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Membrane-and-Cryogenic-Assisted Hydrogen Separation and Purification Process

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ABSTRACT

Hydrogen (H_2) is a clean energy carrier that has the potential to reduce carbon emissions. Currently, H_2 is being produced from fossil fuels. The major drawback of fossil-based H_2 production is the production of CO_2 and other impurities along with it. H_2 rich syngas has gained attention recently. In syngas, H_2 is the main component along with carbon dioxide, carbon monoxide, and nitrogen. To separate and purify H_2, the pressure swing adsorption (PSA) method is adopted. PSA can produce high purity H_2 but with low recovery. In this study, membrane and cryogenic distillation-based separation methods are analyzed and evaluated for the separation and purification of H_2 from syngas. The cryogenic process achieved high H_2 purity (99.999%) with high recovery (99.999%), yet the major challenge is high energy consumption (2.53 kWh/kgFeed). The membrane process, on the other hand, consumes less energy (0.88 kWh/kgFeed) but produces H_2 with low purity (98.85%) and recovery (89.91%). The economic analysis of these processes showed that the membrane process is cost-effective with less TCI (34.36 m$) than the cryogenic process (38.21 m$).

Keywords: Syngas, organic Rankine cycle, cryogenic distillation, CO_2 solidification, membrane process, hydrogen

NOMENCLATURE

Abbreviations	
PSA	pressure swing adsorption
PEMFC	Proton exchange membrane fuel cell
VLE	Vapor liquid equilibrium
WGS	Water gas shift
MITA	Minimum internal temperature approach
TCI	Total capital investment

1. INTRODUCTION

Due to ever-increasing world energy demand and carbon emissions, the use of clean energy fuels is increasing. Hydrogen is one of the clean energy fuels that have the potential to reduce carbon emissions and produce energy [1]. Currently, hydrogen is largely being produced from natural gas (NG) through the steam methane reforming process and from coal through the gasification process [2]. These sources of hydrogen production i.e., fossil fuels are the major source of carbon emissions. Renewable sources such as biomass-based are gaining attention owing to low carbon emissions. Therefore, hydrogen-rich syngas produced from biomass has been considered as a game-changer in shifting towards clean fuels.

Hydrogen is the major component in syngas along with impurities such as carbon dioxide (CO_2), carbon monoxide (CO), and nitrogen (N_2). The impurities must be removed before hydrogen utilization. Conventionally, hydrogen purification is carried out through the pressure swing adsorption (PSA) process. The PSA process purifies hydrogen (up to 99.999% [3]) by adsorbing impurities in a high-pressure column. When the adsorbent is saturated, it is desorbed by lowering the pressure of the column removing the impurities. The major limitation of PSA is low hydrogen recovery (up to 70% [4]). The other technologies such as membrane and cryogenic can be explored to achieve high purity with high recovery. Recently, a review was published by Bernardo et al. [5] on membrane-based separation processes for hydrogen separation and purification. They have analyzed carbon molecular sieve membranes (CMSM), ionic liquid-based membranes (ILM), Palladium based membranes (PM), and electro chemical-based membranes. CMSM have the limitation of brittles and vulnerability to humidity which limits its commercial applications. ILM is relatively new and has a large potential to overcome CMSM limitations. PM membranes are new and expensive. Other catalyst-based membranes can provide high selectivity and high H_2 flux, but the cost is high. They conclude that the membranes have the potential to produce high purity H_2 (up to 99.97%) at a low cost [5]. The cryogenic distillation process for the separation and purification of H_2 has not been evaluated much mainly because of very low-temperature operation due to the presence of H_2 with the boiling point of -251℃ at 1 atm. Lin et al. [6] separated H_2 and liquefied synthetic natural gas through the distillation process. The maximum methane purity was reported as 99.99% from atmospheric distillation. However, they have not reported H_2 purity in the product [6]. Recently. a study was published by Asadnia et al. [7] in which a cryogenic distillation process was adopted to separate hydrogen from a mixture of hydrocarbons and nitrogen. They reported H_2 purity as 88.05% in the final product [7].

Membrane and cryogenic distillation based H_2 separation and purification processes have the potential to produce high purity H_2 with high recovery, yet this potential have not been explored much. In this study, a membrane and CO_2 anti-sublimation assisted cryogenic distillation process is proposed to separate and purify H_2 from syngas. The proposed processes are evaluated in terms of product purity, energy consumption, and process economics.

