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Techno-economic modeling of carbon dioxide hydrate formation for carbon sequestration

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HIGHLIGHTS

- Techno-economics of a 1 Megaton (Mt)/yr CO_2 hydrate formation reactor is studied.
- Electrical energy requirement is 713 MWh/day (or 260kWh/ton).
- Cost of hydrate formation over a 30 yr period is $ 36/ton.
- Refrigeration & compression account for 41 % & 27 % of total cost, respectively.
- Concept of seabed sequestration of CO_2 as sealed hydrate plugs is introduced.

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ABSTRACT

Significant carbon sequestration capacity (up to 10 Gigatons/yr) will be needed by 2050 to limit the Earth's temperature rise to <1.5 °C. Current worldwide sequestration capacity is only ~40MT/yr, which highlights the need for the development of new and scalable sequestration approaches. One promising approach for long-term sequestration of carbon dioxide (CO_2) is the deposition of CO_2 hydrates (ice-like solids of water and CO_2) on the seabed with artificial sealing (or under marine sediments). Technologically, this involves formation of CO_2 hydrate foam, transport of the foam to the sequestration site, compaction into hydrate plugs, sealing and then disposal. Critical to the techno-economic success of this concept is the ability to rapidly form hydrates. The present group has achieved very high rates of formation of hydrate foam by bubbling CO_2 gas at high flow rates in a bubble column reactor (BCR). This study utilizes recent experimental results on ultra-fast hydrate formation to conduct a detailed techno-economic analysis of the hydrate foam-making process. All analysis is conducted for a 1 Megaton/yr sequestration project with project life of 30 years. Our analysis shows that the energy requirements (assumed as electrical in this study) for hydrate formation equal 260 kWhr/ton and the total cost of hydrate foam production is $36/ton. The biggest cost component is energy, which accounts for 51 % of total cost. A 1 Megaton/yr project will require an initial capital investment of $150 M. Such a project will consume 0.66 million cubic meters of seawater/yr. Contributions of various key processes to the total cost are quantified. Process-wise, the biggest contributors to total cost are refrigeration and gas compression, which account for 41 % and 27 % of the total cost, respectively. Cost of the BCR is only 0.1 % of the total investment cost. Also, gas recirculation in the BCR contributes minimally (0.14 %) to the overall energy requirement. Finally, this study identifies pathways to reduce $/ton costs to increase the viability of this carbon sequestration approach. It is noted that hydrate transportation, compaction and sealing are not included in this analysis which focuses on the techno-economics of rapid hydrate formation only.

1. Introduction

Carbon dioxide (CO_2) levels have been steadily increasing since the industrial revolution, largely due to anthropogenic emissions. The United Nations established the Paris Agreement in 2015 which targets limiting global temperature rise to <1.5 °C above pre-industrial levels [1]. To achieve this, net-zero CO_2 emission targets need to be met by 2050. Carbon capture and sequestration (CCS) technologies are

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increasingly seen as essential to meeting this target [2] in view of the technological, policy-related and societal barriers to rapid decarbonization. According to the Intergovernmental Panel on Climate Change (IPCC), up to 10 gigatons of CO_2/yr will need to be captured and sequestered by 2050 [3]. However, existing global CCS capacity as of 2020 was only ~40 MT/yr [2]. This highlights the need to develop new, scalable, cost-effective CCS approaches.

Conventional carbon capture technology involves the use of chemical solvents/sorbents to capture CO_2 from flue gas streams or air. There exist a wide variety of materials/technologies for carbon capture from various industries or from air or oceanwater. On the other hand, there is only one carbon sequestration technology that is currently being deployed on a large scale [4]. This technique is CO_2 injection in reservoirs or saline aquifers. However, suitable geology for injection is scarce or uncharacterized in many parts of the world. Even in the US, despite decades of research, there exist only 2 Class VI reservoirs which allow CO_2 injection for long-term sequestration only [5]; most injection projects involve enhanced oil recovery. Notably, despite more than 70 pending applications with the Environmental Protection Agency (EPA), no new permits have been issued since 2020, highlighting the challenges and risk assessments needed for permitting [4,6]. Key challenges with geological injection include high monitoring costs (due to large areas and decades-long duration), risks associated with CO_2 leakage, risks of seismic activity and lack of appropriate geology in many large carbon emitting nations like China, India, Japan etc. [7,8]. Alternative sequestration technologies include CO_2 mineralization in geological sites of rocks like basalt [9,10], microbial CO_2 sequestration [11], embedding CO_2 in concrete, chemicals, etc. [12]. While these technologies are promising, they all have challenges. Importantly no such technology by itself is adequate to address gigascale sequestration requirements. **Overall, additional options for sequestration need to be urgently added to the basket of available solutions**. This study analyzes CO_2 hydrates-based carbon sequestration; this topic has gained interest in the scientific community over the last decade [7].

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, ethane, propane, etc.) trapped in a lattice of hydrogen-bonded water molecules [13]. CO_2 hydrates can be synthesized at medium-pressures (>400psig) and low temperatures (<5 °C), with 6 water molecules trapping 1 CO_2 molecule (on-average) [7,13]. Nucleation and growth of CO_2 hydrates has been studied for potential use of CO_2 hydrates for water desalination, gas storage, gas separation, gas transport, etc. [13–17]. However, there are very few studies on the techno-economics of hydrates-based systems. Economics associated with propane hydrates-based desalination was studied and the cost was estimated to be only $\$1.11/m^3$ of water [18]. Studies on hydrates-based carbon capture from syngas streams yielded a cost of $ 25/ton CO_2 [19]. Additionally, the energy consumption for hydrates-based CO_2 separation from CO_2/H_2, along with subsequent transport and sequestration of slurries has also been studied [20]; it was seen that gas separation accounted for 70 % of total energy consumption.

This study focuses on hydrates-based marine sequestration of CO_2. The general topic of marine geological sequestration of CO_2 has gained recent interest [21], which can be attributed to its wide-ranging applicability, relative safety (sequestration sites can be far away from aquifers), and stable conditions near the seafloor. Major methods for marine sequestration as per literature include sequestration as hydrates in shallow sediments (approximately 300 m below seabed) [22], sequestration in sub-seabed aquifers [23], and CO_2-CH_4 replacement sequestration [24]. While these technologies seem promising, their implementation is hindered by challenges which include lack of permeability in shallow sediments, high pipeline pressures, low CO_2-CH_4 replacement efficiency and damage to the marine ecosystem in the event of a leak, etc. [21].

