

INVESTIGATING MEMBRANE MATERIALS FOR SUSTAINABLE HYDROGEN PRODUCTION FROM BIOMASS FOR USE IN THE ENERGY SECTOR

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Rezumat. Studiul explorează potențialul materialelor membranare în producția de hidrogen sustenabil din biomasă, concentrându-se pe utilizarea acestuia în sectorul energetic. Prin integrarea tehnologiilor avansate de membrană, se vizează optimizarea proceselor de conversie a biomasei în hidrogen, fără emisii de CO₂. Analiza se concentrează pe caracteristicile de selectivitate și permeabilitate ale diferitelor membrane, evaluând eficiența și sustenabilitatea procesului. Utilizarea hidrogenului rezultat în sectorul energetic poate contribui la reducerea dependenței de sursele de energie fosile și la promovarea unei economii mai curate și mai durabile.

Abstract. The study explores the potential of membrane materials in sustainable hydrogen production from biomass, focusing on their utilization in the energy sector. Integrating advanced membrane technologies aims to optimize biomass conversion processes into hydrogen without CO₂ emissions. The analysis focuses on the selectivity and permeability characteristics of different membranes, evaluating the efficiency and sustainability of the process. Using resulting hydrogen in the energy sector can reduce dependence on fossil energy sources and promote a cleaner, more sustainable economy.

Keywords: Hydrogen; Membrane; BECCS; Biomass; CO₂ capture

1. Introduction

Hydrogen has a significant potential as an energy vector in transitioning to a low-carbon, renewable energy economy. The main reasons why hydrogen is seen as a viable option in this respect include its energy storage capacity, its versatility in use (from fuel cell vehicles to energy storage and electricity generation), and the fact that it can be produced from renewable sources such as wind, solar or biomass. In addition, hydrogen has a high potential to reduce carbon dioxide emissions in the sectors where it is used, helping to combat climate change.

Developing efficient hydrogen separation technologies is essential to facilitate its use as an energy source. Currently, the most common method of hydrogen

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production involves steam methane reforming (SMR), which produces hydrogen together with carbon monoxide as a by-product. To use the produced hydrogen in specific applications, it is essential to efficiently separate it from other gases resulting from the production processes [1-3].

One promising method for hydrogen separation is the use of semi-permeable membranes. This technology is based on the selective diffusion of hydrogen through a membrane while other gas components are retained or passed elsewhere. The basic principle is that hydrogen molecules are small enough to diffuse through the pores of the membranes while other larger or heavier molecules are blocked.

Compared to other hydrogen separation methods, such as adsorption, cryogenic distillation, or chemical processes, membrane technology offers several advantages. A significant advantage of membrane hydrogen separation is energy efficiency. The process requires less energy than other techniques, such as cryogenic distillation, which involves very low temperatures and high energy consumption. Membrane technology is also considered a more environmentally friendly method, not involving toxic chemicals or massive energy consumption [4].

Another essential feature of membrane technology is its ability to operate on a small or large scale, allowing it to be deployed in various applications, from industrial production to portable hydrogen generation systems. Membrane technology can also be efficiently integrated into existing process flows, facilitating its use in the energy and clean technology industries.

In conclusion, hydrogen is a crucial energy carrier in the transition to a low-carbon economy, and efficient hydrogen separation technologies, especially membrane-based ones, play a pivotal role in its development and deployment in various applications. The advantages of membrane-based technology over other separation methods highlight the potential of this technology to facilitate the use of hydrogen as a sustainable and clean energy source in the future.