2. PROBLEM STATEMENT: CHALLENGES AND ISSUES IN HYDROGEN PURIFICATION

Hydrogen purification is a challenging issue mainly because high purity H_2 with high recovery is required in certain applications. Liquid H_2 production, Proton exchange membrane fuel cell and electronic industry strict the H_2 purity specification at ultra-high purity [8]. Conventionally, the pressure swing adsorption method is adopted to produce high purity H_2. The major challenge in the PSA process is low recovery (~80% [5]). The other technologies such as membrane and cryogenic distillation process must be explored to study the purification and recovery of H_2. The distillation process involving vapor liquid equilibrium (VLE) can be exploited to obtain an extremely high purity of H_2 [9]. This method relies on the relative volatility (α) of the mixture which indicates the degree of separation difficulty between the more volatile and less volatile components of a mixture. In the case recovery of H_2 from N_2, CO and CO_2 mixture, owing quite significant difference in the boiling point of H_2 and adjacent component i.e., N_2, make the system a candidate for VLE-based separation. However, due to the presence of H_2 in the mixture, the separation becomes challenging owing to very low-temperature operation. Further, the existing CO_2 in the mixture, very cold temperature inducing to solidification of CO_2. This is because the freezing temperature of CO_2 is far higher than H_2 boiling temperature at atmospheric pressure. To tackle this issue, CO_2 is firstly removed from the mixture through the anti-sublimation phenomenon. CO_2 is solidified in a specially designed chamber releasing CO_2-free product gas. After CO_2 removal, the remaining mixture can be separated by cryogenic distillation. The separation phenomenon is explained through a ternary diagram for H_2, N_2 and CO, as shown in Figure 1.

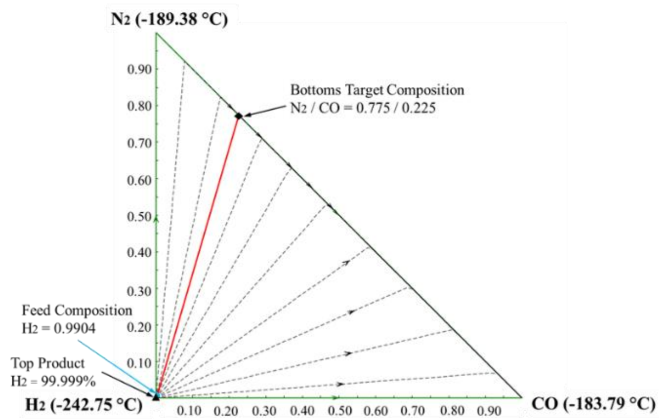

Figure 1 Ternary diagram of H_2, CO_2 and N_2

According to Figure 1, to achieve high H_2 purity at the top of the distillation column, the bottom composition comprises 0.775 N_2 and 0.225 CO. Another, major challenge in VLE-based separation i.e., distillation is high energy consumption owing to low-temperature operation.

The membrane process, on the other hand, can also be used to separate and purify hydrogen. The major challenge in the membrane process is achieving high purity with high recovery. The membrane-based gas permeation capability to separate two gases are determined by the ratio of their permeabilities or the membrane selectivity (α_{ij}); for example, the ratio for H_2 and CO_2 can be presented in equation 1 [10].

$$\alpha_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}} = \left[\frac{D_{H_2}}{D_{CO_2}}\right]\left[\frac{K_{H_2}}{K_{CO_2}}\right] \quad (1)$$

The ratio of two gases diffusion coefficients D_{H_2}/D_{CO_2} is decided by the relative sizes of the components. Thus, the smaller molecule permeation is always faster in comparison to larger elements. The ratio K_{H_2}/K_{CO_2} is the ratio of sorption coefficient that allows the sorption of the more condensable component. Accordingly, the mobility and sorption selectivity effect on the separation H_2 and CO_2 is not uniform. The selection of membrane material type is important. The mobility and selectivity terms rely upon the polymer type [11]. Because of H_2 molecule is smaller than CO_2 and the normal boiling point H_2 is lower than CO_2 [12]. H_2 permeance is faster than CO_2 in the glassy polymer but slower than CO_2 in the rubbery polymer membrane. Other components in the mixture are N_2 and H_2O. In the rubbery polymer, the permeability of N_2 is somewhere near H_2 and H_2O is the fastest among the mixture. In this study, due to low composition the component beside H_2 and CO_2, the remaining components permeability are assumed. N_2 permeability is similar to H_2, H_2O permeability is faster than CO_2 and CO are rejected into retentate.

