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HYDRATES BASED CARBON CAPTURE SYSTEM IN TEXAS: A TECHNO-ECONOMIC PERSPECTIVE

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ABSTRACT

This work analyzes the techno-economic factors associated with the production of blue H_2, and hydrates-based capturing of CO_2 produced by sorption-enhanced steam methane reforming (SESMR) of methane from landfill gas (LFG) across various counties in Texas. The SESMR system is coupled with a hydrates-based carbon capture system, and the energy and cost of setting up and running such a hydrates-centered capture facility have been estimated. In doing so, the amount of water and energy required to compress and refrigerate the gas down to hydrate-forming conditions and the capital and operating costs involved in setting up and running such a facility are evaluated in detail. The cost of producing hydrogen (without the carbon capture system) from this analysis is estimated at \$0.5/kg of H_2. The total cost (CAPEX+OPEX) for capturing one metric ton of CO_2 ranges from \$96 (Harris County) to \$145 (Brazoria County). Notably, adding a thermodynamic promoter such as Tetrabutylammonium bromide (TBAB) to the hydrate precursor mixture to achieve favorable thermodynamic formation conditions increases the overall cost (\$107-\$137/metric ton of CO_2 captured). This can be attributed to the increased water requirement necessitating a higher number of reactors, higher refrigeration capacity, and labor costs. The minimum hydrogen cost required for a positive combined net present value (NPV) for a coupled SESMR + hydrate-based carbon capture system for a 30-year project duration is estimated at \$0.9/kg and \$2.4/kg of H_2 for Harris and Brazoria counties, respectively. Furthermore, a 5-year payback period would require a minimum cost corresponding to \$1.35/kg (Harris) and \$4.95/kg (Brazoria) of H_2, demonstrating that the coupled system would be economical only for counties that have a significant hydrogen production potential.

Keywords: Hydrates, Carbon capture and sequestration, Steam methane reforming, techno-economic analysis.

1. INTRODUCTION

The recent surge in the development and adoption of carbon capture and sequestration (CCS) practices targeted towards achieving the 1.5 ºC limit set by the Paris climate agreement is critical to mitigating the deleterious effects of climate change. Environmental carbon dioxide (CO_2) levels have dangerously increased following the industrial revolution, attributable in large part to anthropogenic factors which have invariably been linked to climate change and elevated global temperatures. Active deployment of carbon capture and sequestration practices and usage of alternative cleaner fuels then become inevitable in the face of increasing adoption of fossil fuel-based energy sources that power up nearly every facet of human life.

Clathrate hydrates were discovered in 1810 by Sir Humphrey Davy and are water-based crystalline solids consisting of a guest molecule (such as methane, CO_2, etahne, propane, etc.) trapped in a lattice of hydrogen-bonded water molecules. CO_2 hydrates in particular have received a lot of attention as one of the potential CCS pathways owing to their desirable long-term sequestration properties. Some of these properties include a high storage capacity (184 unit volume of gas at STP conditions in one unit volume of hydrates), higher density than seawater (1040 to 1160 kg/m^3), and stability at moderate oceanic and permafrost depths at a temperature below 10 ºC. Due to these properties, CO_2 hydrates could be potentially stored in deep oceanic basins and permafrost regions, sub-seafloor saline formations and depleted/existing natural gas hydrate reservoirs (via CH_4-CO_2 exchange), provided they meet the thermodynamic criteria (pressure and temperature conditions) required for stable storage [1]. [2] Such hydrates are typically formed when a mixture of water and gas such as CO_2 is subjected to moderately high pressure (~400 psi) and low-temperature (~4 °C) conditions. While the thermodynamics and kinetics underlying hydrate formation in the presence/absence of various promoters have been investigated in detail, the techno-

economic factors underlying the scalable adoption of hydrate technology in the carbon capture industry deserve special attention.

The nucleation and growth of CO_2 hydrates has been extensively studied in the last few decades due to the potential use of CO_2 hydrates for water desalination, gas storage, gas transport, etc. [add any generic ref, like Koh's book, if needed] The formation of CO_2 hydrates in known to be a stochastic and slow process. Studies have worked on improving the nucleation time for formation of CO_2 hydrates and have shown >1000x decrease in nucleation time [cite our previous Mg and Al papers, and maybe a couple more of other groups from those papers]. The growth rate of CO_2 hydrates can be promoted by chemical and mechanical promoters [CO_2 hydrate properties and applications: A state of the art: Saeid Sinehbaghizadeh, Agus Saptoro, Amir H. Mohammadi]. Chemical promoters include the use of TBAB, THF, SDS etc., while mechanical promotion involves the use of stirring, porous media, bubble column reactors and water-sprays. The best reported growth rate in literature was used for the techno-economic analysis in this work [cite that paper here and add 1 line describing there approach].

Although hydrates-based CO_2 capture (HBCC) is considered a promising technology, it's technoeconomic viability and the potential challenges associated with its implementation are currently being studied [Nguyen etal AE-2022, Rezai et al-2022-IJHE]. The CO_2 intake capacity of HBCC is found to be much higher than the conventional MEA based CO_2 absorption for the same amount of water [Nguyen-ref50,51]. HBCC is found to produce a hydrogen stream as pure as 92 vol% from syngas (60 vol% H_2, 40vol% CO_2) [Nguyen-ref 55]. Aspen HYSYS has been used to simulate an HBCC process with and without chemical promoters. It is found that combination of membrane separation with HBCC with TBAB as a promoter has the least total energy consumption. The corresponding cost was obtained to be 24.97$/ton CO_2.