2. Hydrogen production technologies - development of membrane technologies

Hydrogen production is essential as a renewable and clean energy source. Several methods are used to produce hydrogen, each with specific advantages and disadvantages depending on cost, efficiency, and environmental impact. The main techniques used to produce hydrogen are described below:

- a. Steam methane reforming is the most common industrial method of producing hydrogen. This method involves the chemical reaction of methane (CH_4) with steam (H_2O) to produce hydrogen (H_2) and carbon
-

- monoxide (CO). The reaction occurs at high temperatures and pressures, using catalysts to facilitate the reaction. SMR uses fossil fuels such as natural gas or oil as feedstock.
- b. Electrolysis of water is a method of hydrogen production that uses electricity to split water into hydrogen and oxygen. This reaction takes place in an electrochemical cell, where water undergoes electrolytic decomposition. The process can be powered by renewable energy (e.g., from solar or wind sources), making water electrolysis a potential method of producing green hydrogen.
 - c. Photolysis is a method that uses sunlight to split water into hydrogen and oxygen. This technique relies on using photochemical catalysts to absorb light and facilitate the molecular decomposition of water into hydrogen and oxygen. Photolysis is a promising approach to sustainable hydrogen production because it uses direct solar energy.
 - d. Some phototrophic bacteria can produce hydrogen by anaerobic photosynthesis. These organisms use sunlight to break down organic substances or inorganic compounds, generating hydrogen as a by-product. The method involves using microorganisms as biocatalysts and has the potential for sustainable hydrogen production from biological sources.
 - e. The membrane's hydrogen separation process is based on the different permeability properties of gases through semi-permeable membranes. This process uses selective hydrogen diffusion through membranes to separate hydrogen from other gases such as methane, carbon dioxide, or carbon monoxide.

Semi-permeable membranes allow hydrogen to pass through while blocking other gases based on differences in the molecular sizes and diffusion rates of these gases. Hydrogen, the smallest and lightest gas, diffuses through the membrane faster than more significant gases. The performance of a membrane in separating hydrogen is determined by two main characteristics: permeability and selectivity. Permeability is the ability of the membrane to allow hydrogen to pass through. The higher the permeability, the more hydrogen can pass through the membrane in a given time. Selectivity is the ability of the membrane to separate hydrogen from other gases. A membrane selective for hydrogen will effectively block other gases, such as methane or carbon dioxide, allowing only hydrogen to pass through [5].

There are different types of membranes available for gas separation. Polymeric membranes are the most common and affordable type of membrane used for hydrogen separation. They are made of organic polymers and are defined by good hydrogen selectivity. Metallic membranes are made of metallic materials to resist

high temperatures and pressures. They are used for industrial applications under extreme conditions. Ceramic membranes are composed of inert ceramic materials known for their durability and chemical resistance. Ceramic membranes are ideal for hydrogen separation at high temperatures. Key factors influencing a membrane's performance in hydrogen separation include selectivity, permeability, pressure and temperature resistance, durability, and manufacturing cost.

An essential element in the production and use of hydrogen is the efficient separation of pure hydrogen from gas mixtures resulting from production processes. Integrating hydrogen separation technologies with energy production methods can optimise processes and reduce hydrogen separation and purification costs.

Hydrogen separation technologies, such as semi-permeable membranes, adsorption, and distillation, can be integrated into hydrogen production process streams to achieve purified and high-quality hydrogen. For example, using semi-permeable membranes in an SMR plant can efficiently separate hydrogen from carbon monoxide and other waste gases, producing a pure hydrogen stream.

Integrating hydrogen separation technologies with production methods can also help improve overall process efficiency and reduce energy consumption. Significant savings can be achieved by implementing integrated systems combining hydrogen production and separation.

3. Description of methodology and materials used

The mathematical equations describing the physical principle of operation of polymer membranes in hydrogen separation are shown below. Gas diffusion in polymer membranes is described by Fick's law, which represents the transition of the mass flow of a gas through the membrane corresponding to a concentration gradient of that gas. Therefore, the mass flux of hydrogen (J_{H_2}) passing through the membrane can be expressed by the diffusion equation (1).

$$J_{H_2} = D_{H_2} \cdot \frac{\partial c_{H_2}}{\partial x} \quad (2)$$

Where: J_{H_2} – represents the mass flow of hydrogen through the material studied, in kg/m²/s; D_{H_2} – represents the diffusion coefficient of hydrogen in the studied material, in m²/s; c_{H_2} – represents the concentration of hydrogen in the membrane, in kg/m³; x – the direction of travel of the gas stream in the membrane.

