

# Analyses of one-step liquid hydrogen production from methane and landfill gas

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## Abstract

Conventional liquid hydrogen (LH<sub>2</sub>) production consists of two basic steps: (1) gaseous hydrogen (GH<sub>2</sub>) production via steam methane reformation followed by purification by means of pressure swing adsorption (PSA), and (2) GH<sub>2</sub> liquefaction. LH<sub>2</sub> produced by the conventional processes is not carbon neutral because of the carbon dioxide (CO<sub>2</sub>) emission from PSA operation. A novel concept is herein presented and flowsheeted for LH<sub>2</sub> production with zero carbon emission using methane (CH<sub>4</sub>) or landfill gas as feedstock. A cryogenic process is used for both H<sub>2</sub> separation/purification and liquefaction. This one-step process can substantially increase the efficiency and reduce costs because no PSA step is required. Furthermore, the integrated process results in no CO<sub>2</sub> emissions and minimal H<sub>2</sub> losses. Of the five flowsheets presented, one that combines low and high temperature CO/CH<sub>4</sub> reforming reactions in a single reactor shows the highest overall efficiency with the first and second law efficiencies of 85% and 56%, respectively. The latter figure assumes 10% overall energy loss and 30% efficiency for the cryogenic process. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Liquid hydrogen; Cryogenic separation; Chemical simulation; Steam methane reforming; Water gas shift reaction

## 1. Introduction

In addition to being a propellant for space vehicles, liquid hydrogen (LH<sub>2</sub>) can be utilized for on-board hydrogen storage in polymer electrolyte membrane fuel cell (PEMFC) powered vehicles. On-site production of LH<sub>2</sub> can facilitate its use in transportation applications. Presently, LH<sub>2</sub> is produced by liquefaction of high purity gaseous hydrogen (GH<sub>2</sub>) generated by steam methane reformation (SMR) followed by pressure swing adsorption (PSA) purification, with up to 85% H<sub>2</sub> recovery and at 99.95% purity. One major disadvantage of PSA is that the effluent, containing high concentrations of carbon monoxide (CO), H<sub>2</sub> and methane (CH<sub>4</sub>), is burned to recover the energy value of the combustible gases, thereby wasting CH<sub>4</sub> and CO as potential H<sub>2</sub> producing species as well as increasing the emission of greenhouse gases. Besides H<sub>2</sub> recovery efficiency, H<sub>2</sub> purity is another important parameter when used especially in PEMFC and rocket propulsion applications that typically require hydrogen purity at 99.9995% level or higher. For example,

very low-levels (~10 ppmv) of contaminants such as CO and hydrocarbons can deactivate platinum catalysts used in PEMFC membrane electrode assemblies [1]. It is apparent that GH<sub>2</sub> production through PSA purification may not be sufficient for many applications and deep removal of CO and other contaminants is often required. Various techniques including CO preferential oxidation, CO methanation and electrochemical water gas shift reaction have been used to achieve high hydrogen purity [1].

The cryogenic separation and purification process is a well-established technology for recovery and purification of hydrogen in refineries and the petrochemical industry [2]. Conventional cryogenic H<sub>2</sub> purification utilizes partial condensation to separate H<sub>2</sub> from impurities with higher boiling points, such as H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, and hydrocarbons. Because of the high relative volatility of H<sub>2</sub> as compared to these impurities, cryogenic processes can separate H<sub>2</sub> from off-gases with a very high recovery efficiency at purity levels that far exceed those obtained from PSA or membrane separation processes [3,4].

It should be noted that the efficiency of a cryogenic system is a strong function of heat recovery. The optimization of the heat exchanger system is essential in improving its first and second law efficiencies. Before chemical engineering simulation became widely available, process design and efficiency

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### Nomenclature

CE	cooling energy
CompE	compressor energy requirement
CondE	condenser energy requirement for the distillation column
HE	heating energy
HX	heat exchanger
$n_{\text{LCO}_2}$	number of moles of liquid carbon dioxide
$n_{\text{LH}_2}$	number of moles of liquid hydrogen
$R_{\text{CO}_2/\text{LH}_2}$	amount of carbon dioxide (g) produced per gram of liquid hydrogen collected
$R_{\text{Energy}/\text{LH}_2}$	input energy per mole of liquid hydrogen collected
ReE	reboiler energy requirement for the distillation column

### Greek letters

$\eta_{\text{Carnot}}$	Carnot efficiency
$\eta_{\text{Separation}}$	cryogenic hydrogen separation efficiency
$\eta_{1\text{st}}$	first law efficiency
$\eta_{2\text{nd}}$	second law efficiency

determination were very difficult and time consuming. For this reason, the development and widespread application of cryogenic separation processes have been limited. If cryogenic purification and  $\text{H}_2$  liquefaction could be combined into a single process, the capital cost of the cryogenic separation would be a small portion on the  $\text{LH}_2$  production cost. The objective of this paper is to demonstrate the viability of using  $\text{CH}_4$  and landfill gas (LFG) as feedstocks for producing hydrogen. Five scenarios have been flowsheeted and analyzed in this paper utilizing Aspen Technologies chemical process simulation (CPS) platforms.

## 2. $\text{LH}_2$ production and the efficiency of cryogenic separation

Fig. 1 depicts a schematic diagram of the  $\text{LH}_2$  production process. Hydrogen rich gaseous mixture is produced via methane autothermal reformation followed by cryogenic separation. In the cryogenic process, water vapor is separated in the first stage of the process and liquid  $\text{CO}_2$  removed from the gas stream in

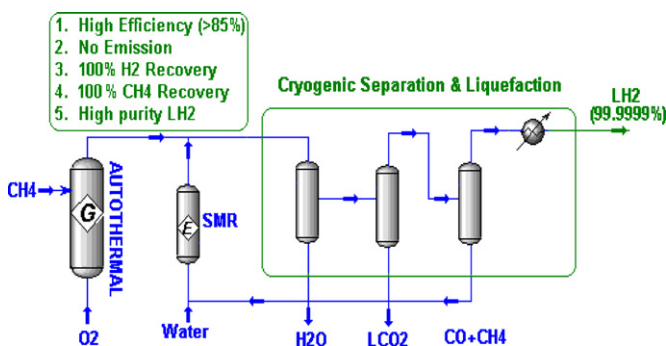
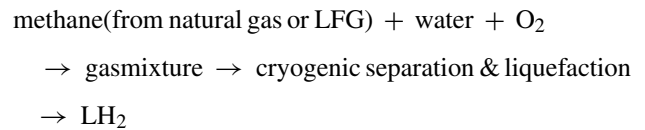