This study investigates the techno-economic factors underlying the utility of using hydrates as a tool to capture and store CO_2 generated by steam methane reforming (SMR) of landfill gas (LFG) collected by various counties across Texas. Specifically, a hydrates-based carbon capture system has been coupled with an SMR system to generate H_2 from landfill gases and store CO_2 in the form of hydrates. The hydrogen produced by SMR is a clean fuel that can be used in a fuel cell to produce electricity, generating just heat and water as byproducts. While the cost of hydrogen production has been evaluated, the techno-economic factors involved in setting up a hydrates-centered facility for carbon capture across various counties in Texas have also been analyzed in detail. In doing so, the energetics associated with the compression and refrigeration process required for hydrate formation have been delineated, and an analysis of the capital and operating costs associated with such a production facility has been carried out. This study constitutes a starting point for assessments of the technical and techno-economic viability of a hydrates-centered future for the carbon capture and natural gas industry.

2. TECHNICAL ANALYSIS

2.1 LFG data

The landfill methane outreach program (LMOP) database contains data on the location and the amount of landfill gas (LFG) collected for more than 2600 municipal solid waste landfills; this can be accessed from the EPA website [3]. This databank (as outlined in Table 1) is used to estimate the amount of LFG collected across various counties (that have a functioning landfill site and an active gas collection system in place) across Texas. The top 10 counties collecting about 75% of the total LFG in Texas (4.5 million m3/day) have been considered for the present analysis.

2.2 Sorption-enhanced steam methane reforming

Steam methane reforming (SMR) is a very commonly used procedure for generating hydrogen from methane (termed as blue hydrogen when paired with a carbon capture system) and currently accounts for about 48% of the hydrogen produced globally. The hydrogen produced from the SMR reaction can be used in fuel cells to generate electricity for a wide range of applications, including transportation, refineries for hydrocracking and hydro-desulfurization (HDS) operations, and production of fertilizers. However, SMR results in significant CO_2 emissions, addressed in the present analysis by coupling the sorption-enhanced membrane reactor (SESMR) system with a hydrates-based carbon capture system, as illustrated in Figure 1.

Sr no	County	Landfill ID	LFG collected (MMSCFD)
1	Harris	1479	9.05
		1465	13.82
		1811	1.18
2	Dallas	11761	2.61
		1475	1.08
		1459	11.38
		1456	5.68
3	Bexar	1509	9.19
		1820	6.59
4	Fort Bend	1812	10.49
		12101	5.08
5	Denton	1480	2.84
		1805	1.29
		1461	9.10
6	Tarrant	1467	4.13
		1463	3.43
7	Galveston	1808	2.77
		1810	3.96
8	Collin	12201	5.87
9	Travis	1464	4.32
		1511	1.33
10	Brazoria	1497	3.87

Table 1. Details of landfills and the amount of gas collected across different counties in Texas. Data obtained from EPA website [3].

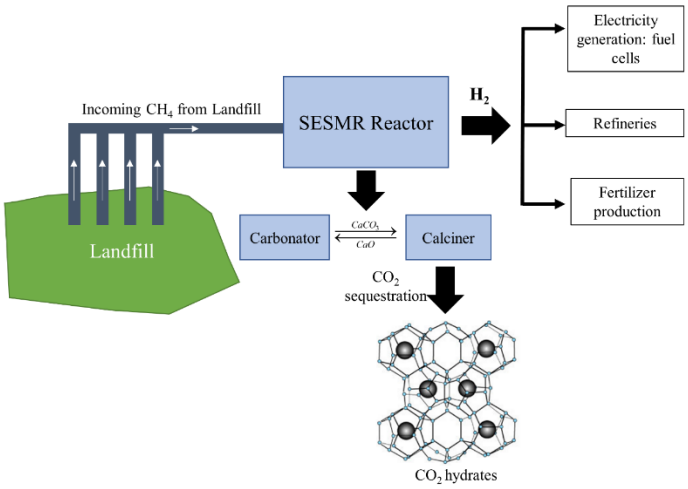


FIGURE 1: ILLUSTRATIVE CONCEPT OF LFG-BASED BLUE HYDROGEN GENERATION VIA SESMR AND CO_2 CAPTURE VIA HYDRATES.

The chemical reactions taking place during a typical SESMR process are:

$$CH_4+H_2O \rightarrow CO+3H_2 \quad \Delta H^0_{298}=206 kJmol^{-1} \quad (1)$$
$$CO+H_2O \rightarrow CO_2+H_2 \quad \Delta H^0_{298}=-41 kJmol^{-1} \quad (2)$$
$$CH_4+2H_2O \rightarrow CO_2+4H_2 \quad \Delta H^0_{298}=165 kJmol^{-1} \quad (3)$$
$$CO_2+CaO \rightarrow CaCO_3 \quad \Delta H^0_{298}=-177.9 kJmol^{-1} \quad (4)$$

Sorption enhanced reforming reaction is a technique that simultaneously produces hydrogen while capturing carbon dioxide and includes catalytic SMR, water gas shift and a CO_2 chemical sorption system using a solid sorbent that aids in improving hydrogen production yields. The carbon dioxide produced during the reaction is captured using CaO adsorbent in a carbonator which is regenerated back in a calciner. In the present analysis, this system is coupled with a CO_2 hydrates-based CCS system wherein the CO_2 emitted by the calciner is further processed to be captured in the form of hydrates. In order to evaluate the amount of CO_2 and H_2 that can be produced via SMR of landfill gases in Texas, results from a previously reported ASPEN Plus process simulation[4] have been used. This study reported production yields of 1.2 mol H_2/mol CH_4 and 0.2 mol CO_2/mol CH_4 at a process temperature of 773K [4].