Henry's law can describe hydrogen concentration in the membrane as a function of Henry's constant, (H_{H_2}), and partial pressure of hydrogen in the gas, (p_{H_2}).

$$c_{H_2} = H_{H_2} \cdot p_{H_2} \quad (2)$$

The general equation for diffusion in porous or inhomogeneous media (equation 3) describes the variation over time of the hydrogen concentration in the membrane.

$$\frac{\partial c_{H_2}}{\partial t} = \frac{1}{r} \cdot \frac{\partial}{\partial r} \left(D_{H_2ef} \cdot r \cdot \frac{\partial c_{H_2}}{\partial r} \right) \quad (3)$$

Where: t – represents the time; r – is the radial coordinate of the membrane; D_{H_2ef} – is the effective diffusion coefficient of hydrogen in the membrane.

Initial data on syngas composition and operating conditions of the gasification process, including flow rates, pressures, and temperatures, are presented in Table 1.

Table 6. Initial syngas data

No.	Parameter	UM	Value
1	Biomass flow rate	kg/h	2850
2	Air flow rate	kg/h	4 572.69
3	Gasification temperature	°C	900
4	Syngas flow rate	kg/h	7 422.64
5	ER report	-	0.25
6	Syngas composition		
7	H ₂ O	vol.%	3.79443
8	H ₂	vol.%	22.62315
9	CH ₄	vol.%	0.006981
10	CO	vol.%	31.49516
11	CO ₂	vol.%	4.0383
12	O ₂	vol.%	0
13	N	vol.%	38.042
14	H ₂ S	vol.%	0

Table 2 shows the properties (permeability and selectivity) of the material used to make the membrane investigated in this study.

To determine the performance of the hydrogen production process, the following indicators have been defined based on equations 4-9.

Table 2. MTR membrane properties [6]

No.	Material type	Parameter	Value
1	Proteus™ (MTR)	H ₂ permeance, GPU	300
2		H ₂ /CO ₂ selectivity	15
3		H ₂ /CO selectivity	75
4		H ₂ /N ₂ selectivity	150

H₂ separation efficiency was calculated (H_2^{ef}) using relation 4.

$$H_2^{ef} = \frac{H_{2,p}}{H_{2,syn}} \cdot 100, [\%] \quad (4)$$

$H_{2,p}$ – molar concentration of H₂ in the permeate, in mol H₂;

$H_{2,syn}$ – molar concentration of H₂ from syngas, in mol H₂.

Total electric power, (P_{el}), is the sum of the electrical powers installed in the equipment (P_s – thermal steam generator; P_{kc} – electrical power of the compressor for syngas compression; P_{vp} – electrical power of the vacuum pump; P_{kt} – the electrical power of the compressor for compressing the permeate for transport according to equation 5.

$$P_{el} = P_s + P_{kc} + P_{vp} + P_{kt}, [kW] \quad (5)$$

Total specific energy consumption, (C_{sp}), is the ratio of electrical power required, (P_{el}) in kW, and permeate flow, (B_p), in kg/h, according to equation 6.

$$C_{sp} = \frac{3,6 \cdot P_{el}}{B_p}, \left[\frac{MJ}{kg} \right] \quad (6)$$

The specific energy consumption required for the capture process, (C_{cap}), is determined as the ratio of the electrical power required for the capture process (includes only the equipment P_{kc} - electrical power of the syngas compressor; P_{vp} - electrical power of the vacuum pump, both in kW) to the permeate flow rate, (B_p) in kg/h, according to equation 7.

$$C_{cap} = \frac{3,6 \cdot (P_{kc} + P_{vp})}{B_p}, \left[\frac{MJ}{kg} \right] \quad (7)$$

To determine the specific energy consumption for H₂ capture, C_{H_2} , the total electrical power required for the capture process (P_{el}), related to the H₂ flow rate in the permeate (B_{H_2}), in kg/h, is taken into account according to equation 8.

$$C_{H_2} = \frac{3,6 \cdot P_{el}}{B_{H_2}}, \left[\frac{MJ}{kg} \right] \quad (8)$$

For the evaluation of hydrogen purity in the permeate stream ($H_{2,purity}$), relation 9 was used, which considers the specific parameters of the separation process and the synthesis gas composition, thus providing essential information for process control and optimization.

$$H_{2,purity} = \frac{H_{2,mol}}{B_{permeat}} \cdot 100, [\%] \quad (9)$$

Where: $H_{2,mol}$ – is the molar flow rate of H₂ in the permeate stream, in kmol/h;
 $B_{permeat}$ – is the permeate flow rate, in kmol/h.