Fig. 1. Schematic diagram of innovative liquid  $\text{H}_2$  production process.

the second stage. Finally, in the third stage,  $\text{H}_2$  is separated from the gaseous mixture containing  $\text{CO}$  and  $\text{CH}_4$ . The mixture is then fed into the steam methane reformer to produce additional hydrogen that is then mixed with the primary stream from the autothermal reactor and sent to the cryogenic separation unit. Low temperature and high purity  $\text{H}_2$  extracted from the  $\text{CO}$  and  $\text{CH}_4$  mixture is then cooled to form  $\text{LH}_2$ , without any  $\text{H}_2$  losses. Since there is no outlet for either  $\text{CO}$  or  $\text{CH}_4$ , theoretically, the recovery of  $\text{CO}$  and  $\text{CH}_4$  should be 100%.  $\text{CO}_2$  collected in the cryogenic process has high purity making it useful in a variety of applications. Because thermal heat and cooling energy can be recovered using heat exchangers, this process can be more efficient than the conventional  $\text{LH}_2$  plants. The overall process can be summarized as follows:



As discussed above, a cryogenic separation process can be cost effective and efficient if  $\text{H}_2$  separation and liquefaction are combined into a single process. But, this makes thermodynamic calculation of cryogenic separation efficiency more complicated. The energy required for cryogenic separation of  $\text{H}_2$  from a gas mixture consists of two parts:  $\text{H}_2$  separation energy and  $\text{H}_2$  liquefaction energy. The cooling energy input for separating components of a gas mixture can be recovered to a large extent by using heat exchangers. Therefore, the total energy needed for  $\text{LH}_2$  production, by the cryogenic process of Fig. 2, using hydrogen rich gas mixture containing  $\text{CO}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  is:

$$\begin{aligned} \Delta H_{\text{Total}} = & (\Delta H_{\text{Cooling}} + \Delta G_{\text{Separating}} + \Delta H_{\text{Recovering}})_{\text{Gas mixture}} \\ & + (\Delta H_{\text{Liquefaction}})_{\text{Hydrogen}} \end{aligned} \quad (1)$$

where  $\Delta G_{\text{Separating}}$  is the Gibbs free energy change for separating a component in the mixture. During the cryogenic separation,  $\text{H}_2$  is cooled progressively until liquefied. Therefore, the cryogenic separation efficiency (First Law efficiency) for  $\text{LH}_2$  production is:

$$\eta_{\text{Separation}} = \frac{(\Delta H_{\text{Cooling}} + \Delta H_{\text{Liquefaction}})_{\text{Hydrogen}}}{\Delta H_{\text{Total}}} \quad (2)$$

In principle, the separation efficiency can be determined from thermodynamics. However, due to the complexities involved in determining heat recoveries in the heat exchangers, its evaluation is somewhat difficult. Furthermore, separation temperatures are different from one component to another and vary with system pressure. Calculation of the cooling energy and heat recovery is also complicated. Additionally, in a cryogenic process, at elevated pressures, a gas mixture cannot be considered an ideal gas, thus, leading to further complications. Accordingly, the precise determination of separation efficiency would be difficult using conventional thermodynamic methods.

For this work, we have used Aspen Technologies' CPS platforms. Fig. 2 illustrates a HYSYS flowsheet for separating and liquefying  $\text{H}_2$  from a hydrogen rich gas mixture. We note that

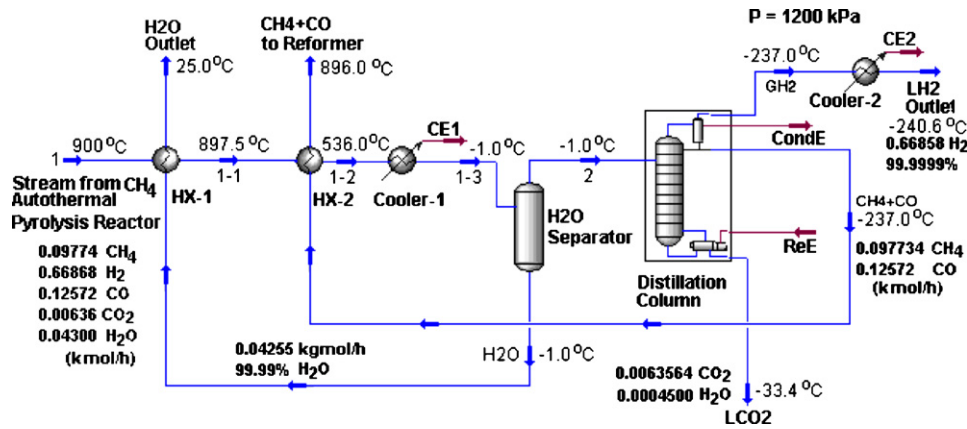


Fig. 2. Separation efficiency calculation ( $P = 1.2 \text{ MPa}$ ,  $\Delta H_{\text{Total}} = 2.666 \times 10^4 \text{ kJ h}^{-1}$ , hydrogen recovery exceeds 99.99%).

at cryogenic state and elevated pressures, both vapor and liquid phases are far from being ideal. In our simulation, the Peng Robinson Equation of State was selected as the fluid package since it is considered applicable to both non-ideal vapors and solutions. The tray efficiencies of the distillation column (Fig. 2) are assumed to be 95%. Idealized heat exchangers were assumed with no heat loss. Stream 1 is a feed stream containing  $\text{H}_2$  rich gas mixture from an autothermal  $\text{CH}_4$  pyrolysis reactor containing  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$ . The composition of the mixture is calculated from a Gibbs reactor using AspenPlus™ CPS. The inlet stream to the Gibbs reactor contains 0.452 kmol of  $\text{CH}_4$  and 0.0904 kmol of  $\text{O}_2$ , respectively, at a temperature of  $900^\circ\text{C}$  and 1200 kPa. In order to calculate the total energy requirement ( $\Delta H_{\text{Total}}$ , Eq. (2)) for cooling and liquefaction of pure  $\text{H}_2$ , a simple flow diagram (Fig. 3) was used—subject to conditions identical to those in Fig. 2. Based on Figs. 2 and 3, the energy input to both pure  $\text{H}_2$  liquefaction ( $0.66858 \text{ kmol h}^{-1}$ ) and gas mixture can be determined.