This study focuses on an alternative approach for hydrates-based sequestration and involves sequestration on the seabed (Fig. 1). It is noted that geological sites where CO_2 hydrates can be thermodynamically stable (and where long-term sequestration would be technically viable) include subsea porous media under marine sediments, on the seabed with appropriate sealing, and deep under the permafrost regions [7,25,26]. Among these, sequestration on the seabed poses the least engineering challenges [4]. However, sequestering on the seabed will need sealing to prevent dissociation of hydrates in seawater, as was seen in previous field tests [27,28]; this will involve the use of sealing materials which are bio-friendly, non-degradable, mechanically burst resistant and CO_2 impermeable. Overall, our concept involves rapid

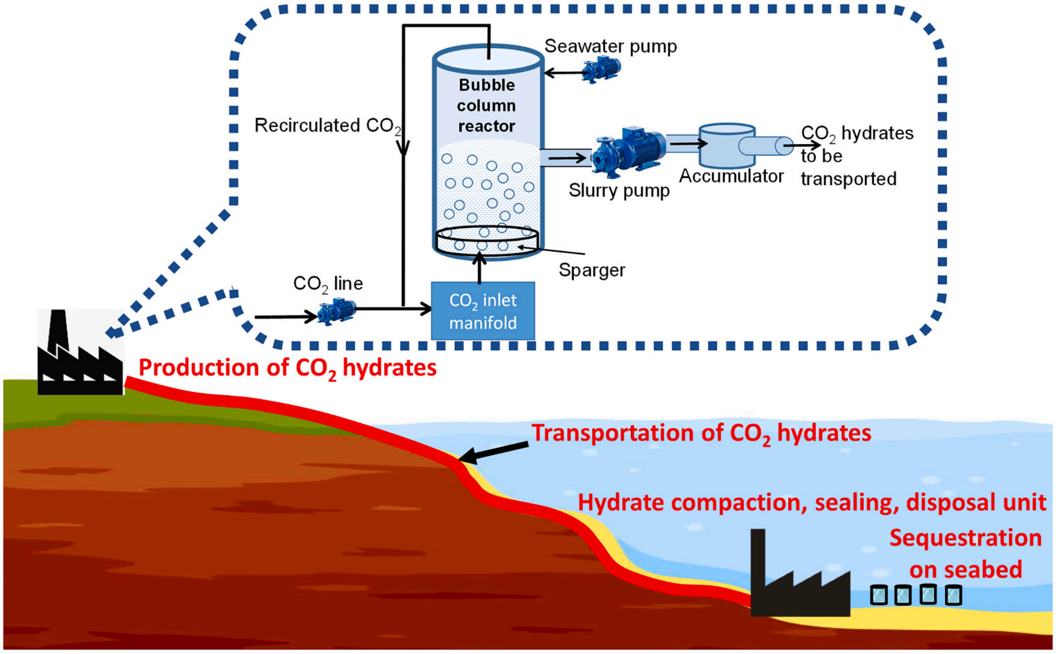

Fig. 1. Schematic illustration of the concept of hydrates-based carbon sequestration on the seabed. This study analyzes the techno-economics of hydrate foam formation in a bubble column reactor. Other aspects involved in sequestration are not analyzed presently.

synthesis of hydrate foam in a bubble column reactor, pipeline transportation to sequestration site, compaction of hydrates into plugs (to remove excess water and increase density), sealing and then disposal. A key advantage of this approach is its high storage density, wherein 1 Megaton CO_2 can be sequestered in a 1 km^2 area as a 3 m thick layer of solid hydrate on the seabed [7]. This area requirement is at least 10 times smaller than the area footprint of geological injection projects, which also reduces monitoring and remediation/intervention costs. The higher density of hydrates (1040–1160 kg/m^3) compared to seawater further helps long-term sequestration. Another key value proposition of hydrates-based sequestration is that hydrates can be made from relatively impure CO_2 streams (50–60 % purity), thereby reducing overall CCS costs.

While there are numerous studies on CO_2 hydrate formation, with some analyzing the techno-economics of hydrates-based carbon capture [19,29], there is no study on the techno-economics of hydrates-based carbon sequestration using captured CO_2. Furthermore, while hydrates-based sequestration has been discussed in literature, it is limited to the CO_2-CH_4 replacement method, and sequestration under the seabed under shallow sediments wherein the sealing mechanism for long-term sequestration is provided by the geological landscape (in contrast to our approach which relies on artificial sealing).

This study conducts a detailed techno-economic assessment of the hydrate foam formation process. We recognize that foam transportation, compaction, sealing are important aspects of the overall technology. However, they are very distinct from hydrate formation, and hence not included in this study, which focuses on techno-economics of hydrate formation only. Hydrate foam-formation projects could be developed topside (e.g., on decommissioned oil-gas platforms) in close proximity to sequestration sites, on the coast, or subsea (on the seabed). Subsea hydrate formation is very attractive since the required thermodynamic conditions naturally exist. However, the installation and operational challenges of running a hydrate formation process subsea are largely unknown, besides there is no cost data available to conduct even a preliminary techno-economic analysis. For this reason, this study analyzes hydrate formation on the seacoast for which there is sufficient existing data available.

In summary, this study analyzes the techno-economics of forming CO_2 hydrates in bubble column reactors (BCR) noting that such a study can inform other hydrates-based applications as well. Hydrate foam formation for a 1 Megaton/yr project is considered, which is typical of industrial sequestration projects. Capital expenditures (CAPEX) and operating expenditures (OPEX) are estimated for a 30-yr long project. A key consideration in the analysis of any hydrates-based systems is the production rate, noting that hydrates form at very slow rates. Significantly, hydrate formation rates used in the techno-economic analysis are based on recent experimental results from our group [30], which demonstrate 6× faster hydrate formation than state-of-art. The fraction of CO_2 gas converted to hydrates per pass through the BCR (conversion fraction) is a key process parameter, which determines the extent of recirculation. The influence of conversion fraction on the techno-economics is analyzed. The contribution of various processes (compression, cooling etc.,) and components like land, working capital etc., to the total cost is quantified. Potential pathways to reduce the total cost are outlined with the objective of making this technology cost-competitive.