The range of parameters analyzed in this study is presented in Table 3. In this study, two different scenarios were analysed. The first scenario involved the use of a single step for hydrogen separation. In the second scenario, two serialized steps were used for hydrogen separation. Both scenarios involved the use of a compressor station ($P_{K1}; P_{K2}$) and a vacuum pump ($P_{VP1}; P_{VP2}$). In the first scenario, only the compressor station (case a) or the simultaneous use of the compressor station and the vacuum pump (case b) were considered. In the second scenario, the compressor pressure before the first stage was kept constant at 4 bar, while the vacuum pump pressure was supposed to be 0.5 and 1 bar, respectively.

Table 3. Range of variation of the analysed parameters

<i>Parameters</i>	<i>U.M.</i>	<i>Values</i>
First stage		
Compression pressure (P_{K1})	bar	1.5; 2; 3; 4
Vacuum pump pressure (P_{VP1})	bar	0.5; 0.7; 1
Transport required pressure	bar	700
Transport required temperature	°C	300
H ₂ permeance	GPU	300
Steam flow for WGS reactor	kg/h	1 500
H ₂ capture efficiency	%	90
Second stage		
Compression pressure (P_{K2})	bar	2; 3; 4
Vacuum pressure (P_{VP2})	bar	0.5; 1

4. Results and discussions

4.1. Establishment of the operating parameters of the gasification process

Figure 1 shows the evolution of hydrogen concentration for different fluxes as a function of steam flow rates injected into the conversion reactor (WGS). This study considered a variation of the injected steam flow rate between 500 and 10 000 kg/h. Thus, the extent to which the steam flow rate influences the syngas composition and, more specifically, the value of the H₂ volume concentration was studied. For example, for a steam flow rate of 10 000 kg/h, the conversion result showed a negative heat output, suggesting that the energy required to produce steam exceeded the heat output of the syngas generated. This observation highlights an inefficient scenario, underlining the need to adjust process parameters to ensure efficiency and sustainability.

Thus, our initial conclusion is that changes in steam flow rates significantly influence the performance of the conversion process, and identifying optimal flow rates is crucial to achieving satisfactory thermal efficiency. These results underline the importance of further studies to optimise this process to reduce energy consumption and maximise efficiency. In conclusion, the gasification

regime analysed below is defined by a steam flow rate of 1 500 kg/h, for which an H₂ concentration of at least 30% and a lower heating value of about 6 000 kJ/kg were obtained (Figure 2).