2.3 Hydrates-based carbon capture

The CO_2 emitted by the calciner could either be collected and stored in tanks, following which it has to be subjected to a compression and refrigeration process along with water to store it in the form of hydrates. To estimate the amount of water required to convert this CO_2 into hydrate, gas uptake capacity, as reported in the work of Mohammadi and Jodat [5], has been used. At a thermodynamic formation condition of 3.2 MPa and 276.15 K, a gas uptake capacity of about 60 mmol of gas/mol of water was obtained at about 120 mins, which is one of the best in class reported values. It is noted that the maximum theoretical uptake rate that can be obtained for CO_2 hydrates, assuming that all the cages will be occupied, is about 174 mmol of gas/mol of water. However, the numbers achieved in practical conditions are lower than this value due to inefficient cage-filling process during hydrate formation. The present analysis assumes that CO_2 capture via hydrate formation will occur as batch processes comprising two hours each. A duration of two hours was used since the hydrate formation rate was observed to saturate around this time [5].

2.4 Hydrates-based carbon capture

The calculation procedure to compress the gas to CO_2 hydrate forming conditions (3.2 MPa and 3 °C) is detailed in this section. A compression time of ten minutes is assumed to compress the gas available in two hours from atmospheric pressure (it is assumed that the collected gas will be available at ambient pressure and temperature conditions) to 3.2 MPa. The compression time has been decided while considering the inlet flow rate constraints for a centrifugal compressor. The compression head (H_{is}) is calculated using [6]:

$$H_{is} = \frac{R}{M}\frac{Z_{avg}T_1}{\frac{(k-1)}{k}}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 1\right] \quad (5)$$

In the above equation, R is the universal gas constant 8.314 kJ/(kmol.K), M is the molecular mass in kg/kmol, Z_{avg} is the average compressibility factor (Z_s+Z_d/2) evaluated at the suction and discharge conditions using Peng-Robinson equation of state, T is the absolute temperature in K, k is the isentropic exponent (C_p/C_v) and p is the absolute pressure in kPa. An isentropic compression process with an isentropic efficiency (η_s) of 0.83 has been used to evaluate the actual compression power (Ghp) in kW as a function of the inlet mass flow rate (w) and compression head (H_{is}) using:

$$Ghp = \frac{wH_{is}}{3600\eta_{is}} \quad (6)$$

The inlet mass flow rate is evaluated using:

$$w = \frac{QMp_1}{8.314T_1Z_1} \quad (7)$$

In the above equation, Q is the inlet volumetric flow rate in m^3/h.

Since the gas in the present analysis has to be compressed to very high hydrate forming pressures (translating to a very high overall compression ratio), the compression process is carried out in multiple stages based on the guidelines for designing compressors as detailed ahead [6]:

1. The overall compression ratio is divided into an equal number of stages such that the compression ratio per stage is lesser than four (r<4) while considering intercooler pressure loss (10 psi).
2. At the end of every stage, the outlet pressure and temperature are evaluated for the calculated compression ratio assuming an isentropic process (η_s=0.83).

3. The compression power per stage is calculated using equations 5 and 6.
4. The gas will be subjected to an intercooling process to bring the temperature at the discharge stage down to ambient conditions before it enters the next stage.
5. The electrical energy requirements are evaluated using a COP of 4.

Figure 2 illustrates the multistage compression process modeled for compressing the gas to 3.2 MPa in the present study.

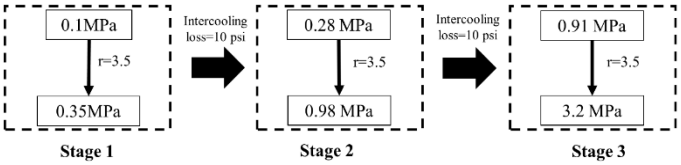


FIGURE 2: THREE-STAGE COMPRESSION PROCESS FOR COMPRESSING THE GAS TO HYDRATE FORMING CONDITIONS (3.2 MPA).

2.5 Energetics of hydrate formation process: Refrigeration

Refrigeration energy accounts for the energy required to cool the reactor down to hydrate formation temperatures (considered as 3 ºC in the present study). This occurs in three stages: Stage 1 consists of sensible heating, the energy required to bring the reactor vessel + water + gas mixture to hydrate forming temperatures (HFT). Stage 2 comprises the dissociation energy, which accounts for the latent heat released when the water molecules rearrange to form solid hydrate structures in the reactor vessel. Stage 3 is related to the energy required to maintain the system at HFT, which would account for the heat losses in the system.