In the case of 71.02% of  $\text{GH}_2$  concentration in the gas mixture, the separation efficiency defined by Eq. (2) is  $\eta_{\text{Separation}} \% = (2.281 \times 10^4 / 2.666 \times 10^4) \times 100\% = 85.56\%$ . In other words, 86.56% of the energy is used for  $\text{LH}_2$  production, while 13.44% is consumed for cryogenic separation of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ , and  $\text{CH}_4$ . It should be noted that several factors contribute to the separation efficiency. For example, concentration of  $\text{H}_2$  plays an important role in the efficiency calculations. Eq. (2) predicts that for two extreme conditions (*i.e.* the inlet  $\text{H}_2$  concentrations of 100% and 0% to the cryogenic separation and liquefaction system shown in Fig. 2) efficiencies are 100% and 0%, respectively. Fig. 4 depicts the cryogenic separation efficiency as a function of inlet  $\text{GH}_2$  concentration. The efficiency

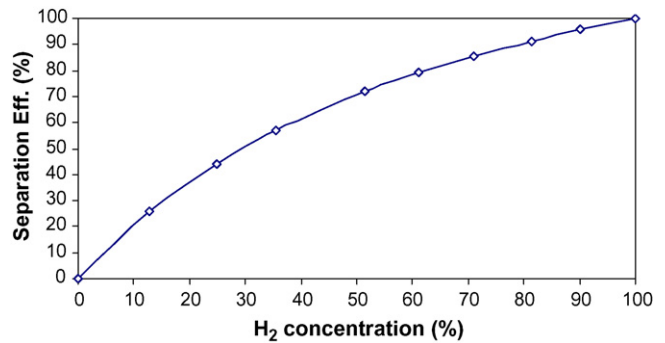


Fig. 4. Separation efficiency vs. inlet  $\text{GH}_2$  concentration.

increases nonlinearly with increasing  $\text{GH}_2$  concentration. If a separation efficiency of 70% is required, concentration of inlet  $\text{GH}_2$  must be higher than 50 mol% in the gaseous mixture. On the other hand, if the  $\text{H}_2$  recovery rate is defined as  $(\text{LH}_2 \text{ outlet flow rate}) / (\text{GH}_2 \text{ flow rate}) \times 100\%$ , Figs. 2 and 3 show that the recovery rate in a cryogenic separation system increases with increasing inlet  $\text{GH}_2$  concentration. The extent of  $\text{H}_2$  in the outlet  $\text{CO}$  and  $\text{CH}_4$  streams is affected by the separation efficiency of the distillation column. The components  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{O}$  do not significantly influence the separation efficiency since the cooling energy required for separating these species can be recovered in the heat exchangers. The outlet  $\text{CO}_2$  in liquid form ( $\text{LCO}_2$ ) makes it easier to transport, store and/or sequester. Note that required  $\text{LH}_2$  purity does not have a strong effect on the separation efficiency because the relative volatility of  $\text{H}_2$  to  $\text{CH}_4$  in a typical cryogenic process is greater than 200 [2].

### 3. Processes for $\text{LH}_2$ production from methane and landfill gas

There are several conventional technologies for production of  $\text{H}_2$  from  $\text{CH}_4$ , including steam reforming (SMR), partial oxidation, pyrolysis, autothermal pyrolysis, and autothermal SMR. Carbon monoxide ( $\text{CO}$ ), the intermediate generated from these processes (except in the case of pure  $\text{CH}_4$  pyrolysis that produces

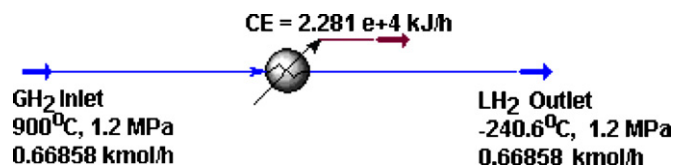


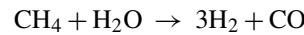
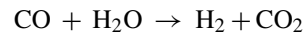
Fig. 3.  $\text{H}_2$  cooling and liquefaction energy calculation ( $P = 1.2 \text{ MPa}$ ,  $\Delta H_{\text{CE-2}} = 2.281 \times 10^4 \text{ kJ h}^{-1}$ ).

only solid carbon and H<sub>2</sub>), can undergo high and low temperature water gas shift reactions (WGSR) to produce more H<sub>2</sub> and CO<sub>2</sub>. Therefore, by combining these processes with a cryogenic separation process, a number of flow diagrams for production of LH<sub>2</sub> directly from CH<sub>4</sub> can be conceived. In order to reduce the production of CO<sub>2</sub>, we selected CH<sub>4</sub> autothermal pyrolysis for GH<sub>2</sub> production. The energy required for CH<sub>4</sub> pyrolysis is derived from partial combustion of CH<sub>4</sub>, in which enough heat is generated to allow decomposition of any remaining CH<sub>4</sub>, resulting in a thermo-neutral process. The outlet stream from the autothermal reactor consists of CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O. The gaseous mixture is separated cryogenically into individual components. In some case studies no CO and CH<sub>4</sub> separation were needed, and the mixture was combined with H<sub>2</sub>O and recycled to a high temperature gas conditioning reactor (HTGCR) or a low temperature gas conditioning reactor (LTGCR) to generate more H<sub>2</sub>. The product stream from either HTGCR or LTGCR was mixed with the main stream from the CH<sub>4</sub> autothermal pyrolysis reactor and sent to the separation unit. Based on the processes discussed above, five flowsheets were constructed for LH<sub>2</sub> production as follows:

- *Flowsheet I.* CH<sub>4</sub> and CO are not separated; the gaseous mixture enters HTGCR and LTGCR.
- *Flowsheet II.* CH<sub>4</sub> and CO are not separated; both gas mixtures enter HTGCR.
- *Flowsheet III.* CH<sub>4</sub> and CO are separated; CH<sub>4</sub> enters SMR and CO enters WGSR.
- *Flowsheet IV.* CH<sub>4</sub> and CO are separated; CH<sub>4</sub> is sent back to autothermal pyrolysis while CO is fed to WGSR.
- *Flowsheet V.* LH<sub>2</sub> is produced from landfill gas; a mixture of CH<sub>4</sub> and CO enters HTGCR.