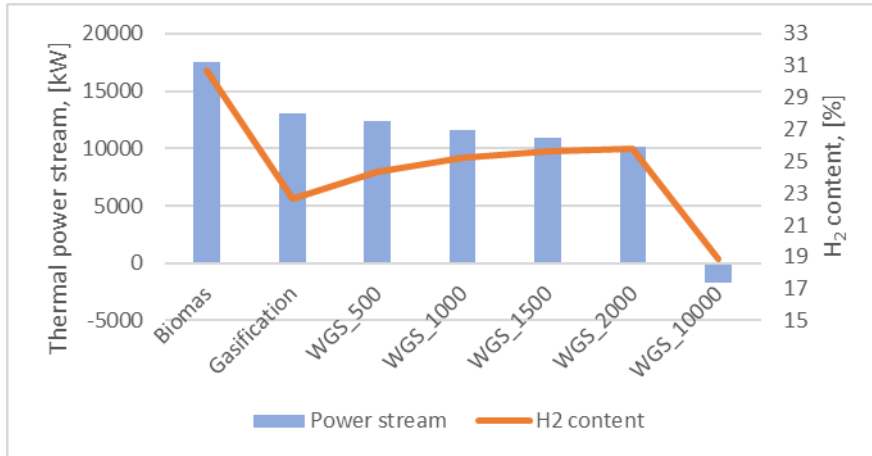


Fig. 1. Thermal power of different streams and H₂ content variation

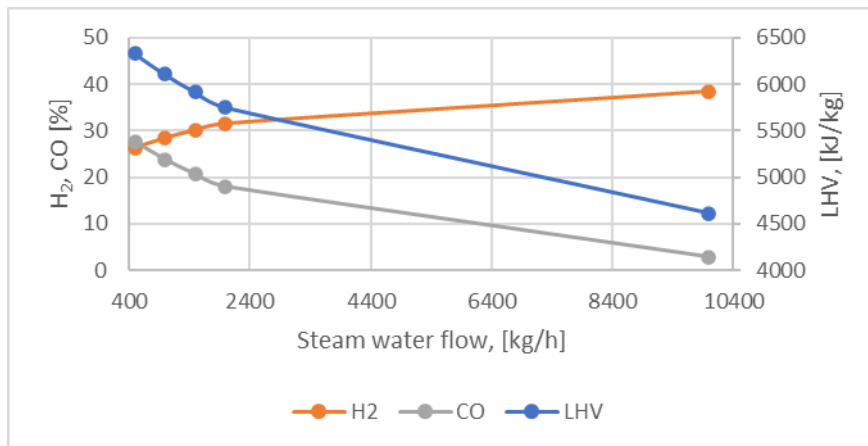


Fig. 2. CO, H₂, LHV variation according to steam water flow

4.2. Influence of compressor operating parameters on membrane module performance

The first phase studied how increasing compressor pressure influences the membrane's performance and surface area size. It can be seen in Figure 3 that as the compressor pressure rises, the membrane surface area decreases due to the higher permeability of the membrane in hydrogen separation; this is true regardless of the gasification regime under consideration. Increasing the flow rate of steam injected into the gasification reactor favored reducing the membrane surface area due to higher hydrogen concentration in the syngas.

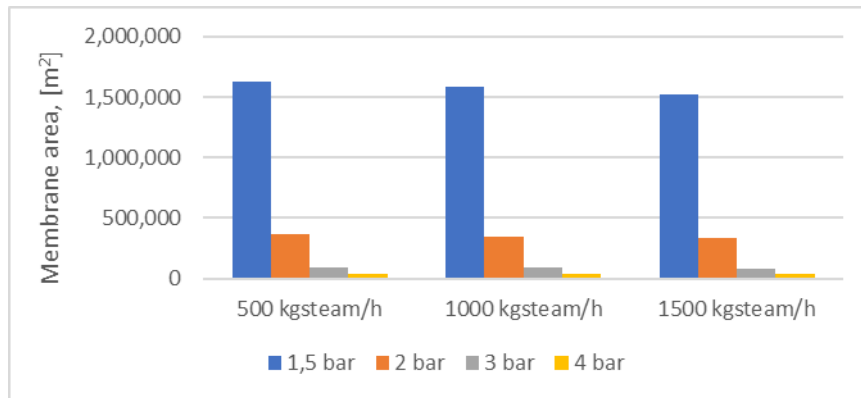


Fig. 3. Compressor pressure influence on membrane area

Table 4 shows the performance of the membrane module as a function of compressor pressure. The efficiency for each case analysed was considered to be 90%. The most crucial parameter analysed is the H₂ purity in the permeate. It is observed that H₂ purity rises as compressor pressure increases due to the decrease in membrane surface area required to reach 90% efficiency.

Table 4. Membrane module performances according to different compressor pressure

Steam flow: 1 500 kg/h	UM	Syngas compressor pressure, [bar]			
		1.5	2	3	4
Membrane area	m ²	1 525 000	338 000	83 400	36 650
Total power consumption	kW	5 515.9	4 984.8	4 580.9	4 459.6
Specific total energy consumption	MJ/kg	4.15	5.02	6.71	8.33
Specific capture energy consumption	MJ/kg	0.09	0.30	0.78	1.31
Purity	vol %	39.92	48.06	58.93	65.78
Specific H ₂ energy consumption	MJ/kg	102.89	92.90	85.39	83.16

The total specific energy consumption varied between 4-8 MJ/kg considering the total energy consumption of the equipment used and between 0.09-1.31 MJ/kg considering only the equipment specific to the H₂.