In order to evaluate the energy required for sensible cooling, it is crucial to determine the reactor volume and thickness that would contribute to the thermal mass of the system. To do so, it is assumed that the maximum diameter and height of the reactor are 3m and 6m (aspect ratio=2), respectively. In cases where the amount of CO_2 + water exceeds this volume, a system of parallel reactors would be used. It is noted that the reactor dimensions are similar to the one used in a previous study analyzing CO_2 capture by hydrate formation for gas emission in the steelmaking industry [7]. The reactor wall thickness should be sufficient to withstand hoop and longitudinal stresses for the working design pressures (considered as 10 MPa, which is three times the hydrate forming pressures considered in this study). Accordingly, the wall thickness was evaluated using the following equation as per ASME Section VIII, paragraph UG-27 (used for calculating the thickness of thin-walled pressure vessels):

$$t_1 = \frac{PD}{2SE - 1.2P} \quad (8)$$

$$t_2 = \frac{PD}{4SE + 0.8P} \quad (9)$$

In the above equations, t_1 and t_2 are the thicknesses corresponding to longitudinal and circumferential stresses, respectively. P is the pressure (design pressure=10 MPa), D is the diameter, S is the maximum allowable stress for the reactor material (considered as T316 SS in this study), and E is the welded joint efficiency. The thicker value of the two is taken as the wall thickness, and 0.125 inches is added to this value to account for corrosion over time as per standard practice. Welding factor (E) is 1 and 0.85 for a seamless and welded pipe, respectively. While evaluating S, a safety factor of 4 has been assumed, so the maximum allowable stress for the reactor material is $1/4^{th}$ times the maximum tensile strength (T_{max}) for reactor material (T_{max} for T316SS typically lies around 80,000 psi).

Once the reactor dimensions and the amount of water and gas in each system are determined, the number of reactors required for every County and the sensible energy required to bring this system down to hydrate forming temperatures is evaluated. Heat losses are calculated for this reactor system using a thermal resistance circuit analogy and assuming a natural convection boundary condition around the reactor walls. Dissociation energy is evaluated using a value of 60kJ/mol [8] for CO_2 hydrates. The final refrigeration energy is evaluated by summing up the sensible/dissociation heat requirements and heat losses; the electrical energy is evaluated using a COP of 4.

3. ECONOMIC ANALYSIS

The economic analysis was carried out using an itemized cost estimation to evaluate the unit production cost ($/kg$H_2$) for the SESMR and carbon capture cost ($/metric ton of CO_2) for the hydrates-based carbon capture facility. The economics for setting up and running the facility were classified as capital expenditure (CAPEX) and operating expenditure (OPEX), respectively.

The capital cost and the operating cost for the SESMR process have been adopted from the work of Lee et al. [4], wherein a detailed techno-economic investigation was carried out using an Aspen plus process simulation and itemized cost estimation. CAPEX consists of the equipment costs involved in each process. For the SESMR process, the capital costs include the reactor, compressor, carbonator, calciner and supplement cost (assumed as 20% of the total CAPEX in this analysis). The operating cost includes electricity, labor, membrane, maintenance and other costs. In order to scale up the CAPEX, an exponent of 0.6 is used with the annual hydrogen production capacity (six-tenth rule), whereas operating cost is assumed to increase proportionally with the production capacity [4]. It is noted that the values for electricity cost, discount rate and project year to estimate the annual CAPEX and OPEX used in the analysis of Lee et al. [4] have been modified to reflect the cost of electricity in Texas and the discount rate and project year used in the present analysis.

An itemized cost estimation for evaluating the capital cost for a hydrates-based carbon capture system would include compressors, reactors, refrigeration systems and supplement cost (assumed as 20% of the total CAPEX). The investment cost for the compressors is estimated using the following Douglas correlation [9]:

$$\text{Cost} = \left(\frac{M\&S}{280}\right) 517.5(bhp)^{0.82}(2.11 + F_c) \quad (10)$$

In the above equation, M&S is the Marshall and Swift equipment cost index (2171.6 for 2020), bhp is the brake horsepower and F_c is the correction factor equal to 1.15 for a centrifugal compressor [7].

The investment cost for the reactor (pressure vessel) is estimated using the following [9]:

$$\text{Cost} = \left(\frac{M\&S}{280}\right) 101.9D^{1.066}H^{0.802}(2.18 + F_c) \quad (11)$$

In the above equation, D and H are the diameter and height of the reactor vessel (in feet), respectively. F_c is the correction factor for pressure vessel reactors, which would depend on the material of the vessel and the operating pressure.

In order to estimate the capital cost of refrigeration systems, values reported in the work of Luyben [10] for a single-stage ammonia-based refrigeration system have been used, and a scaling factor of 0.6 with the refrigeration load has been used to scale up the capital cost for industrial-scale systems considered in the present study.

To convert the capital cost into an annual cost, it has to be multiplied by a capital recovery factor (CRF). In order to evaluate the CRF, a discount rate of 10% was used, which is consistent with established practices on valuations of energy and water-related projects [11], [12]. A project period of 30 years was used, which is consistent with the 3+ decades of steady emissions from landfills [12], [13]. Accordingly, a capital recovery factor of 0.106 was used to evaluate the annual capital cost/metric ton of CO_2 captured, as per the following:

$$\text{Capital cost}\left[\frac{\$}{\text{metric ton}_{CO_2}}\right] = \frac{\text{CRF x Total Capital cost}}{\text{Amount of } CO_2 \text{ produced annually}} \quad (12)$$

An average electricity price of $22/MWh (based on the average wholesale electricity price in 2020 (as per EIA data) [14]) was used to evaluate the operating electrical energy costs for compression and refrigeration processes. Maintenance and other costs were assumed to be 2% and 1% of the total CAPEX, respectively [4]. To evaluate the labor cost for the hydrates-based capture system, it was assumed that one operator could handle two machines and a labor rate of $20/hr was used [15].