2. Methodology

2.1. Hydrate formation rate measurements which inform present techno-economic analysis

The analysis used in this study is based on recent experimental findings from the group [30], that report >6 times higher hydrate formation rates compared to the fastest reported in literature. This result is even more significant as no traditional chemical promoters were used (e.g., sodium dodecyl sulfate (SDS)), which would lead to significant environmental concerns. This increased rate is the result of coupling magnesium-based promotion of hydrate formation [15] with high gas flow rates in an open-system bubble column reactor (BCR), with constant inflow and outflow of gas. This approach continuously renews the gas-water-hydrate interface thereby significantly increasing hydrate growth rate. Experiments were conducted [30] with seawater (deionized (DI) water with 3.5 wt% NaCl added) and DI water at operating temperature (T_o) ranging from 1 to 2 °C, pressure (P_o) of 2.86 MPa (400psig) and 3.54 MPa (500psig), and inlet gas flow rate of 1.2 kg/h. It is known that the addition of salt slows down hydrate formation [31], and it was indeed observed so in our experiments at low pressure (2.86 MPa). However, at the higher pressure of 3.54 MPa, saltwater hydrate formation rates were nearly as high as those with DI water, which is a significant finding. From an applications perspective, the use of seawater for hydrate formation offers significant advantages since desalination-related costs can be eliminated. The present techno-economic analysis therefore considers hydrate formation with saltwater at $P_o = 3.54$ MPa and $T_o = 1$ °C.

The current analysis assumes that the performance of BCRs will scale linearly with reactor size (volume); this is a reasonable assumption if the process intensification conditions can be maintained. Our experiments [30] were conducted in a 650 ml reactor and yielded hydrate formation rates of ~2 kg/h/lit of reactor volume, which would translate to 12.5 tons of CO_2 sequestered per year. Presently, we assume that a CO_2 sequestration rate of 1 Megaton/yr reactor can be linearly scaled from our current reactor. This sequestration rate is the amount of CO_2 consumed to form hydrate foam inside the bubble column reactor. Excess CO_2 needed for pre-dissolution of CO_2 in water, and any CO_2 lost during transportation, sealing and disposal is not considered in the present study. This requires an inlet gas flow rate of 1.54×10^5 kg/h and water flow rate of 7.83×10^5 kg/h for a 12 m tall ($H_g = 2$ m, $H_w = 10$ m as per Fig. 2) and 3 m diameter reactor operating at $P_o = 3.54$ MPa and $T_o = 1$ °C. In our experiments [30], we measured a 50–70 % conversion fraction of the inlet gas per pass; in this study the unreacted gas will be modeled as recirculated. Also, this study considers a wider range of conversion fraction (25–75 %) for the same inlet gas flow rate, noting that a 1MT/yr sequestration plant would correspond to 75 % conversion.

2.2. Scope of the techno-economic analysis

Fig. 2 is a schematic depiction of the process for producing CO_2 hydrate foam by bubbling CO_2 gas in stagnant water in a BCR. The dotted region indicates the domain that is analyzed in the present techno-economic model. Experimental results show that hydrate growth originates from the interface and spreads towards both sides of the interface. Therefore, a headspace of 2 m is provided in the BCR for hydrate foam growth. A feed gas stream of pure CO_2 is supplied at P_{Cs}, T_{Cs}, considered to be equal to STP for this study. The cost of CO_2 is not considered as the focus of this study is to evaluate sequestration costs only. The feed gas is first compressed to operating pressure (P_o) using a three-stage compression process described in section 2.3. The gas is cooled back to atmospheric temperature after each compression stage and then cooled to operating temperature (T_o). The feed gas is mixed with the recirculated gas (exiting reactor at P_o, T_o) using a gas mixer, the cost of which is included in auxiliary equipment costs. The combined gas stream undergoes further compression and intercooling (represented by RGC in Fig. 2) so that it can be pumped into the BCR for hydrate formation. The corresponding inlet pressure is P_i, as represented by eq. 1 shown below, where ρ_g is the gas density, g is the gravitational constant, η is the initial bubble diameter, and γ is the surface tension of water. The inlet gas is assumed to have an initial bubble diameter (η) equal to 0.25 mm and is assumed to be distributed uniformly across the reactor using a sparger.

