CO₂ Transportation via Hydrates and Liquefaction: Technical Analysis and Comparison

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ABSTRACT
Carbon capture, utilization, and storage (CCUS), has been deemed an essential component for climate change mitigation. Commercialization of CCUS requires an efficient transportation method of the captured carbon dioxide (CO₂). Previous works have investigated the technological aspects for conventional CO₂ transportation by pipelines and ships, along with the risk and security issues. Transportation of CO₂ through gas hydrates is extremely attractive alternative as 1m³ of hydrate may contain 150-180Sm³ of CO₂. However, the industries are hesitant to implement the gas hydrate technology for CO₂ transportation as there is a lack of pilot studies proving the applicability. This work aims to make a feasibility study on the gas hydrate-based CO₂ transportation. The technical analysis has been performed in terms of CO₂ storage capacity, utility costs, CO₂ handling method and the costing for loading and offloading carrier. The results have been compared with CO₂ transportation through liquefaction method. Calculations have shown that for a 1m³ ship capacity, 867.97 moles of CO₂ can be transported as hydrates, and about 24,553.73 mols of CO₂ can be transported in liquefied state. Thus, in terms of volume it is considered not feasible to transport CO₂ as hydrates. However, comparing other factors, it is found that CO₂ hydrates-based transportation is a better option than liquefaction for sources with lower emissions as involved CAPEX and OPEX is lower as compared to liquefying the similar amount of CO₂.

Keywords: CO₂ transportation, gas hydrate, liquefaction, technical analysis

1. INTRODUCTION
Mitigating climate change has become a hot issue in the international community. Fair numbers of researchers and engineers consider anthropogenic CO₂ emissions from various sources (Figure 1) to be the main factor causing the greenhouse effect and global warming. [1]

Figure 1: Sources of CO₂ emissions [2]

According to Smit et al., large-scale carbon capture, utilization, and storage (CCUS) is our ultimate weapon in the global war against climate change [3][4]. CCUS is regarded as one of the most promising technologies for reducing the anthropogenic greenhouse gas. However, the commercialization of CCUS requires an efficient transportation method of the captured carbon dioxide (CO₂) [5]. Transportation of CO₂ is a fundamental chain of the CCUS flow, which is characterized by high investment and high energy consumption in the integrated CCUS technology [3]. The transportation of CO₂ gas is studied mainly to reduce transportation costs as well as improve transport security and reliability. The most efficient transportation method is known through a detailed technical analysis.
feasibility study. It is necessary to classify and study various transportation methods with regards to cost, capacity, distance, transportation means and storage type. All of these are done to prove the feasibility of a process. Currently, there are CO$_2$ transportation methods which includes CO$_2$ through pipelines and CO$_2$ through shipping. For longer distance of transportation, shipping has been confirmed to be a better option. Under shipping, liquefaction and hydrates are commonly known methods. Previous works have investigated the technological aspects for conventional CO$_2$ transportation by pipelines and ships, along with the risk and security issues [6]. Transportation of CO$_2$ through gas hydrates is attractive alternative as 1m$^3$ of hydrate may contain 150-180 Sm$^3$ of CO$_2$ [7]. However, the industries are hesitant to implement the gas hydrate technology for CO$_2$ transportation as there is a lack of pilot studies proving the applicability. As the gas hydrates technology is relatively new, researchers are often neglecting the possibilities of transporting CO$_2$ through hydrates.

Gas hydrates are solid crystalline inclusion compounds comprising of water cavities which entrap small gas molecules. CO$_2$ hydrates are formed in combination of water when subjected to low temperatures and high pressures.[8] Various industries have been studying and identifying options of transporting CO$_2$ as gas hydrate pellets. [9][10] The major reasons of not implementing the hydrate technology are the possible costly replacement of currently available liquefaction facilities, and the unestablished efficiency of hydrate transportation. It is essential to study the possibility of CO$_2$ hydrate transportation as the new method can often be more economical and beneficial to us. In this work, CO$_2$ transportation via gas hydrates and liquefaction are compared in terms CO$_2$ storage capacity, utility costs, CO$_2$ handling method and the costing for loading and offloading carrier.