The overall unit cost for the production/capture system was evaluated using the following:

$$\text{Unit gas capture/production cost} = \frac{\sum_i \text{CAPEX}_i(\$y^{-1}) + \sum_j \text{OPEX}_i(\$y^{-1})}{\text{Amount of gas produced/captured annually}} \quad (13)$$

The overall economics of combining a SESMR system with a hydrates-based carbon capture system has been evaluated using two commonly used metrics: PayBack Period (PBP) and Net Present Value (NPV). NPV measures the time-adjusted returns from a project, whereas PBP provides the time required to recover the investment in a project. The NPV of the combined SESMR+CCS can be evaluated using the following:

$$NPV = \sum_{j=1}^{n} \frac{I_{t=j}}{(1+r)^j} - \left[C_0 + \sum_{j=1}^{n} \frac{OC_{t=j}}{(1+r)^j}\right] \quad (14)$$

In the above equation, I is the income that could be obtained via hydrogen every year, r is the discount rate, n is the project period, C_0 is the capital expenditure and OC is the operating cost. Payback period can be obtained from the time when NPV becomes equal to 0. A net positive NPV indicates that the projected earnings for a project are higher than the anticipated costs in present dollars. It is assumed that positive and negative NPV values indicate investments that would be profitable and those that would incur a net loss, respectively. Higher values of NPV indicate a higher value for a particular long-term investment, whereas a shorter PBP is indicative of a shorter payback or breakeven period.

4. RESULTS AND DISCUSSION

Figure 3 illustrates the amount of CO_2 and H_2 (in million metric tons) that can be captured/produced via steam methane reforming of LFG collected from the top 10 counties in Texas. The highest CO_2 capture and H_2 production potentials are for Harris County, which generates the highest amount of landfill gas (Table 1), yielding about 0.05 and 0.01 million metric tons of CO_2 and H_2 every year. The collective annual CO_2 capture and H_2 production potential for all the counties are about 0.24 and 0.07 million metric tons, respectively. It is noted that the amount of CO_2 captured via SMR of LFG in Texas is a small percentage of the annual CO_2 emissions in the United States, amounting to about 5256 million metric tons in 2019 [16].

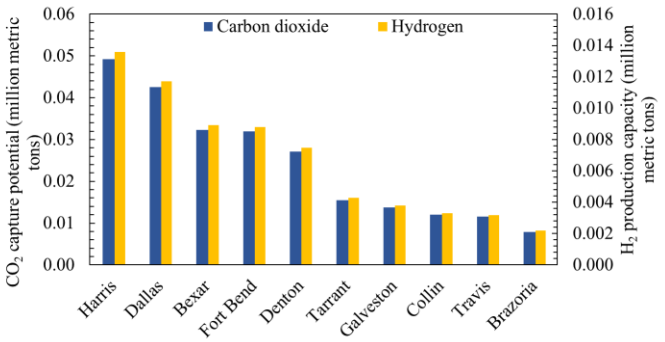


FIGURE 3. TOTAL AMOUNT OF CO_2 AND H_2 THAT CAN BE COLLECTED/PRODUCED ANNUALLY (IN MILLION METRIC TONS) FOR THE TOP 10 COUNTIES IN TEXAS.

The collective amount of hydrogen produced from the top 10 landfills collecting counties in Texas, when used in a fuel cell with 60% efficiency (HHV=39.7 kWh/kg), would produce enough energy (~160 GWh) to power about 15,000 homes every year based on the average annual electricity consumption for a U.S. residential utility customer in 2020 [17]. A preliminary techno-economic analysis for the SESMR technology in Texas suggests a hydrogen production cost of $0.5/kg of H_2 for all the counties considered in the present analysis. It is noted that this does not include the cost of natural gas in the operating cost as it would be available essentially free from landfill gas. However, if the LFG production is low for specific counties, natural gas can be purchased externally and converted into H_2 to keep the reactor running or to scale up the production to reduce overall

costs. When the cost of natural gas is factored in OPEX, the cost becomes \$1.5/kg of H_2, which is in line with the numbers reported in literature wherein hydrogen production cost from steam methane reforming ranges from \$1.25/kg for large systems to \$3.5/kg for small systems [18]. It is noted that these numbers have been evaluated for the SESMR process alone. An in-depth analysis where SESMR is coupled with a carbon capture system is detailed ahead.

Figure 4 quantifies the amount of water that would be required every day to capture all the CO_2 in the form of hydrates for two different test cases. Test case 1 corresponds to a gas uptake rate of 60mmol of CO_2/mol of water, as reported in the work of Mohammadi and Jodat [5]. Test case 2 corresponds to the theoretical maximum gas uptake capacity (174 mmol of CO_2/mol of water) that can be achieved for pure CO_2 hydrates. While a 100% capture efficiency is difficult to achieve in practice, the gas uptake rate can be enhanced by using various mechanical agitation methods and the use of nanoparticles or surfactants such as SDS to increase the gas-water contacts. The highest water requirement is for Harris County (0.92 million liters/day); this is about 0.05% of the water (1700 million liters/day) that is treated by the city of Houston every day [19].

