to produce syngas with an adjustable H₂:CO ratio. *Ind Eng Chem Res* 2018;57(31):10663–74.
- [20] Jarunthammachote S, Dutta A. Equilibrium modeling of gasification: Gibbs free energy minimization approach and its application to spouted bed and spout-fluid bed gasifiers. *Energy Convers Manag* 2008;49(6):1345–56.
- [21] Jafarbegloo M, Tarlani A, Mesbah AW, Sahebdehfar S. Thermodynamic analysis of carbon dioxide reforming of methane and its practical relevance. *Int J Hydrogen Energy* 2015;40(6):2445–51.
- [22] Chan SH, Wang HM. Effect of natural gas composition on autothermal fuel reforming products. *Fuel Process Technol* 2000;64(1–3):221–39.
- [23] Aspen Technology Inc.. <http://www.aspentech.com/>. [Accessed 19 August 2021].
- [24] Carlson. Don't gamble with physical properties for simulations. *Chem Eng Prog* 1996;35–46.
- [25] Posada A, Manousiouthakis V. Heat and power integration of methane reforming based hydrogen production. *Ind Eng Chem Res* 2005;44:9113–9.
- [26] ASPEN physical property system – physical property methods and models 11.1. ASPEN Technology Inc.; 2001.
- [27] Grover BS. PSA tail gas preheating. US: United States Patent; 2012. 8,187,363 B2.
- [28] Nemet A, Klemeš JJ, Varbanov PS, Mantelli V. Heat Integration retrofit analysis-an oil refinery case study by Retrofit Tracing Grid Diagram. *Front Chem Sci Eng* 2015;9(2):163–82.
- [29] Kemp IC. Pinch analysis and process integration: a user guide on process integration for the efficient use of energy. 2nd ed. Amsterdam, Boston: Butterworth-Heinemann; 2007.
- [30] Peng XD. Analysis of the thermal efficiency limit of the steam methane reforming process. *Ind Eng Chem Res* 2012;51(50):16385–92.

- [31] Pal DB, Chand R, Upadhyay SN, Mishra PK. Performance of water gas shift reaction catalysts: a review. *Renew Sustain Energy Rev* 2018;93:549–65.
- [32] Wang Z, Cao XM, Zhu J, Hu P. Activity and coke formation of nickel and nickel carbide in dry reforming: a deactivation scheme from density functional theory. *J Catal* 2014;311:469–80.
- [33] Ginsburg JM, Piña J, El Solh T, de Lasa HI. Coke formation over a nickel catalyst under methane dry reforming conditions: thermodynamic and kinetic models. *Ind Eng Chem Res* 2005;44(14):4846–54.
- [34] Muraza O, Galadima A. A review on coke management during dry reforming of methane. *Int J Energy Res* 2015;39(9):1196–216.
- [35] Rego De Vasconcelos B, Zhao L, Sharrock P, Nzihou A, Pham Minh D. Catalytic transformation of carbon dioxide and methane into syngas over ruthenium and platinum supported hydroxyapatites. *Appl Surf Sci* 2016;390:141–56.
- [36] Rego de Vasconcelos B, Pham Minh B, Lyczko N, Phan TS, Sharrock P, Nzihou A. Upgrading greenhouse gases (methane and carbon dioxide) into syngas using nickel-based catalysts. *Fuel* 2018;226:195–203.