Flowsheet I is shown in Fig. 5 and the process can be separated into three sections:

- CH<sub>4</sub> autothermal decomposition.* CH<sub>4</sub> and O<sub>2</sub> gases are heated to 900 °C and mixed in a Gibbs reactor operating isothermally. Because the objective of this simulation was to calculate the energy requirement, CH<sub>4</sub> decomposition during the heating process was assumed not to occur but take place in the isothermal Gibbs reactor. The ratio of CH<sub>4</sub> to O<sub>2</sub> (CH<sub>4</sub>:O<sub>2</sub> = 5:1) indicates that 20% of the CH<sub>4</sub> is oxidized to produce the heat required for the pyrolysis of the remaining CH<sub>4</sub> [2]. After separating solid carbon, the gas mixture containing CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>O was then sent to cryogenic separation.
- Cryogenic separation.* Here, H<sub>2</sub>O and pure CO<sub>2</sub> are separated as liquids while the remaining gas mixture is distilled to separate the high purity GH<sub>2</sub> from CH<sub>4</sub> and CO. Low temperature GH<sub>2</sub> is then liquefied to LH<sub>2</sub>. A gaseous stream containing CH<sub>4</sub> and CO is not separated and is recycled to the recirculation loop.
- HTGCR and LTGCR recirculation loop.* H<sub>2</sub> is produced from the remaining CH<sub>4</sub> and CO in HTGCR and LTGCR, based on the HYSYS 3.0.1 equilibrium reactions:



The outlet stream (R6) is mixed with the main stream 1–0 from section (I) and sent to section (II) for the component separation.

The thermal heat energy generated in the process is recovered via many ideal heat exchangers having heat recovery efficiency equal to 100%. The details of the heat exchanger arrangement are shown in Fig. 5. Likewise, Figs. 6–9 depict Flowsheets II–V. Note that Flowsheet V was developed for the production

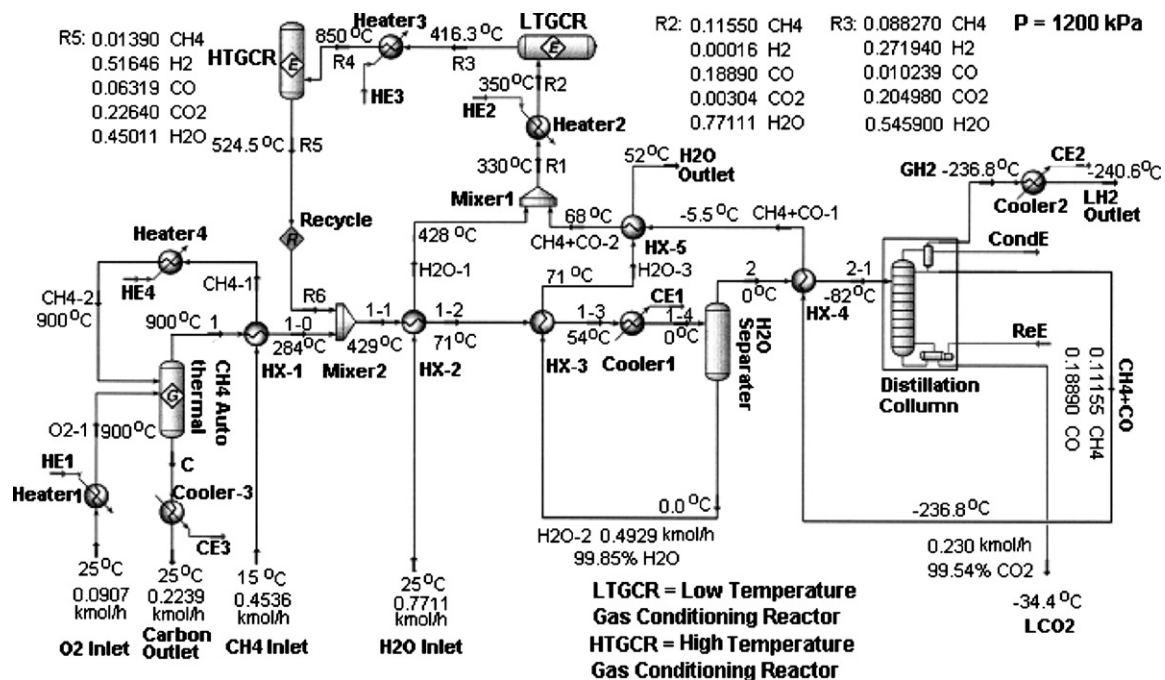


Fig. 5. Flowsheet I (no CH<sub>4</sub> and CO separation, the gaseous mixture undergo HTGCR and LTGCR).

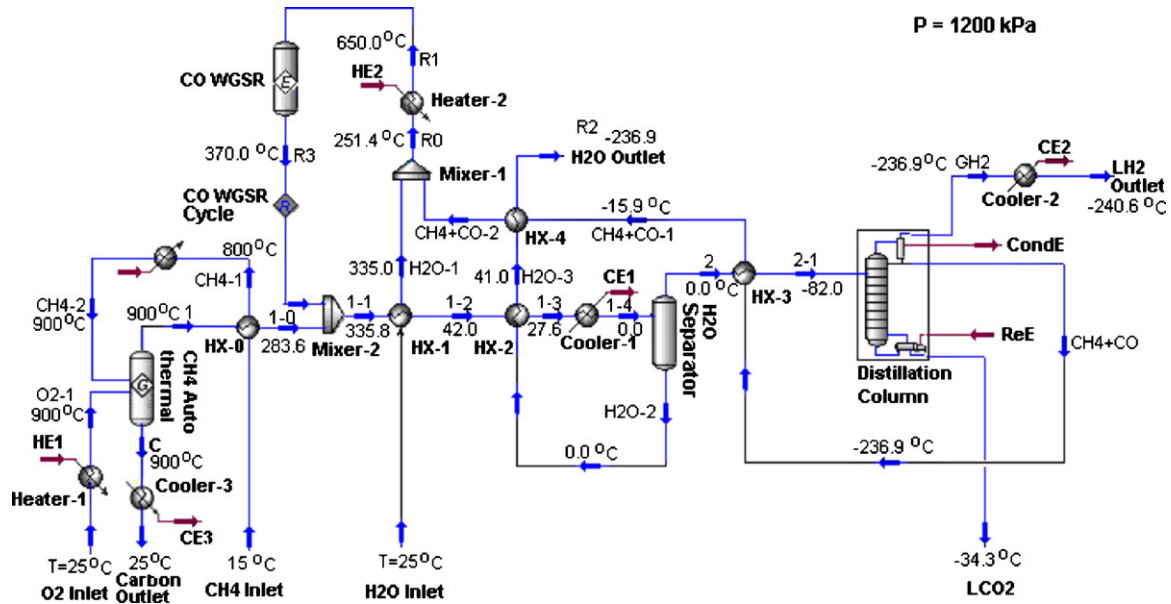


Fig. 6. Flowsheet II (no methane and carbon monoxide separation, no SMR).