$$P_i = P_o + \rho_g g H_w + 2\gamma/\eta \quad (1)$$

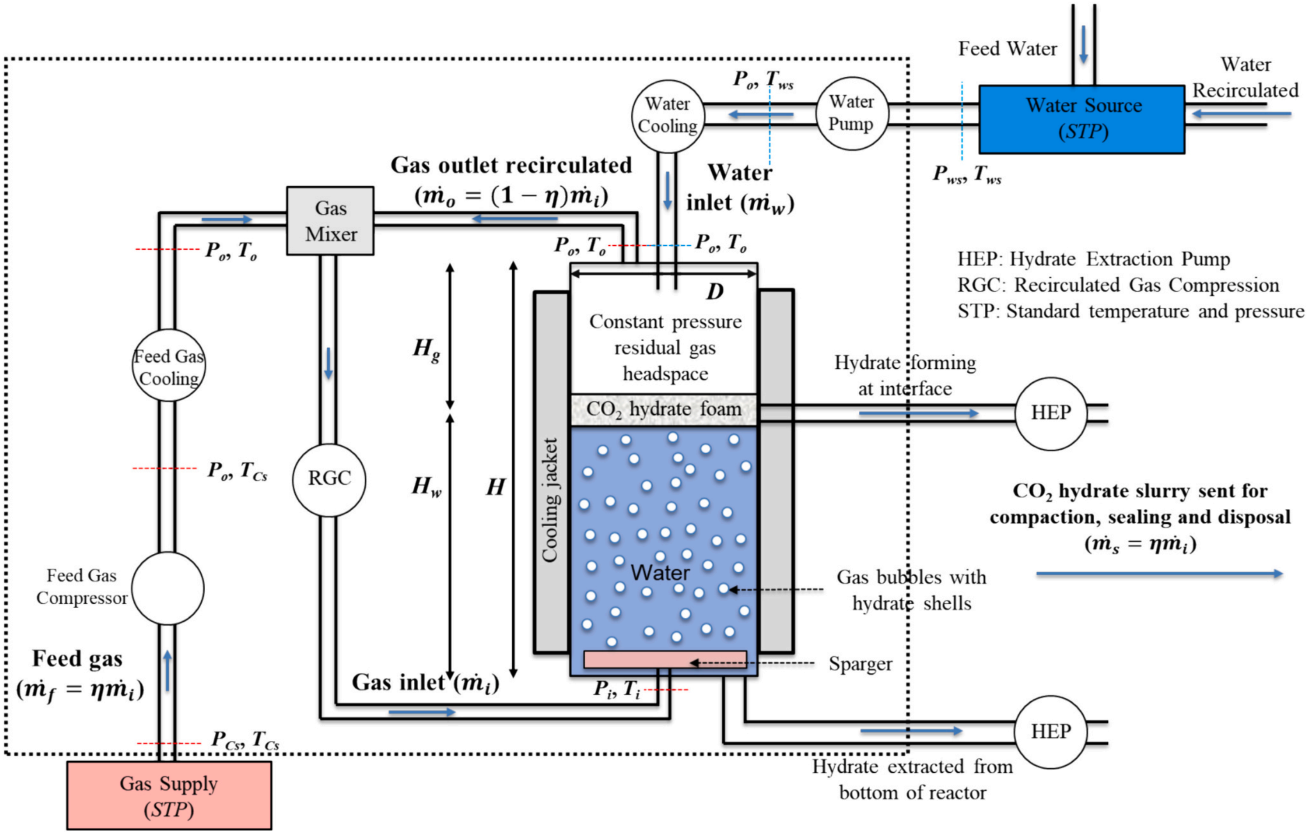

Fig. 2. Schematic depiction of production of CO_2 hydrate foam (dotted lines represent the domain considered in the present techno-economic analysis).

It was observed from experiments [30,32] that hydrate shells that turn into hydrate foam accumulate either on the gas-water interface or sink to the bottom of the reactor. Two hydrate extraction pumps are therefore located at these two locations on the BCR. As mentioned previously, techno-economic analysis of these pumps is not included in the present study (which focuses on formation only). The heat generated from hydrate formation, heat gain from walls of reactor and other heat gain processes need to be compensated for by the cooling jacket placed around the reactor to maintain its operating temperature. To maintain continuous hydrate formation, a constant feedwater (seawater) stream is provided to the reactor from the gas headspace. The introduction of feed water from the top of the BCR also helps break down the hydrate shells into hydrate foam which can then be extracted for a continuous process. The feed water stream is seawater which enhances the techno-economic proposition of this concept as it eliminates the cost of procurement and transportation of freshwater (also P_{ws}, T_{ws} is at STP). Feedwater is cooled to operating conditions before injection into the reactor.

2.3. Estimating the energy consumption for hydrate formation

The process to compressing CO_2 to the operating pressure is carried out in three stages based on the guidelines for designing compressors [33]. A compression ratio of 3.6 and an intercooler pressure loss of 10 psi is considered. The outlet temperature after each compression stage (T_{out}) is estimated using an isentropic efficiency of $\eta_s = 0.83$ as shown in eq. 2. After each compression stage, the temperature is cooled back to inlet temperature. The compression head (H_{is}) is evaluated using eq. 3, which is then used to estimate the gas horsepower (*ghp*) as shown in eq. 4. Summing the *ghp* for the three-stage compression of feed gas, along with the compression for recirculation provides the net energy requirement for the compression process.

$$T_{out} = \frac{T_{in}}{\eta_{is}}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 1\right] \tag{2}$$

$$H_{is} = \frac{R}{M}\frac{Z_{avg}T_{in}}{(k-1)/k}\left[\left(\frac{p_2}{p_1}\right)^{\frac{k-1}{k}} - 1\right] \tag{3}$$

$$ghp = \frac{m_{\dot{CO_2}}H_{is}}{\eta_{is}} \tag{4}$$

In the above equations, R is the universal gas constant, M is the molar mass of CO_2, Z_{avg} is the average compressibility factor evaluated at the suction and discharge conditions using Peng-Robinson equation of state [34], T_{in} is the absolute temperature at suction, p_2 and p_1 are absolute pressures at discharge and suction respectively, k is the isentropic exponent and is considered to be 1.289, and $m_{\dot{CO_2}}$ is the mass flow rate of CO_2 at any given section. Further details on energetics of gas compression are reported in [33,35].

Next, the net refrigeration load or total cooling requirement to maintain continuous operation of the reactor at 1 °C is estimated. This includes the energy needed for cooling of feed gas, feed water, removing the heat released during exothermic hydrate formation and other heat gained by the BCR from outside convection. The refrigeration load for feed gas cooling includes the energy requirement to cool down the gas from T_{out} (eq. 2) to T_{in} after each compression stage (termed as intercooling), and then to further cool down the compressed gas to operating conditions. Feed water cooling includes the cooling of water from source conditions, which are considered to be ambient conditions, to the operating conditions. The corresponding cooling energy required for gas and water can be evaluated as equal to $\dot{m}\Delta h$, where $\dot{m}$ is the mass flow rate of gas or water, and Δh is the enthalpy difference between the source and the operating conditions. The specific heats and enthalpy (h) used for this analysis are estimated for different conditions from the CoolProp library in Python. The cooling to compensate heat losses is estimated by conduction across stainless steel walls of given thickness of 11.7 cm, assuming a 5 °C temperature difference across the walls of the reactor. This corresponds to a conduction loss of 73 kW. The cooling energy required to remove the heat of hydrate formation can be evaluated as $\dot{m}_s \Delta H$ where ΔH is the heat of release for hydrate formation (ΔH = 60 kJ/mol), and $\dot{m}_s$ is the sequestration scale, which is the rate at which CO_2 is converted to hydrates. The electrical energy requirement is evaluated from total cooling energy needed using a COP of 4.