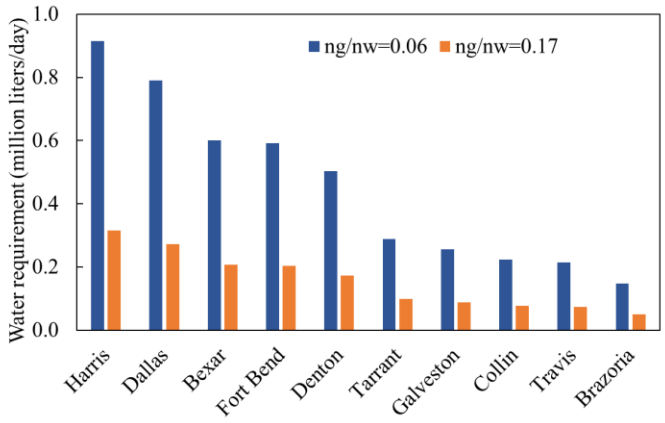


FIGURE 4. AMOUNT OF WATER REQUIRED DAILY FOR CAPTURING ALL THE CO_2 COLLECTED AS HYDRATES.

Figure 5 outlines the total electrical energy required daily to compress, refrigerate and maintain the gas at thermodynamic hydrate formation conditions (3.2 MPa @ 3 ºC for CO_2 hydrates). The refrigeration process takes up most of the energy, accounting for about 64% of the electrical energy. The collective daily total electricity requirements for all the counties (145 MWh) corresponds to 0.01% of the total net electricity generated every day in Texas during the month of June [20].

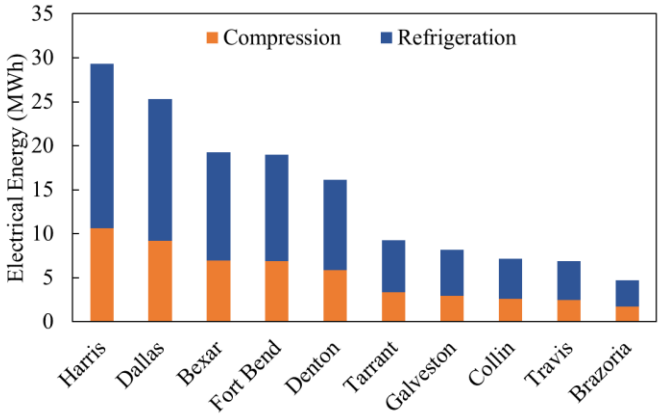


FIGURE 5. ELECTRICAL ENERGY REQUIREMENTS FOR COMPRESSION AND REFRIGERATION PROCESS

Figure 6 outlines the capital cost requirements for compressors, pressure vessel reactors and refrigeration systems to set up CO_2 capture facilities across various counties in Texas. Compressors account for a majority of the capital costs (average contribution ~67%). Similar trends have been reported in past studies where compressor groups have accounted for about 83% of the total investment cost [7].

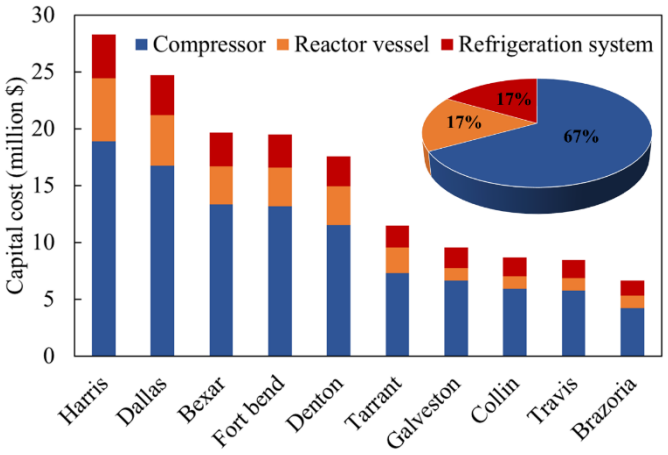


FIGURE 6. CAPITAL COST FOR COMPRESSORS, REACTOR VESSELS AND REFRIGERATION SYSTEM

Table 2 outlines the itemized cost estimations for the annual capital and operating cost to set up hydrate-based carbon capture centers across the top 10 counties in Texas. Annual capital costs are at least three times higher than the operating costs, and therefore one approach to lowering the carbon capture cost would be to bring down the capital costs (compressors which account for a majority of the CAPEX) while keeping the operating costs constant. The high capital cost due to compressors could potentially be decreased if the hydrate forming conditions could be brought down to lower pressures using thermodynamic promoters such as TBAB (Tetrabutylammonium bromide), TBAF (Tetrabutylammonium fluoride) and TBPB (Tetrabutylphosphonium bromide) [21]–

[23]. Such tetraalkylammonium halide salts form hydrates under atmospheric conditions and are termed semiclathrate hydrates since their cage structures are composed of water and the relatively large salt molecule (water-anion framework encapsulating the cation inside the cage that keeps the structure stable) and dodecahedral empty cages capable of storing small sized gas molecules like CO_2. This inherently translates to a very low gas uptake capacity than the pure sI hydrates, wherein gas molecules could potentially occupy all the cages. It is noted that while such tetraalkylammonium halide-based semiclathrate hydrates could bring down hydrate forming pressures, the increase in the amount of water required to capture the same amount of gas when compared to sI hydrates could potentially translate to higher capital cost for reactor vessels and operating costs for refrigeration and labor expenses.