4.3. Influence of vacuum pump parameters on membrane permeances

Only one case was studied for integrating the vacuum pump, and that was to provide a pressure of 0.5 bar for the permeate. Thus, considering the same analysis indicators and 90% capture efficiency, it was observed that the H₂ purity in the permeate increased by about 19% compared to the variant without a vacuum pump for the same syngas pressure. Adding the vacuum pump and maintaining the same syngas pressure (4 bar) increased the driving force, reducing

about 64% of the membrane surface area but increasing about 74% of the specific energy consumption. Table 5 shows the values obtained for the performance indicators considering the same variation of syngas pressure.

Table 5. Membrane module performances according to different compressor pressure

<i>Vacuum pressure: 0.5 bar</i>	<i>UM</i>	<i>Syngas compressor pressure, [bar]</i>			
		<i>1.5</i>	<i>2</i>	<i>3</i>	<i>4</i>
Membrane area	m ²	137 500	64 000	24 450	13 300
Total power consumption	kW	4 849.5	4 687.1	4 652.8	4 672.2
Specific total energy consumption	MJ/kg	7.34	8.99	12.03	14.52
Specific capture energy consumption	MJ/kg	0.37	0.77	1.62	2.47
Purity	vol %	59.91	66.55	74.18	78.35
Specific H ₂ energy consumption	MJ/kg	90.39	87.36	86.73	87.15

4.4. Integration of two-stage H₂ separation

The performance of the membrane system consisting of 2 separation steps was analysed considering the same indicators above. To simplify the analysis, the pressure of the first compressor was taken as 4 bar, and the pressure of the vacuum pump belonging to the second membrane module as 0.5 bar. The pressure of the second compressor varied between 2 and 4 bar, and the pressure of the vacuum pump belonging to the first membrane module was 0.5 and 1 bar.

Therefore, the results obtained for the two scenarios (two-stage and single-stage) were compared regarding H₂ purity in the permeate (Figure 4). It can be seen that the H₂ purity is over 90% for $P_{VP2} = 1$ bar and over 95% for $P_{VP2} = 0.5$ bar. Figure 5 shows the specific energy consumption for the two scenarios analysed.

However, a high energy consumption is required to achieve the desired purity, which is about six times higher than in the first scenario. An economic calculation is needed to choose the optimal variant.