2.4. Estimating the costs associated with key processes

The key processes for hydrate formation include compression, refrigeration, and gas and water pumping into a BCR. The investment cost of compressors is estimated using the Douglas correlation [36] as shown in eq. 5 where M&S is the Marshall and Swift equipment cost index (2171.6 for 2020), *bhp* is the brake horsepower evaluated from eq. 4 as described in [33], and $F_{c,c}$ is the correction factor equal to 1.15 for a centrifugal compressor [37].

$$Compressor\ Cost = \left(\frac{M\&S}{280}\right) 517.5 (bhp)^{0.82} \left(2.11 + F_{c,c}\right) \tag{5}$$

The thickness of the BCR is estimated equal to 11.3 cm based on a working pressure of 10 MPa (such that a factor of safety of 3 is established). This thickness is sufficient to withstand the hoop and longitudinal stresses, and was evaluated using the guidelines in ASME section VIII, paragraph UG-27. The investment cost of the reactor is estimated using eq. 6 provided below [35], where M&S is the same as that of compressors, D and H are diameter and height of the reactor vessel, and $F_{c,v}$ is the correction factor for the reactor vessel and equals 9.175.

$$Reactor\ Cost = \left(\frac{M\&S}{280}\right) 101.9 D^{1.066} H^{0.802} \left(2.18 + F_{c,v}\right) \tag{6}$$

The seawater pumping and electricity costs are estimated using the seawater desalination report for the Texas water development board [38], wherein a pump efficiency of 75 % is considered and the annual electricity requirement is reported for continuous operation. The capital cost of refrigeration is evaluated using a single-stage ammonia-based refrigeration system with a scaling factor of 0.6 with the refrigeration load estimated using eq. 7; this is adopted from the study of Luyben [39].

$$Refrigeration\ Cost\ (\$) = (Net\ Refrigeration\ Laod\ in\ MW)^{0.6} * 1.936 * 10^{6} \tag{7}$$

2.5. Estimating the total capital investment (TCI) or CAPEX

The net capital expenditure (CAPEX or TCI) in this study is evaluated using the methodology provided in [18,36]. The CAPEX comprises of fixed capital investment (FCI), working capital and startup costs. Working capital includes the raw material for one-month supply, accounts receivable, accounts payable, taxes payable, etc. This study considers that 15 % of the TCI be allocated as working capital. Startup costs include start-up labor, loss in revenue during debugging of the processes, etc., and is considered to be 10 % of the fixed capital investment (FCI). FCI comprises of direct capital costs (DCC), indirect capital costs (ICC) and contingency costs (C_{cont}). Direct capital costs (DCC) comprise of total installed cost of key equipment (TIC) and supplementary costs (C_{supp}). TIC includes the installed cost of gas compressors, bubble column reactor, refrigeration systems and water pumps. Supplementary cost includes land cost (2 % of TIC), water intake and disposal infrastructure (10 % of TIC), and site development and auxiliary equipment (15 % of TIC). Indirect capital costs include the cost of insurance, freight and tax (1.5 % of DCC), overhead cost (15 % of DCC), engineering cost (3.5 % of DCC), and project development (0.5 % of DCC). A contingency cost (C_{cont}) equal to 20 % of DCC is considered to account for unpredictable events such as storms, floods, strikes, errors in estimates, design changes, etc. All these components of CAPEX are summarized in Table 1.

Table 1
Summary of costs in total CAPEX (TCI) of $150 M for a 1MT/yr hydrates-based sequestration project.

Cost type	Cost component	Evaluation method	Cost (in million $)
TIC	Gas compressors	Eq. 4 [36]	37.3
	Water pumps	[38]	1.24
	Refrigeration system	[39]	24.0
	Bubble column reactor	Eq. 3 [35]	0.2
Supplementary cost (C_{supp})	Land cost	2 % of TIC	1.3
	Water intake and disposal infrastructure	10 % of TIC	6.3
	Site development and auxiliary equipment	15 % of TIC	9.4
ICC	Insurance, freight and tax	1.5 % of DCC	1.2
	Overhead cost	15 % of DCC	12.0
	Engineering cost	3.5 % of DCC	2.8
	Project development	0.5 % of DCC	0.4
Contingency (C_{cont})	To account for unpredictable events	20 % of DCC	16.0
Working Capital	Raw material for one-month supply, accounts receivable, accounts payable, taxes payable, etc.	15 % of TCI	21.8
Startup Costs	Start-up labor, loss in revenue during debugging of process, etc.	10 % of FCI	11.2

2.6. Estimation of OPEX and annualized CAPEX

The operational expenditure (OPEX) comprises of operational costs associated with compression, intercooling, cooling (to cool feed gas, feed water, reactor and account for other heat gains), labor costs, maintenance costs, and other costs. Maintenance and other costs were assumed to be 2 % and 1 % of the total CAPEX, respectively [40]. To evaluate the labor costs, a correlation [41] was used to obtain the number of operating personnel at a given time to be equal to 4. Each operator is assumed to work 5 shifts per week, and the plant runs 365 days with 3 shifts per day. This adds up to a total of 18 operators. A mean salary of 75,000 USD is considered for the operators. In practice, the entire process could be automated, so this should be considered a starting point. All of the energy requirements required for hydrate production are assumed to be met by electricity. An electricity price of $ 71.3/MWh was used to estimate the cost of energy; this is the average price in 2022 for industrial applications in the state of Texas as per the US Energy Information Administration (EIA) [42]. The sensitivity of OPEX to the price of electricity was considered, with the price varying from $ 10–110/MWh.