of LH<sub>2</sub> from landfill gas (LFG), in which LFG is purified by a cryogenic process to produce pure CH<sub>4</sub> and N<sub>2</sub>. CH<sub>4</sub> is then fed into an autothermal reformer to generate solid carbon and a hydrogen rich gas mixture. Before the cryogenic purification process, hydrogen sulfide (H<sub>2</sub>S) must be removed from LFG to avoid the deactivation of catalysts. Oxygen is also removed from LFG prior to the cryogenic separation process. Because LFG is saturated with water vapor at room temperature and 1 atm, H<sub>2</sub>O concentration can be calculated using HYSYS program as depicted in the landfill gas inlet stream. Although cryogenic LFG purification is a capital intensive process, the combination of purification and LH<sub>2</sub> production may result in

some benefits. Firstly, CH<sub>4</sub> recovery can reach 99.99% with purity levels as high as 99.93%. Even though a higher purity can be achieved by adjusting the cooling temperature in the N<sub>2</sub> separator, obtaining higher CH<sub>4</sub> purity requires considerable energy input. For example, when methane purity is 99.93% and nitrogen purity is 99.96%, CondE-3 and ReE-3 are, respectively, 5246 kJ h<sup>-1</sup> and 2244 kJ h<sup>-1</sup>. If the purity levels are increased to 99.99% for CH<sub>4</sub> and 99.996% for N<sub>2</sub>, CondE-3 and ReE-3 energy requirements increase to 70,410 kJ h<sup>-1</sup> and 67,410 kJ h<sup>-1</sup>, respectively. Secondly, in a cryogenic process, individual components can be extracted as valuable co-products in the process, e.g. high purity liquid N<sub>2</sub> and CO<sub>2</sub>. It must be

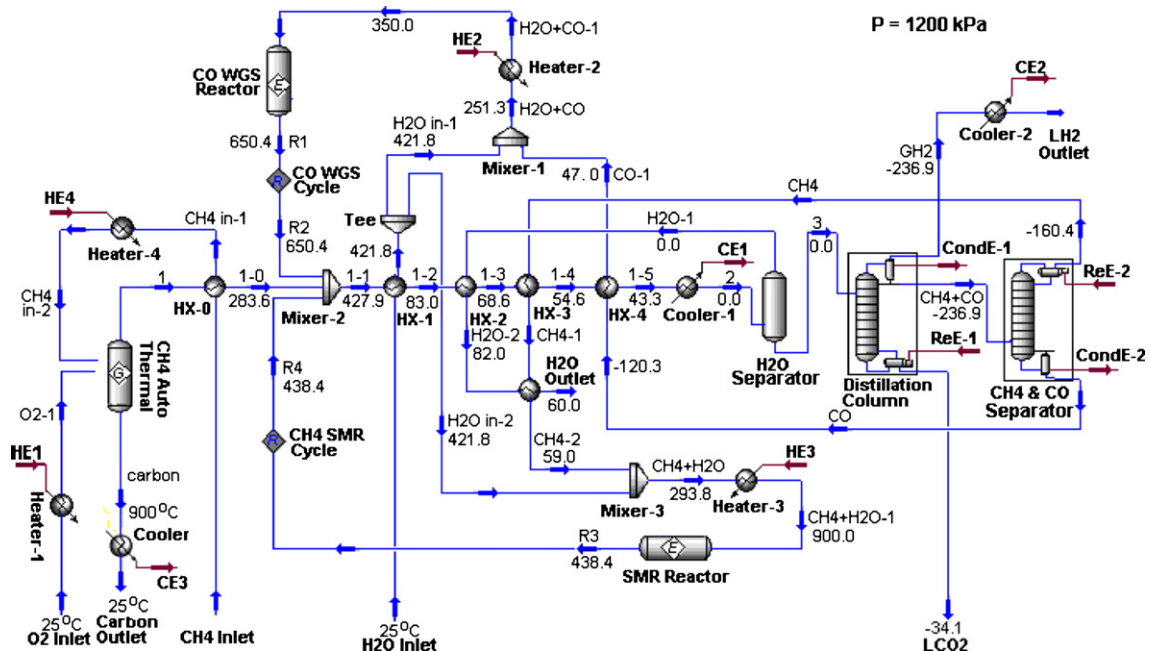


Fig. 7. Flowsheet III (CO and CH<sub>4</sub> are separated; CO undergoes WGSR while CH<sub>4</sub> SMR).