3. PROCESS DESCRIPTION AND SIMULATION

The membrane and cryogenic distillation processes are simulated in Aspen Hysys® v11. Peng-Robinson [13] is used as an equation of state to calculate thermodynamic properties. The feed composition and conditions, taken from [14], are presented in Table 1. The following important assumptions are taken to simulate the process:

- There is no heat loss to the surroundings.
- There is no pressure drop in exchangers.
- The minimum approach temperature approach (MITA) in multi-stream exchangers is ~3.0°C.
- The compressors are expanders efficiencies are taken as 80 and 85 %, respectively.

Table 1 Syngas feed conditions and composition [14]

Feed composition	**Mole%**
Carbon monoxide	24.18
Carbon dioxide	0.57
Nitrogen	0.74
Hydrogen	74.51
Feed conditions	
Temperature (°C)	25
Pressure (bar)	31.01
Flow rate (kg/s)	32.52

Initially, the CO is converted into H_2 through water gas shift (WGS) reaction (as shown in equation 2) in high temperature and low-temperature shift converters. CO_2 is produced alongside H_2.

$$CO + H_2O = CO_2 + H_2 \quad (2)$$

The WGS product is further purified to get high purity H_2 product. The details of the membrane process and cryogenic distillation process are provided in sections 3.1 and 3.2, respectively.

3.1 Membrane process

Besides many applications of the membrane in gas processing, H_2 and CO_2 separation is one common application. Membrane modules separate gases through permeate and retentate. Generally, the membrane scheme is represented by two steps and two stages [11] as shown in Figure 2 (a).

In this work, between two major components, H_2 and CO_2, the H_2 proportion is the highest in the mixture, and the CO_2 selective membrane is selected for separation [15]. In industrial membrane application, the spiral wound module is one of the most common membrane modules for the separation of CO_2 [16]. The Spiral wound module is modelled following a cross-flow pattern [17] which approximates the actual spiral wound membrane separator. The transport mechanism of gas permeation in the dense membrane can be described by the solution-diffusion model [11,18] by equation 3.

$$J_i = \frac{D_i K_i^G}{l}(p_{io} - p_{il}) = \frac{P_i^G}{l}(p_{io} - p_{il}) \quad (3)$$

where J_i (m^3(STP)/m^2 h) is the flux of the gas component *i*, D_i is the membrane diffusion coefficient (cm^2/s) of component *i*, K_i^G is the sorption coefficient (cm^3(STP)/cm^3 cm·Hg) of component *i*, *l* is the membrane thickness, p_{io} and p_{il} are the partial pressures of component *i* on either side of the membrane (surface *o* and *l*), and P_i^G is the gas-phase permeability coefficient.

To maximize the separation, three membrane modules of the spiral wound are applied by combining the configuration of a two-step and two-stage membrane. Due to the membrane is CO_2 selective, a two-step membrane is utilized to recover H_2 through retentate. Aspen custom modeler (ACM) is used to model the membrane. The permeability values are H_2 = 74 and CO_2 = 814 barrer with CO_2/H_2 mixed gas selectivity is 11.1 [15].

3.2 Cryogenic process

Distillation based separations based on differing the α and phase behavior are relatively simple and widely adopted in the gas industry. A larger difference in α signify easier separation [19,20]. The rough estimation of α in an ideal gas is defined through the derivation of Clapeyron's equation (4) [21],

$$\ln \alpha_{ij} \approx e^{\beta(T_{bj}-T_{bi})/T_B} \tag{4}$$

where

$$\beta = \frac{\Delta H^{vap}}{RT_B}\ ; \qquad T_B = \sqrt{T_{bi}T_{bj}} \tag{5}$$

where ΔH_{vap}, R, i, j, T_{bi}, and T_{bj} are the specific heat of vaporization, universal gas constant, component i, component j, boiling point component i, and boiling point component j, respectively. From equation 4, the rough estimation of α is equivalent to the difference of the boiling point difference, the greater boiling point different from unity, the greater is α. The large α values in the mixture imply that a simple separation is applicable. Reversely, if the value of α is almost unity, a more complex separation method is required.