To compare the relative importance of CAPEX and OPEX, the overall investment cost (total CAPEX) is converted into an annual CAPEX by using the capital recovery factor (CRF) as shown in Eq. 8. A discount rate of 10 %, and a project period of 30 years is used to obtain a CRF of 0.106. The values for the life and discount rate are consistent with existing sequestration projects [4] and other established practices on valuations of energy and water-related projects [43].

$$Annual\ CAPEX\ (\$/ton) = \left(\frac{CRF*Total\ CAPEX}{Sequestration\ scale}\right) \tag{8}$$

Key assumptions/limitations associated with the current modeling approach are summarized below:

- Challenges associated with materials compatibility with seawater have not been analyzed. The reactor is considered to be made of stainless steel. For subsea applications, water contacting surfaces will need to be coated with a seawater-resistant material or the reactor will need to be built of specialty alloy steels. However, this might not

affect the total costs significantly, as per current findings detailed later.
- Pressure head losses in heat exchangers for gas and water cooling are unaccounted for.
- The economics associated with hydrate extraction from the reactor, transportation, compaction, sealing and disposal is not accounted for. Water recirculation can be implemented after hydrate compaction to reduce water pumping and cooling costs, which has also not been accounted in the present study.
- Experimental results for hydrate formation in a lab-scale reactor are assumed to scale linearly with volume for the industrial scale reactor; this can be achieved if the process intensification conditions are maintained in large reactors. It is observed in our experiments [30] that the number density of bubbles and the gas-water interfacial area are the key parameters which determine scalability of hydrate formation in a BCR. If these parameters can be made to scale linearly with volume, the linear scaling approximation will be accurate.

3. Results and discussions

3.1. Energy requirements for a 1 Megaton/year project

The total energy (electrical) requirement for a 1 Megaton per year project is estimated at 713 MWh per day. The highest energy requirement (Fig. 3) is for cooling to offset the exothermic hydrate formation process (36.8 %). This requirement is directly proportional to the scale of the sequestration project and will be unchanged if hydrates are formed subsea. Energy requirements to compensate for other losses such as conduction losses will be lower if processing is done subsea (where ambient temperature is lower); however, the energy requirements for compression will increase correspondingly. Furthermore, depending on the location, the conditions subsea could likely cause liquid CO_2 formation which will reduce the hydrate formation rates.

Feed gas compression accounts for 31.6 % of the total energy requirement. The feed gas compression energy requirement is directly proportional to the gas flow rate through the feed gas compressor (eq. 4), which is the same as the rate at which CO_2 is being sequestered (or sequestration scale). The high energy demand is attributed to the high gas flow rate considered in this study, which allows fast hydrate growth, and the condition to meet 1MT/yr sequestration requirement. This component of cost will increase significantly if hydrates are produced subsea since additional pressurization will be needed.

Energy demand for cooling water (for hydrate formation) accounts for 18.4 % of the total demand; this can be mitigated by water recirculation. Additionally, this component of cost will reduce significantly if hydrates are produced subsea instead of on land (due to the lower ambient temperature).

Feed gas cooling makes a 10.2 % contribution to the overall energy requirement, indicating that atmospheric temperature conditions for feed CO_2 streams align well with a hydrates-based sequestration approach. If the feed gas is pumped to the seabed for hydrate formation, it's temperature will be close to 4 °C instead of 25 °C considered presently. This will reduce the feed gas cooling requirement significantly. The 10.2 % contribution is for cooling from 25 °C to 1 °C, suggesting that further reduction in temperature, e.g. to −1 °C, would not cause a major increase in the energy demand. A lower temperature would also help reduce the compression requirements thereby reducing overall energy consumption. This aspect motivates further studies on this topic to obtain optimized operating conditions from an economic perspective.

Notably, the compression associated with recirculation accounts for only 0.14 % of the total energy consumption. This indicates that a low conversion fraction does not significantly impact the economics of the overall approach. However, a low conversion fraction will result in a smaller scale of sequestration from the bubble column reactor. To increase the scale of sequestration, additional reactors will need to be incorporated, which is realistic given the relatively low water pumping and reactor costs.

3.2. Initial investment cost for a 1 megaton/year project

Fig. 4 illustrates the breakdown of initial investment costs for a 1 Megaton per year sequestration project, corresponding to a 75 % conversion fraction. The total capital investment (TCI) is estimated at $150 million, with compressors accounting for the largest share at 24.8 %. This is attributed to the moderately high-pressure requirement and the multi-stage compression process. This study assumes that CO_2 is

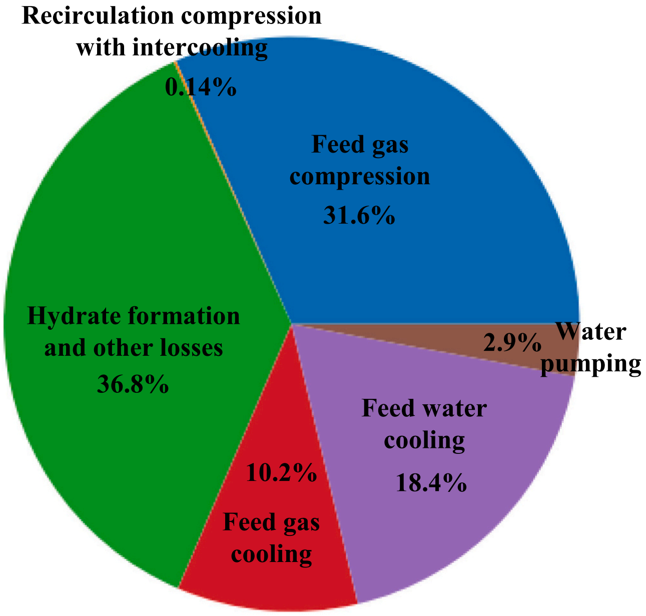

Fig. 3. Relative contribution of various processes to the total energy requirement of 713 MWh/day (or 260 kWh/ton) for a 1MT/yr CO_2 hydrate foam production process.

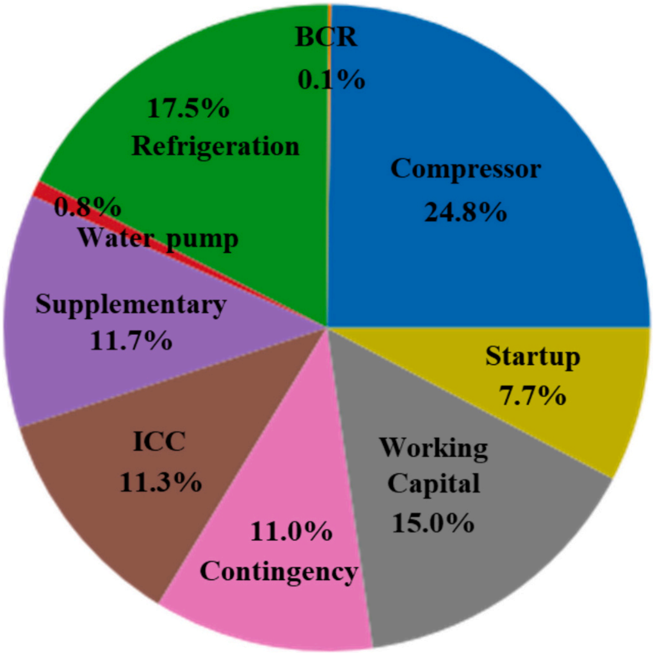

Fig. 4. Components of total capital investment (of $150 M) for a 1 MT/yr CO_2 hydrate foam production process.