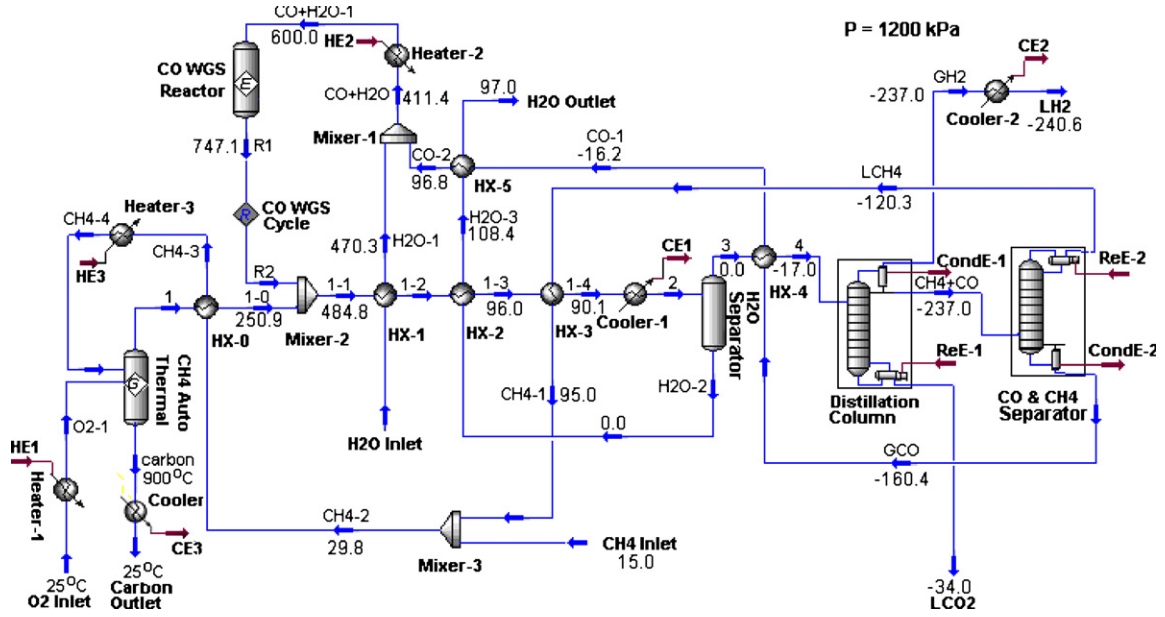


Fig. 8. Flowsheet IV (CO and CH<sub>4</sub> are separated; CO undergoes WGS while CH<sub>4</sub> pyrolysis).

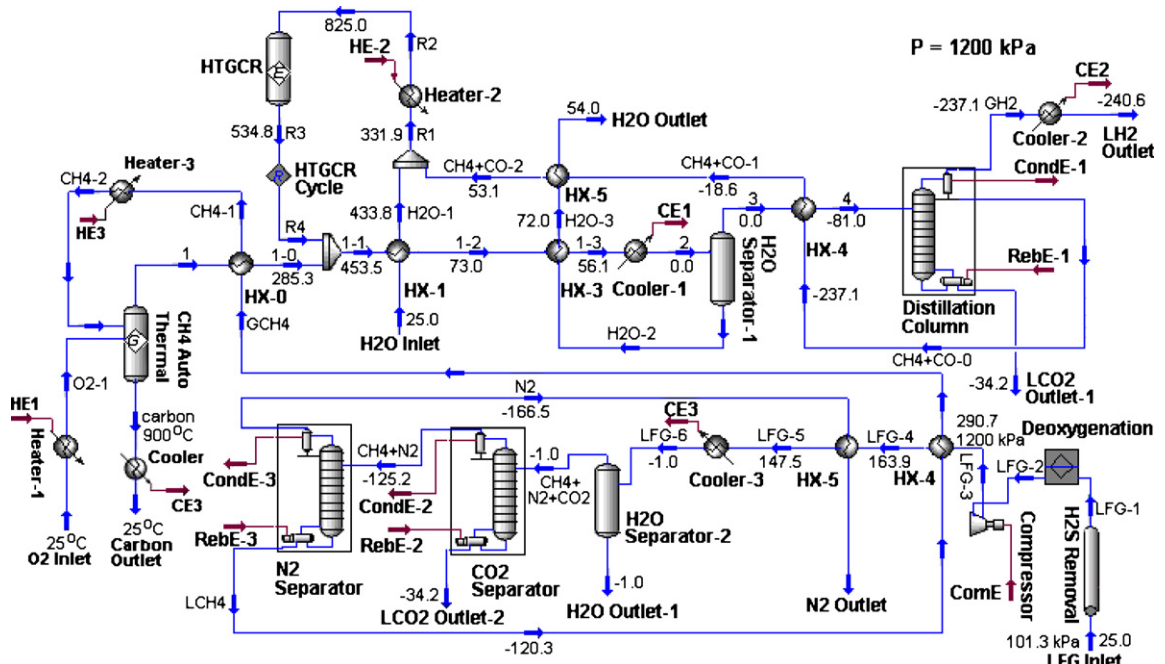


Fig. 9. Flowsheet V. LH<sub>2</sub> production through landfill gas (no CH<sub>4</sub> and CO separation, the gaseous mixture undergo a HTGCR).

pointed out that a practical application of the cryogenic process depends upon both the efficiency and cost of the process.

#### 4. Results and discussion

##### 4.1. The first and second law efficiencies

The first law and second law efficiencies are defined as:

$$\eta_{1st} = \frac{n_{Hydrogen}(\Delta H_{Combustion} + \Delta H_{LH_2})_{Hydrogen}}{(n_{Methane} \Delta H_{Combustion})_{Methane} + \Delta H_{Total}} \times 100\% \quad (3)$$

$$\eta_{2nd} = \frac{n_{Hydrogen}(\Delta G_f^\circ + \Delta H_{LH_2} \eta_{Carnot})}{(n_{Methane} \Delta H_{Combustion})_{Methane} + \Delta H_{Heating} + \Delta H_C / \eta_C} \times 90\% \quad (4)$$

where CH<sub>4</sub> combustion  $\Delta H_{Combustion} = \Delta H_{298K}^\circ = 802.6 \text{ kJ mol}^{-1}$ . Hydrogen high heating value  $\Delta H_{Combustion} = \Delta H_{f298K}^\circ = 285.9 \text{ kJ mol}^{-1}$ .  $n_{Methane}$  and  $n_{Hydrogen}$  refer to number of moles of input CH<sub>4</sub> and H<sub>2</sub> generated, respectively;  $\Delta G_f^\circ = 228.5 \text{ kJ mol}^{-1}$  is the Gibbs free energy change for the formation of 1 mol of water. While H<sub>2</sub> cooling and liquefaction energy  $(\Delta H_{Cooling} + \Delta H_{Liquefaction})_{Hydrogen}$ , calculated from