The product from WGS is sent to water removal prior to cryogenic distillation to avoid any potential freezing of water. The water is removed through Tri-ethylene Glycol (TEG) process. The dry product gas from the TEG unit is sent to the cryogenic distillation unit. The major challenge in this process is CO_2 removal through cryogenic distillation because of the presence of a large amount of H_2 (Boiling point: -251°C). The distillation column operates at a very low temperature which is subject to the freezing of CO_2 in the column. To avoid this phenomenon, a unique separation method is adopted i.e., anti-sublimation. It separates CO_2 in solidified form. The solidification of CO_2 is also applied and validated for biogas upgrading process [22]. The temperature and pressure conditions of CO_2 solidifications are calculated from CO_2 phase diagram. A unique cold box phenomenon is simulated, and solid CO_2 is removed from the inlet gas mixture while the product gas including H_2, N_2 and CO is removed from the top. This $H_2/N_2/CO$ mixture is separated in a cryogenic distillation unit with ultra-high purity H_2 (99.999%) and high recovery (99.999%). The process diagram is shown in Figure 2 (b).

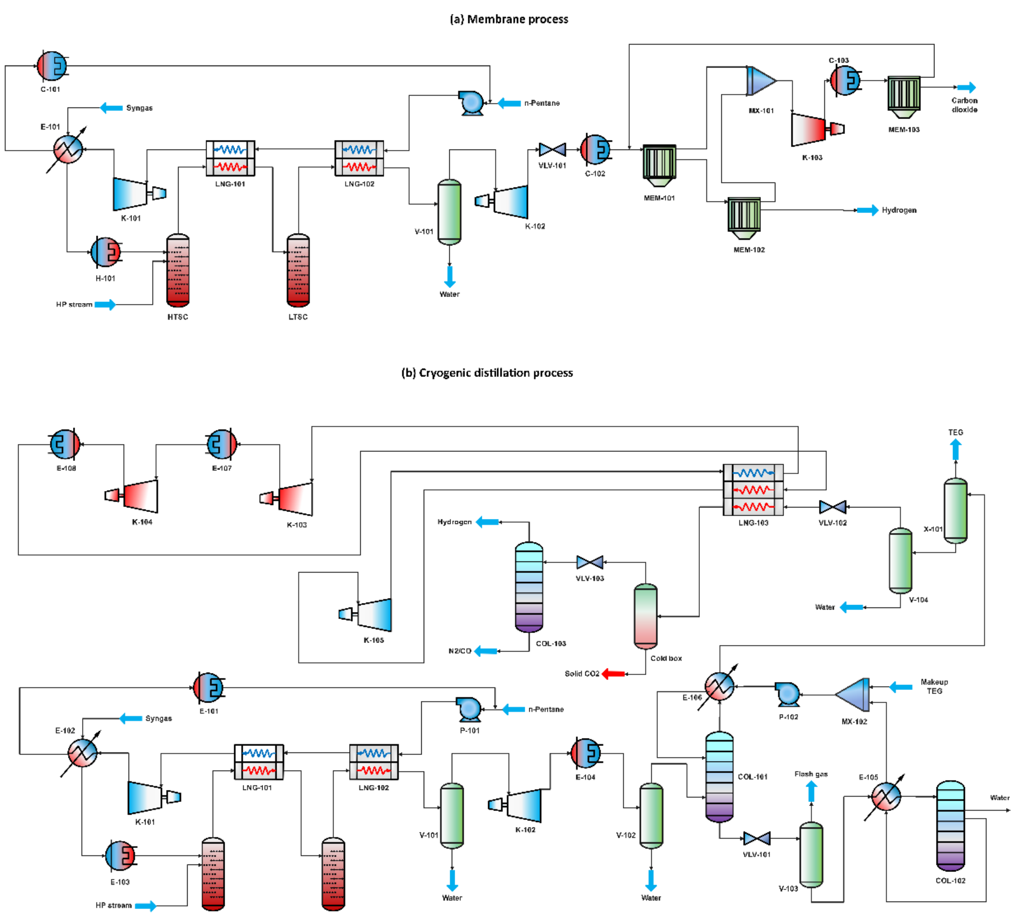

Figure 2 Syngas derived hydrogen separation and purification through (a) membrane process and (b) cryogenic distillation process

4. RESULTS AND DISCUSSION

4.1 Energy analysis

Energy analysis is the major term to discuss within the compared scenarios for hydrogen separation. Two uniquely classified processes have integrated with modern energy-intensive processes to recover energy and get benefitted in both ways. The energy analysis of both proposed technologies is conducted. It is analyzed that the membrane technology is less energy-consuming in comparison to the cryogenic separation process, specified for the syngas feed stream as shown in Figure 3.