CAPEX (million $/year)					
County	**Compression**	**Refrigeration**	**Reactor vessel**	**Supplement**	**Total**
Harris	2.00	0.41	0.59	0.60	3.60
Dallas	1.77	0.37	0.47	0.52	3.14
Bexar	1.42	0.32	0.36	0.42	2.50
Fort Bend	1.40	0.31	0.36	0.41	2.48
Denton	1.23	0.28	0.36	0.37	2.24
Tarrant	0.77	0.20	0.24	0.24	1.46
Galveston	0.70	0.19	0.12	0.20	1.21
Collin	0.63	0.17	0.12	0.18	1.11
Travis	0.61	0.17	0.12	0.18	1.08
Brazoria	0.45	0.14	0.12	0.14	0.84
OPEX (million $/year)					
County	**Electricity**	**Maintenance**	**Other cost**	**Labor**	**Total**
Harris	0.69	0.05	0.03	0.35	1.12
Dallas	0.59	0.05	0.02	0.35	1.01
Bexar	0.45	0.04	0.02	0.35	0.86
Fort Bend	0.44	0.04	0.02	0.35	0.85
Denton	0.38	0.03	0.02	0.35	0.78
Tarrant	0.22	0.02	0.01	0.18	0.43
Galveston	0.19	0.02	0.01	0.18	0.39
Collin	0.17	0.02	0.01	0.18	0.37
Travis	0.16	0.02	0.01	0.18	0.36
Brazoria	0.11	0.01	0.01	0.18	0.31

Table 2. Itemized cost estimation for annual capital and operating cost (in million $) for ten counties in Texas.

Figure 7 quantifies the cost required to capture one metric ton of CO_2 across different counties in Texas. The lowest carbon capture cost corresponds to Harris County ($96/metric ton of CO_2). Brazoria County has the highest carbon capture cost at $145/metric ton of CO_2. This contrast in costs shows that scaling up of this technology could further bring down costs in the future. It is noted that this cost captures both the capital and operating cost for a model hydrate-based carbon capture system, and CAPEX accounts for a significant portion (~75%) of the overall cost.

In order to investigate the effect of using TBAB on the economics of the carbon capture process, the entire analysis was repeated to account for the modified thermodynamic formation conditions and the water/energy requirements for the revised process in the presence of TBAB. The thermodynamic formation conditions in the presence of 10 wt% TBAB correspond to about 11 ^oC at 1 MPa, and therefore the CAPEX and OPEX were reanalyzed for the CO_2 capture system running at 6 ^oC (corresponding to 5 ^oC overcooling) at 1 MPa. It is noted that the system has been subjected to overcooling instead of over-pressurization to reduce the capital cost requirement for compressors. Pressurization, in this case, could be achieved by using two out of three stages for the compression system, as illustrated in Figure 2. In order to estimate the gas uptake capacity, it was assumed that 50% of the uptake capacity reported in the work of Mohammadi and Jodat [5] (40 mmol of gas/mol of water) could be achieved, as the experiments reported in this paper in the presence of 10 wt% TBAB were carried out at higher pressures and lower temperatures (3.2 MPa and 3 ^oC).

Figure 7 quantifies the capital and operating costs in the presence of TBAB, wherein the overall cost is observed to increase ($107-$137/metric ton of CO_2) when compared to the pure CO_2 hydrates case. This finding seems counterintuitive and can be explained by analyzing the changes in CAPEX and OPEX as detailed ahead:

- CAPEX: An increase in the amount of water required due to lower gas uptake capacity in the presence of TBAB leads to an increase in the number of reactors required to accommodate the hydrate precursor mixture, leading to an increased capital cost for reactors and refrigeration systems. However, this is counterbalanced by a significant reduction in the capital cost for compressors, and therefore the overall capital cost required to capture one metric ton of CO_2 decreases.
- OPEX: The increased number of reactors leads to increased labor and electricity costs corresponding to refrigeration while decreasing the electricity costs for the compression process. The net result is an increase in the operating cost since compression energy contributes to a tiny percentage (4-8%) of the overall operating cost.

The combined impact of the abovementioned changes is a net increase in the overall cost for capturing one metric ton of CO_2. However, it is notable that the increase in overall cost is significant (~12%) only for the top 4 counties producing the highest amount of CO_2. The percentage increase falls to around 4% for all the remaining counties except Brazoria, where the overall cost decreases by 6% when TBAB is used. This implies using a thermodynamic promoter such as TBAB might be beneficial only for small-scale carbon capture systems.

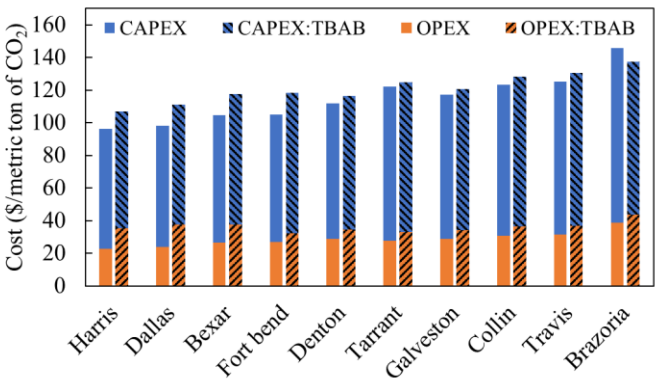
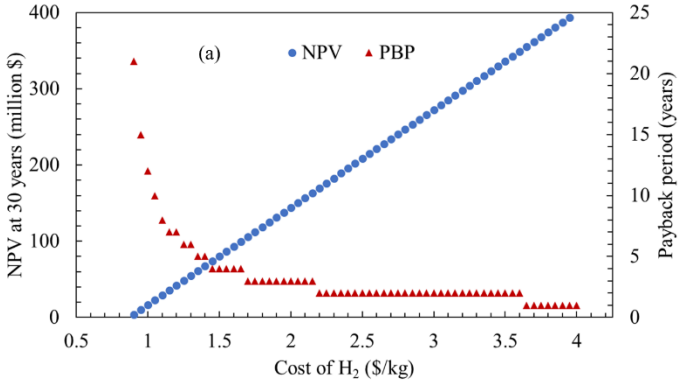