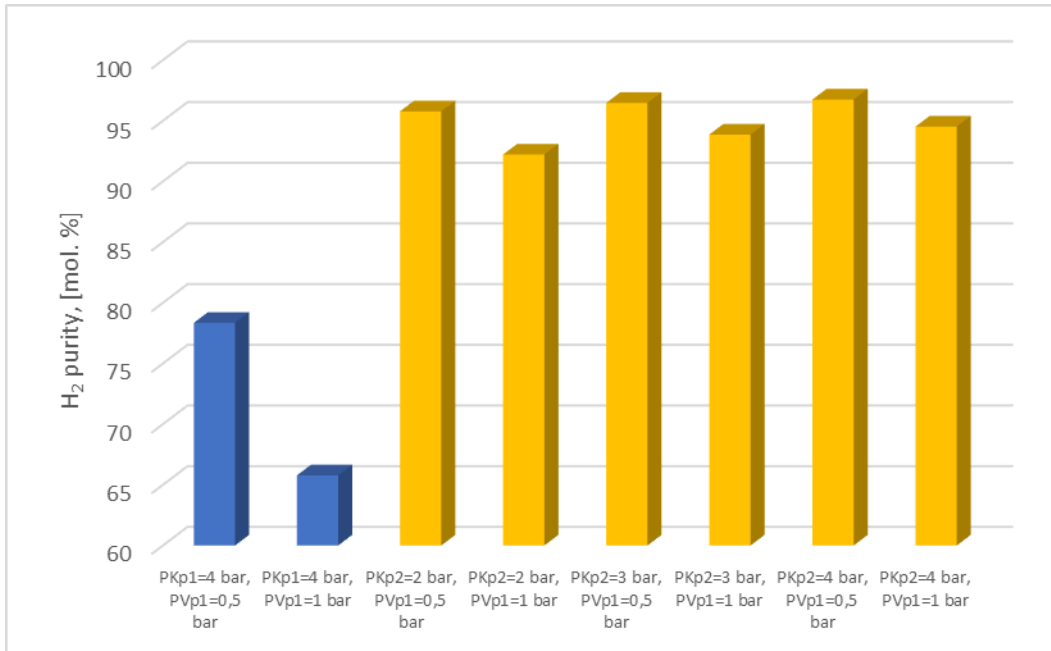


Fig. 4. Comparison between 2 scenarios according to H₂ purity (bleu – one stage yellow – two stages) for different process parameters

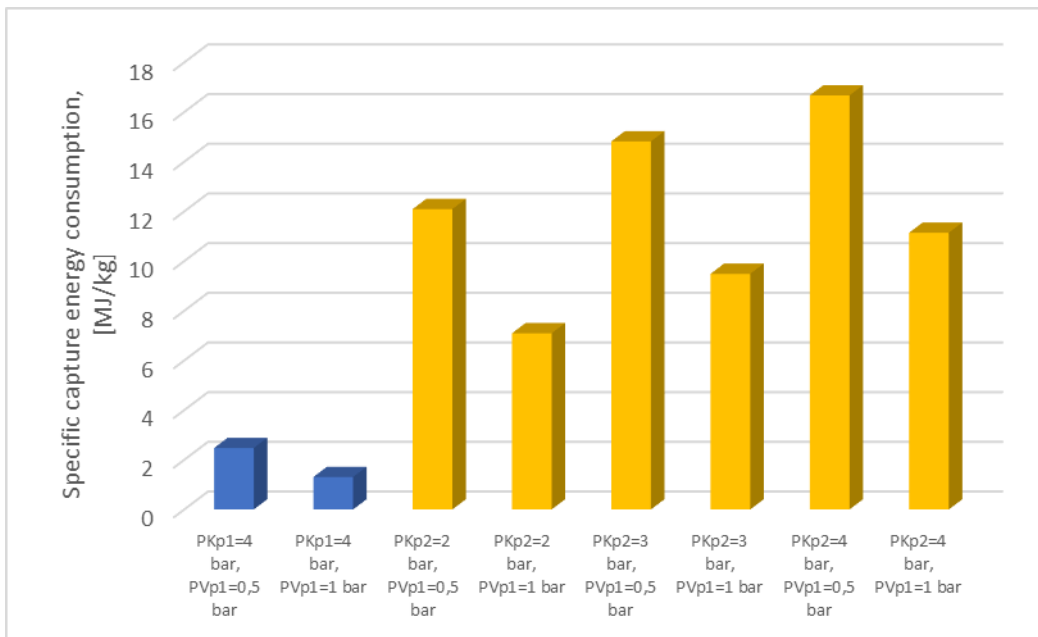


Fig. 5. Comparison between 2 scenarios according to specific energy consumption (bleu – one stage yellow – two stages) for different process parameters

5. Conclusion

Comparing the two scenarios of hydrogen separation from syngas, using a single membrane in the first scenario and two inserted membranes in the second scenario, several important conclusions were drawn from the analysis of the integration of compressor and vacuum pump, with impact on membrane surface area, specific energy consumption, and hydrogen purity.

In both cases studied, the separation efficiency was constant at 90%. However, it was found that to achieve hydrogen purity above 90% in the permeate, it is necessary to integrate two separation steps, i.e., the use of two inert membranes. This significantly increased specific energy consumption in the 12-14 MJ/kg range.

In conclusion, although using two-stage separation can improve hydrogen purity, it comes at a significant cost regarding specific energy consumption. Therefore, optimisation of the separation process remains essential to balance separation efficiency and energy consumption in high-purity hydrogen production.

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