supplied at atmospheric pressure; compression costs will be lower if the carbon capture plant were to supply CO_2 at elevated pressures. The refrigeration system is the second-largest contributor and accounts for 17.5 % of the TCI. These costs will reduce significantly if the hydrate foam production process is carried out in a subsea environment, wherein the ambient temperature is 4 °C instead of the 25 °C, considered in this study. However, subsea installations will turn out to be more expensive. The cost of pumping water and the bubble column reactor are low, and account for 0.8 % and 0.1 % of the TCI. This suggests that if the conversion fraction from a single BCR is low (such as 25 %), the pressurized gas can be redirected to another BCR without a significant increase in total cost. Accordingly, this strategy can enhance the overall conversion of pressurized gas and thereby increase the scale of sequestration achieved.

With the total installation cost of key equipment accounting for 43.2 % of the TCI, the corresponding contributions of the other parts of CAPEX are depicted in Fig. 2. Supplementary costs account for 11.7 % of the total and can increase significantly based on the distance between the capture and storage site as gas transportation costs are not explicitly included in the present study. Furthermore, the cost of water intake and disposal infrastructure (part of supplementary cost), will also increase if the installation is implemented subsea to reduce refrigeration requirements. Indirect capital costs (ICC) depend on the location selected for the proposed project and was evaluated to be 11.3 % of TCI for this study. The working capital and startup costs account for a total of 22.7 % of TCI, with the cost considered for contingency equal to 11.0 %.

3.3. Influence of conversion fraction and price of electricity on total cost

Fig. 5 illustrates the impact of the conversion fraction on the scale and cost of hydrate production. As per the modeling framework utilized in this study, there is a linear increase in sequestration rate with higher conversion fractions. Interestingly, the total cost decreases with increasing conversion fraction. This phenomenon is explained by the fact that both the energy for compression and heat release from hydrate formation, which are the two primary contributors to net refrigeration load, increase proportionally with the sequestration scale. The refrigeration cost rises with the refrigeration load with a power of 0.6 (eq. 7), resulting in an overall cost reduction as the sequestration scale increases. Similarly, although the feed gas flow rate is higher for achieving a greater sequestration rate, the compressor cost rises with flow rate at a power of 0.82 [33], while the sequestration rate increases linearly. Consequently, the total cost reduces from approximately $ 57 per ton to around $ 36 per ton for a conversion fraction change from 25 % to 75 %.

Throughout the examined domain, the relative contributions of capital expenditure (CAPEX) and operational expenditure (OPEX) remain consistent. It is important to note that the reported sequestration costs are for a single reactor. As the number of reactors utilized increases, the costs scale much less than linearly, whereas the sequestration scale increases linearly with the number of reactors. This implies that the cost of production will continue to decrease as the demand for sequestration increases, considering that a single reactor alone can sequester up to 1 Megaton per year.

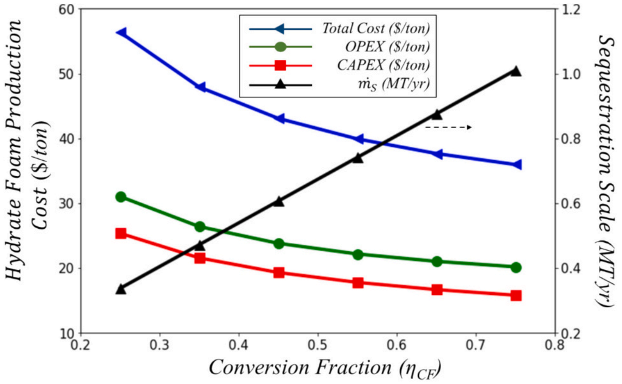

Fig. 5. Influence of CO_2 conversion fraction (per pass) on scale of sequestration and cost of foam production.

Electricity prices exhibit significant variability based on factors such as location, time, and the source of electricity (renewable or non-renewable). In this study, an electricity price of $71.3 per MWh is considered [42]. With an electrical energy demand of 713 MWh per day, the cost contribution attributed to electricity amounts to $ 18.5 per ton out of the total cost of $ 36 per ton, representing approximately 51 % of the total contribution. This underscores the importance of reducing the cost of renewables-based electricity to increase the viability of this concept. Indeed, many novel CCS approaches will be viable only when the costs of renewables-based electricity go down significantly. The impact of electricity prices on hydrate production costs was evaluated for a 1 Megaton per year project, with the results depicted in Fig. 6. The capital expenditure (CAPEX) remains constant as it is unaffected by electricity prices. However, the operational expenditure (OPEX) shows a linear increase from approximately $ 4 per ton to around $ 26 per ton for an increase in electricity prices from $10–110 per MWh.

3.4. Contribution of various components/processes to the total annualized cost (includes CAPEX and OPEX)

Fig. 7 presents the relative contribution of each cost category to the total cost for a 1 Megaton per year project. The cost of hydrate foam production for eventual sequestration is determined to be $ 36 per ton. To obtain the total cost for hydrates-based sequestration on the seabed, additional expenses such as hydrate compaction, sealing, and disposal would need to be factored in. Refrigeration accounts for the largest share in annualized cost (41.2 %), followed by compression at 27 %. Implementing this project on the seabed will reduce refrigeration requirements, thereby lowering overall annualized costs. Additionally, a reduction in electricity prices will reduce the total OPEX. Compression costs are evaluated assuming that the CO_2 gas is provided at standard temperature and pressure (STP) conditions. Shifting to a carbon capture method that supplies CO_2 at a higher pressure would significantly reduce compression costs. Other operating costs, including labor and maintenance, represent 5.0 % of the annualized total cost, while other capital costs, apart from key equipment installation costs, account for 24.9 % of the annualized total cost.