Table 1  
Energy balance and efficiencies of the five scenarios

Energy streams	Scenario I	Scenario II	Scenario III	Scenario IV	Scenario V
HE1 (kJ h <sup>-1</sup> )	2624.0	2624.0	2624.0	3193.0	2624.0
HE2 (kJ h <sup>-1</sup> )	820.0	17,450.0	1574.0	5584.0	21,710.0
HE3 (kJ h <sup>-1</sup> )	20,560.0		23,030.0		
HE4 (kJ h <sup>-1</sup> )	3452.0	3452.0	3452.0	4200.0	3453.0
CE1 (kJ h <sup>-1</sup> )	5840.0	2725.0	4813.0	11,100.0	2973.0
CE2 (kJ h <sup>-1</sup> )	563.6	570.7	568.4	449.8	558.2
CE3 (kJ h <sup>-1</sup> )	-3420.0	-3420.0	-3420.0	-4922.0	-3420.0
CE4 (kJ h <sup>-1</sup> )					6705.0
CondE (kJ h <sup>-1</sup> )	12,910.0	13,010.0	20,880.0	12,350.0	13,060.0
ReE (kJ h <sup>-1</sup> )	911.5	916.3	1173.0	456.3	934.3
CondE-2 (kJ h <sup>-1</sup> )			5369.0	2768.0	9764.0
ReE-2 (kJ h <sup>-1</sup> )			1576.0	768.4	1836.0
CondE-3 (kJ h <sup>-1</sup> )					5246.0
ReE-3 (kJ h <sup>-1</sup> )					2244.0
CompE (kJ h <sup>-1</sup> )					11,010
Total (kJ h <sup>-1</sup> )	44,261.1	37,328.0	61,639.4	35,947.5	78,697.5
LH <sub>2</sub> (kmol h <sup>-1</sup> )	1.1852	1.1852	1.1852	0.9506	1.1852
LCO <sub>2</sub> (kmol h <sup>-1</sup> )	0.2286	0.2286	0.2285	0.1318	0.2290
First law efficiency (%)	85.34	86.81	81.85	87.11	78.70
Second law efficiency (%)	55.21	56.95	52.09	44.83	50.89
ΔH (kJ kmol <sup>-1</sup> LH <sub>2</sub> )	37,345	31,495	52,008	37,816	66,400
Ratio (CO <sub>2</sub> /H <sub>2</sub> ) (g g <sup>-1</sup> )	4.211	4.211	4.209	3.027	4.219

Fig. 2, is equal to  $n_{\text{Hydrogen}} \times 34,120 \text{ kJ h}^{-1}$ . Since LH<sub>2</sub> can serve as a low-temperature heat sink for a heat engine operating between room temperature and  $-240.6 \text{ }^\circ\text{C}$ , the heat flow from the hot source (GH<sub>2</sub> at  $25 \text{ }^\circ\text{C}$ ) to the cold sink (LH<sub>2</sub> at  $-240.6 \text{ }^\circ\text{C}$ ) is:  $\Delta H_{\text{LH}_2} = 8147.68 \text{ kJ mol}^{-1}$ , with Carnot efficiency of  $\eta_{\text{Carnot}} = (298.15 - 32.55)/298.15 \times 100\% = 89.08\%$ .

The work produced from the engine can be calculated as follows:  $\Delta H_{\text{LH}_2} \times \eta_{\text{Carnot}}$ . Considering heat losses and leakage in the cryogenic system, we assume cryogenic process efficiency,  $\eta_{\text{C}}$ , of 30% (input electrical energy to cooling energy required for separation and liquefaction of hydrogen). In addition to the energy required for the entire process, one must consider the heat leakage and heat recovery losses throughout the process. Assume that 10% of total heat is lost in the process; the second law efficiency is assumed to be less than that calculated from Eq. (4) to compensate for the ideal heat exchanger assumption.

To further evaluate an LH<sub>2</sub> production process, two parameters were used that are defined as:  $R_{\text{Energy/LH}_2}$ , that is the total energy consumption per mole of LH<sub>2</sub> produced, and  $R_{\text{CO}_2/\text{LH}_2}$ , that refers to the weight (g) of CO<sub>2</sub> produced per gram of LH<sub>2</sub> generated. These parameters can be used for a general comparison with the conventional processes described in the literature. It should be noted that, since liquid carbon dioxide (LCO<sub>2</sub>) is produced during cryogenic separation, instead of directly releasing this greenhouse gas into the atmosphere, LCO<sub>2</sub> can be used as a co-product or solidified and sequestered to reduce its environmental impact.

$$R_{\text{Energy/LH}_2} = \frac{\Delta H_{\text{Total}}}{n_{\text{LH}_2}} \quad (5)$$

$$R_{\text{CO}_2/\text{LH}_2} = \frac{n_{\text{CO}_2} \times 44}{n_{\text{LH}_2} \times 2} \quad (6)$$

Table 1 lists the energy balance and efficiencies for the five flowsheets discussed above. The first law efficiencies, after taking cooling effect of LH<sub>2</sub> into account, for four of the five scenarios are calculated to be over 81% (except Flowsheet V that is 78.7%). Even with added energy input for separating CO and CH<sub>4</sub>, Scenario IV achieves the highest first law efficiency (87.11%). The first law efficiency for Flowsheet III is calculated to be 81.85%. Since Flowsheet IV does not include an SMR as in Flowsheet III, simulation results indicate that inclusion of an SMR process results in consumption of a large portion of the input energy, while the use of a CH<sub>4</sub> autothermal reformer reduces the total input energy requirement.

A comparison of the Flowsheets I and II reveals that combining HTGCR and LTGCR into one unit would reduce the energy input required, thereby increasing first law efficiency of the process. Although the total energy input for Flowsheet IV is the lowest amongst all the five flowsheets considered (*i.e.*

Table 2  
Total mass balance for Scenario II

Inlet components (kmol h <sup>-1</sup> )	
CH <sub>4</sub>	0.4536
O <sub>2</sub>	0.0907
H <sub>2</sub> O	0.7711
Outlet components (kmol h <sup>-1</sup> )	
LH <sub>2</sub>	1.1852
LCO <sub>2</sub>	0.2290
Carbon	0.2239
H <sub>2</sub> O	0.4922

Table 3  
SMR temperature effects on the stability of Scenario II

Temperature (°C)	HE2 (kJ h <sup>-1</sup> )	CE1 (kJ h <sup>-1</sup> )	CE2 (kJ h <sup>-1</sup> )	CondE (kJ h <sup>-1</sup> )	ReE (kJ h <sup>-1</sup> )	$\Delta H_{\text{Total}}$ (kJ h <sup>-1</sup> )	1–1 flow (kmol h <sup>-1</sup> )	LH <sub>2</sub> (kmol h <sup>-1</sup> )	LCO <sub>2</sub> (kmol h <sup>-1</sup> )	$R_{\text{Energy/LH}_2}$ (kJ kmol <sup>-1</sup> )	$R_{\text{CO}_2/\text{LH}_2}$ (g g <sup>-1</sup> )
500	21740	–5937	629	24300	788	44176	2.673	1.185	0.2290	37279	4.25
550	19800	–3807	605	20580	766	40599	2.452	1.185	0.2288	34261	4.25
600	18500	–2293	588	18110	747	38308	2.305	1.185	0.2287	32327	4.25
650	17750	–1271	577	16530	732	36974	2.212	1.185	0.2286	31202	4.24
700	17960	–426	570	15820	725	37304	2.170	1.185	0.2285	31481	4.24
750	19190	396	567	15840	724	39373	2.173	1.185	0.2285	33226	4.24
800	20790	1322	564	16100	727	42159	2.192	1.185	0.2285	35577	4.24
850	22730	2470	562	16460	730	45607	2.180	1.185	0.2286	38487	4.24
900	24750	3689	558	16920	733	49306	2.225	1.185	0.2286	41609	4.24