Figure 7. COST (CAPITAL + OPERATING) REQUIRED TO CAPTURE ONE METRIC TON OF CO_2 ACROSS DIFFERENT COUNTIES IN TEXAS.

Figures 8 (a) and (b) outline the NPV and PBP for a combined SESMR+CCS system set up at Harris and Brazoria County. A minimum cost of \$0.9/kg of H_2 would be required to have a positive 30-year NPV for Harris County, whereas the number increases to \$2.4/kg of H_2 for Brazoria County. This accounts for both the carbon capture cost and the cost of producing H_2 via SESMR. The payback period depends on the cost of producing hydrogen, with a 5-year payback period requiring hydrogen costs of \$1.35 /kg and \$4.95/kg for Harris and Brazoria County, respectively. Clearly, producing blue hydrogen from LFG looks attractive from a business standpoint only for counties like Harris County, which could produce significant amounts of H_2 and CO_2 due to the economics of scale. To make this technology viable, the H_2 production capacity at counties like Brazoria County would need to be scaled up, with the additional capacity being used for SMR of natural gas.



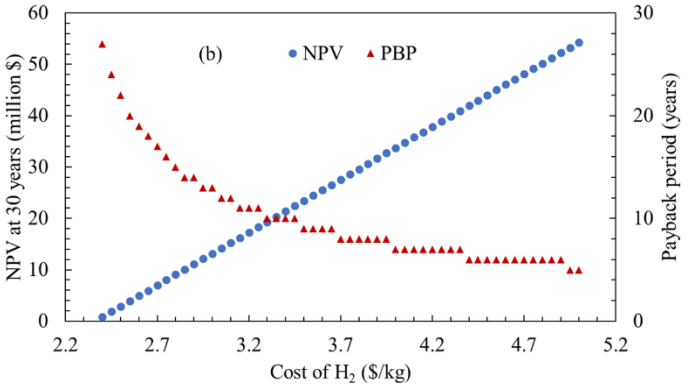


FIGURE 8. NET PRESENT VALUE AT 30 YEARS AND PAYBACK PERIOD FOR A COMBINED SESMR + HYDRATES-BASED CARBON CAPTURE SYSTEM FOR PRODUCING HYDROGEN USING STEAM REFORMING OF LFG IN (A) HARRIS COUNTY (TOP) AND (B) BRAZORIA COUNTY (BOTTOM).

CONCLUSIONS

In summary, this work has analyzed the techno-economic factors involved in producing H_2 and capturing CO_2 produced by sorption-enhanced steam methane reforming of landfill gas across different counties in Texas. The capital and operating costs for the SESMR process for Texas counties are scaled up from previously reported numbers obtained from ASPEN process simulation and itemized cost estimation analysis. The combined hydrogen production potential is about 0.07 million metric tons (enough to power 15,000 homes annually in the U.S.), and the cost of producing this H_2 from LFG stands at \$0.5/kg of H_2 for all the counties considered in the present analysis. This number increases to \$1.4/kg of H_2 if the natural gas for producing hydrogen is purchased externally.

This SESMR system has been used in combination with a hydrates-based carbon capture facility, and the energetics and costs involved in setting up such a facility have been evaluated at length. In doing so, the amount of water required, the energy required for compression and refrigeration, and the capital and operating cost required to set up and run such a facility has been investigated. The collective carbon capture potential for all the counties analyzed in the present chapter amounts to 0.24 million metric tons of CO_2 every year. The water requirements are not significant, with Harris County (which has the highest water requirement amongst all the counties in Texas) requiring only about 0.05% of the total water treated at Houston to convert all the CO_2 gas into hydrates. A total electrical energy of 145 MWh would be required daily to compress and refrigerate the water and gas to hydrate forming conditions, translating to about 0.01% of the total electricity production in Texas. The total carbon capture cost (CAPEX+OPEX) lies in the range of \$96-\$145/metric ton of CO_2 captured and is expected to decrease with subsequent scaling up of the process. Adding a thermodynamic promoter such as TBAB results in a net increase in the overall cost to \$107-\$137/metric ton of CO_2 captured, except for Brazoria County. For Harris County, a minimum cost of \$0.9/kg of H_2 would be required to produce a positive NPV over a 30-

year period, whereas a 5-year payback period would require a minimum cost of $1.35/kg of H_2.

While the present analysis considers separate SESMR and hydrate-based carbon capture facilities for every County in Texas, an alternative approach could be to build a centralized facility to collectively convert all the CH_4 to H_2 while capturing CO_2 in the form of hydrates. Such a facility could utilize the existing natural gas pipelines in Texas to transport CH_4 to the centralized facility and could further bring down the cost of capturing CO_2 and producing H_2 due to the economics of scale.

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