The OPEX to CAPEX ratio is 56 % to 44 %. The largest component of CAPEX is attributed to compressors, accounting for 24.8 % of the total

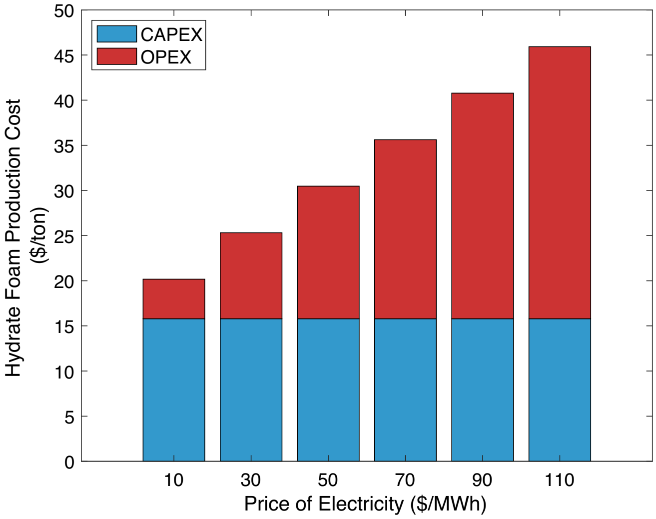

Fig. 6. Influence of price of electricity on the cost of producing hydrate foam.

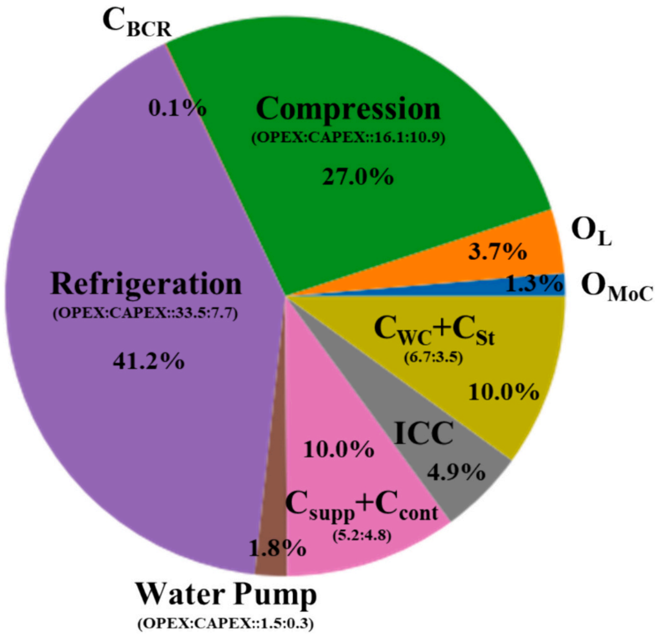

Fig. 7. Contribution of various components/processes to the total cost ($ 36/ton) of a 1MT/yr CO_2 hydrate foam production project.

CAPEX (Fig. 2), or 10.9 % of the total annualized cost. Similarly, cooling represents the largest component of OPEX, constituting 33.5 % of the total annualized cost. Cooling expenses encompass gas cooling, water cooling, and cooling to offset exothermic hydrate formation and other heat gain mechanisms. Out of these, feed gas and feed water cooling requirements would reduce significantly for a seabed application.

According to the U.S. Department of Energy [44], the sequestration cost for a reservoir injection project typically ranges from $8 to $20 per ton, depending on the plant location and basin. Although the production costs for hydrate foams exceed the sequestration cost for a reservoir injection project, it is important to note that these costs are based on a single reactor only, where the reactor accounts for only 0.1 % of the total cost. This clearly suggests that larger capacity projects with more reactors (or larger capacity reactors) will significantly reduce the $/ton metric. Our analysis indicates that a 10 Megaton/yr hydrates-based sequestration project (based on 10 BCRs of the kind discussed presenting) will lead to a $25/ton cost of producing hydrates, which is a very promising prospect.

4. Conclusions

A techno-economic model is developed (based on in-house experimental results) to analyze CO_2 hydrate foam formation in bubble column reactors for hydrates-based carbon sequestration. For a 30-year, 1 Megaton per year project, the total cost of foam production is estimated at $ 36 per ton, with an initial investment cost of $150 million and a daily energy requirement of 713 MWh (equivalent to 260kWh/ton). Notably, the cost contribution of electricity is $18.5 per ton, underscoring the importance of reduced electricity prices for increasing the feasibility of carbon sequestration projects. Primary cost contributions to the total cost originate from refrigeration (41.2 %) and compression (27 %), while costs related to the reactor itself are negligible (~0.1 %). The energy cost associated with CO_2 recirculation is minimal (0.14 %), indicating that operating at low conversion fractions remains a viable option. These findings suggest that larger capacity projects with multiple reactors can reduce annualized costs. Additionally, subsea implementation of this technology holds promise, particularly in cooler oceanic environments where refrigeration costs can be avoided; however, this would entail higher installation costs and gas transportation costs. Another consideration that needs to be analyzed in the future is the techno-economic viability of forming hydrates from impure CO_2 streams, noting that the capture cost increases with higher purity requirements. Overall, this study lays the groundwork for further detailed investigations into hydrates-based carbon sequestration on the seabed.

Author contributions

Awan Bhati designed and conducted the experiments, alongwith the techno-economic analysis, with assistance from Mark Hamalian. V. Bahadur conceptualized and supervised this project. A. Bhati prepared the manuscript and V. Bahadur finalized it for submission.

List of acronyms used in manuscript

CCS	Carbon Capture and Sequestration
BCR	Bubble Column Reactor
HEP	Hydrate Extraction Pump
RGC	Recirculated Gas Compression
STP	Standard Temperature and Pressure
TCI	Total Capital Investment
FCI	Fixed Capital Investment
DCC	Direct Capital Costs
ICC	Indirect Capital Costs
TIC	Total installed cost of key equipment

CRediT authorship contribution statement

Awan Bhati: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Mark Hamalian:** Investigation, Writing – review & editing. **Vaibhav Bahadur:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Two US patent applications related to the research reported in this work have been filed with USTPO by The University of Texas at Austin.

Data availability

Data will be made available on request.

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