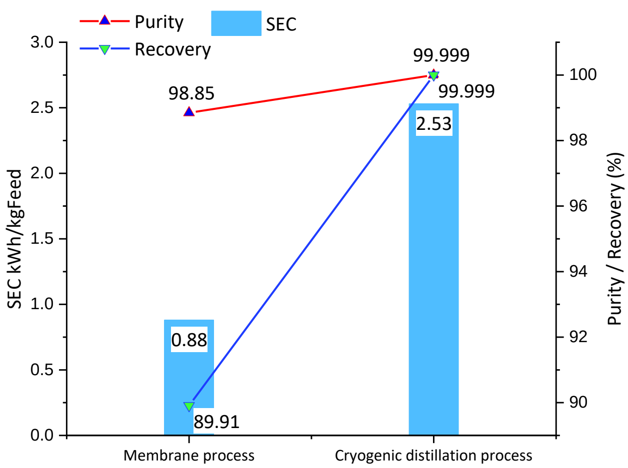

Figure 3 Comparison of membrane and cryogenic processes concerning SEC, H_2 purity and recovery.

On the contrary, it would be biased if SEC is the only criteria of analysis. Although the membrane process is less energy-intensive, its recovery and purity of product H_2 is 89.91% and 98.85% which is less than the cryogenic process having 100% and 99.99%, respectively. Compared to cryogenic, the membrane separation process is an energy-saving process, However, there is still large potential available in terms of product purity and recovery.

4.2 Economic analysis

The economic analysis is conducted to evaluate and compare the proposed cases with the base case. In this study, Guthrie's method (module costing technique) is adopted for economic evaluation [23]. This module costing method is commonly used in estimating the cost of a new chemical plant [23]. Figure 4 shows a TCI comparison between cryogenic and membrane-based technologies. In the cryogenic process, TCI was found to be $38.21M. Compressors contributed the most (52.3%), whereas the heat exchangers contributed the least only 0.4%. Compressors' cost was more owing to the larger compression requirement to attain low temperatures. In contrast, membrane-based process is on the cheaper side. In the membrane process, the compression process is the major contributor in TCI followed by membrane unit.

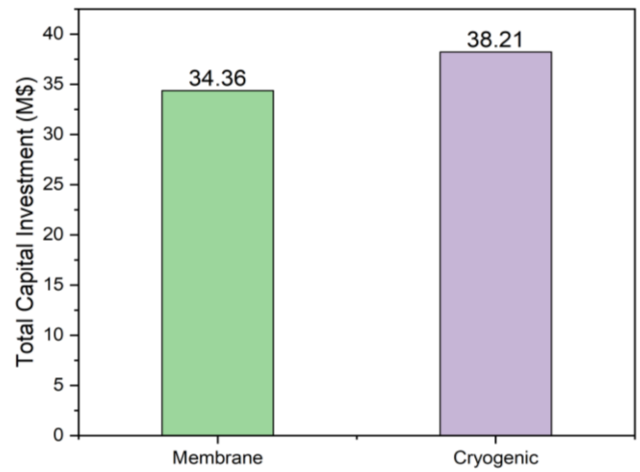

Figure 4 Comparison of membrane and cryogenic processes in terms of TCI.

5. CONCLUSIONS

Conventionally, H_2 separation and purification from syngas has been carried out through the PSA process. PSA process ensures high purity of H_2 but with low recovery. In this study, two unconventional methods have been adopted to analyze H_2 separation and purification. The membrane process consumes less energy with less investment cost as compared to the cryogenic process. Nevertheless, the purity and recovery of H_2 through the membrane process is less than the cryogenic process. In conclusion, the cryogenic process can be adopted to achieve high purity H_2 (99.999%) with high recovery (99.999%) but at an expense of high energy i.e., 2.53 kWh/kgFeed.

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