35,947.5 kJ h<sup>-1</sup>), its second law efficiency is calculated to be the lowest (44.83%) as well. The reason for this is that the amount of LH<sub>2</sub> produced (0.9506 mol) is less than that generated (1.1852 mol) in the other four flowsheets. The second law efficiencies of Flowsheets I and II are similar. Flowsheet II combines HTGCR and LTGCR into one so it is expected that the capital cost for the process will be lower. Results of Table 1 also show that the cooling energy share of the total energy input is a major contributor to the second law efficiency calculations since the cooling process is a generally low efficiency process (about 35%). Increasing CH<sub>4</sub> and CO conversions during HTGCR/LTGCR or SMR/WGSR increases the second law efficiencies of these processes.

#### 4.2. Total material balance and methane conversion

Let us consider Flowsheet II as an example to demonstrate the manner in which the calculation of material balances was carried out. Table 2 shows the total flow rates for components input and output. The material balance calculations were performed as follows.

- Carbon balance =  $0.4536 - 0.2290 - 0.2239 = 0.0007 \text{ kmol h}^{-1}$ .
- Hydrogen balance =  $2 \times 0.4536 + (0.7711 - 0.4922) - 1.1852 = 0.00094 \text{ kmol h}^{-1}$ .
- Oxygen balance =  $0.0907 + (0.7711 - 0.4922)/2 - 0.2290 = 0.0012 \text{ kmol h}^{-1}$ .
- Hydrogen produced from methane =  $2 \times 0.4536 = 0.9072 \text{ kmol h}^{-1}$ .
- Hydrogen produced from water =  $0.711 - 0.4922 = 0.2789 \text{ kmol h}^{-1}$ .
- Percentage of hydrogen from methane =  $0.9072/1.1852 \times 100\% = 76.5\%$ .
- Percentage of hydrogen from water =  $0.2789/1.1852 \times 100\% = 23.5\%$ .

These results indicate satisfactory material balances for all input and output elements. Results also show that more than 75% of total hydrogen is produced from methane while less than 25% comes from water splitting. With an increase of H<sub>2</sub> production through CH<sub>4</sub> pyrolysis, the CO<sub>2</sub> to H<sub>2</sub> ratio will be reduced to 4.21 in comparison to SMR (CH<sub>4</sub> + 2H<sub>2</sub>O = 4H<sub>2</sub> + CO<sub>2</sub>) from

which 50% of H<sub>2</sub> is produced from CH<sub>4</sub> and 50% comes from water. The CO<sub>2</sub> to H<sub>2</sub> ratio is  $1 \cdot 44/(4 \cdot 2) = 5.5$ . Since there is no CO or CH<sub>4</sub> discharged during the process, both CH<sub>4</sub> conversion and H<sub>2</sub> yield would be 100%. These results further illustrate the benefits of using a cryogenic process for LH<sub>2</sub> production.

#### 4.3. Process stability considerations

The stability of a process is a measure of the capability of the process to maintain steady state when operating conditions change. Because CH<sub>4</sub> and CO remain within the cryogenic process and are recycled, the entire process remains in a steady state operating condition when, for example, the catalyst is gradually deactivated or some disturbance occurs within the system. One way to simulate catalyst deactivation in SMR or WGSR is to vary the reaction temperature in order to affect the reaction rate. CO and CH<sub>4</sub> conversion will vary with the reaction temperature. The variation of the conversions within SMR or WGSR will, in turn, affect the steady state of the process. Table 3 depicts that even with a relatively wide variation of the SMR temperature range (from 500 °C to 900 °C), the output LH<sub>2</sub> and LCO<sub>2</sub> remain unchanged. The ratio of total energy per mole of LH<sub>2</sub> produced and the system efficiencies vary slightly. Thus, the cryogenic process described here offers a more efficient alternative to LH<sub>2</sub> production than the present conventional processes.

## 5. Conclusions

Five processes combining separation and production of liquid hydrogen, directly from methane and landfill gas, were described and flowsheeted. The chemical process simulation results for the first and second law efficiencies, the extent of greenhouse gas emissions and process stability considerations show that highly efficient processes for production of high purity LH<sub>2</sub> are possible by integrating H<sub>2</sub> production and liquefaction processes. For an optimized flowsheet, the extent of H<sub>2</sub> recovery can be 99.99% with purity levels as high as 99.9999% and methane conversion efficiencies of up to 99.99%. As a by-product of liquid H<sub>2</sub> production, high purity liquid CO<sub>2</sub> is also generated as a value added co-product. The total thermal efficiencies of the processes considered exceed 81% and 79% for methane and landfill gas, respectively. The highest energy efficiency calculated is 57% for methane and 51% for landfill gas under the assumption of 10%



heat loss and 30% efficiency for the cryogenic process used. The ratio of CO<sub>2</sub> to H<sub>2</sub> mass in these processes falls between 3.027 g g<sup>-1</sup> and 4.219 g g<sup>-1</sup>. If the input electrical energy to the system is generated from a renewable resource, such as solar or wind, conversion of CH<sub>4</sub> to liquid H<sub>2</sub> via processes considered would be essentially zero emission.

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#### **References**

- [1] C. Huang, R. Jiang, M. Elbaccouch, N.Z. Muradov, J.M. Fenton, *J. Power Sources* 162 (2007) 563–571.
- [2] H.C. Rowles, D.M. Nicholas, H.L. Vines, M.F. Hilton, *Energy Prog.* 6 (1) (1986) 25–32.
- [3] N.Z. Muradov, C. Huang, A. T-Raissi, *Proceedings of the 15th World Hydrogen Energy Conference*, Yokohama, Japan, June 27–July 2, 2004.
- [4] N.Z. Muradov, F. Smith, C. Huang, A. T-Raissi, *Catal. Today* 116 (2006) 281–288.