2. EXPERIMENTAL

2.1 CO$_2$ Storage Capacity

Gas hydrates are 85 mole % water and 15 mole % gas[11]. Considering 85:15 mole ratio, the amount of CO$_2$ that can be stored in 1000m$^3$ tank is calculated. The partial volume occupied by CO$_2$ and water in a clathrate hydrate is known by the division of mass by density of the CO$_2$ and water, respectively. While the density of water is 1000kg/m$^3$ the density of the compressible CO$_2$ is 47.7 kg/m$^3$ at 273.3 K and 20.8 bars [12]. The difference density value under 273.3 K and 278.15 K is assumed to be negligible. Once the partial volume is obtained, the number of moles of CO$_2$ that can be stored as hydrates in 1000m$^3$ (basis of comparison) is calculated using the ideal gas law. When CO$_2$ is liquefied, the volume of CO$_2$ is reduced by about a 1/550 ratio [13]. Volumetric conversions are done based on the molar volume of CO$_2$, which is 22.4 dm$^3$/mol at standard temperature and pressure. This will provide a reasonable estimate to visualize the CO$_2$ storage capacity in liquid and hydrate form.

2.2 Cost Estimation for CO$_2$ Transportation via Hydrates and Liquefaction

Practical experience is lacking in this field of CO$_2$ hydrates transportation. Thus, the analysis has to be based on publications and studies alone that were brought together by an extensive literature review. The entire process of CO$_2$ liquefaction and CO$_2$ hydrates formation is studied and its energy requirements is found and then its cost is calculated based on current tariff in Malaysia which is obtained from Tenaga Nasional Berhad (TNB). For this work, the internal refrigeration or better known as self-refrigeration method [14][15] is discussed to be compared with CO$_2$ hydrates. In terms of gas hydrate technology, Literature on CO$_2$ hydrates are limited as it is still mostly in research and development phase. The cost of CO$_2$ hydrate formation is calculated based on the previous experiments [16][17,18]. In However, in cases where the literature is insufficient, the data available on methane hydrates are used. Methane hydrates and CO$_2$ hydrates are considered to be almost the same as they are both sI hydrates and density of methane hydrates is 900 kg/m$^3$ [19] is considered relatively close to the density of CO$_2$-hydrates which is 1198 kg/m$^3$.

2.3 Risk Analysis of CO$_2$ Transportation

All risks involved in transporting liquid CO$_2$ and hydrates is studied thoroughly from literature. Its handling is also kept in view based on required codes and standards applied. Handling of hydrates and its risk factors are found entirely on literature. Current project based on methane hydrates transportation is used as a basis CO$_2$ hydrates transportation.

3. RESULTS AND DISCUSSION

3.1. Related Work

Carbon dioxide phase diagram shows the phase behavior with changes in temperature and pressure. Phase diagram of CO$_2$ has a more typical melting curve, sloping up and to the right. The triple point is −56.6°C and 5.11 atm, which means that liquid CO$_2$ cannot exist at pressures lower than 5.11 atm. At 1 atm, solid CO$_2$ sublimes directly to the vapor while maintaining a temperature of −78.5°C, the normal sublimation temperature. CO$_2$ exists as solid at temperatures below −56.57°C.
At standard conditions (gas), CO₂ is in 2.0 kg/m³ at 0°C and 1 bar. When liquefied, CO₂ is in 1.030 kg/m³ at -22°C and 20 bar. The volume of CO₂ is reduced by about a 1/550 ratio by liquefaction. As of 2018, worldwide, there are only 4 small ships that transports CO₂ in liquid state. If changed to solids, CO₂ will be able to achieve higher volumes as to liquefaction at certain temperature and pressure. This can be proven by a kinetic molecular theory. CO₂ is either in gas or solid phase at atmospheric pressures depending on the temperature. Lowering the temperature at atmospheric pressure cannot by itself cause CO₂ to liquefy, but only to make so-called ‘dry ice’ or solid CO₂. Liquid CO₂ can only exist at a combination of low temperature and pressures well above atmospheric pressure. Storing CO₂ as liquid or solids requires CO₂ to undergo extreme pressure and temperature changes. Gas occupies less volume if it is compressed, and compressed gas is transported by pipeline. Volume can be further reduced by liquefaction, solidification or hydration [21]. Much more energy is required for solidification as compared to the other methods and high energy is proportional to a higher cost. Solid CO₂ or “dry ice” exists at about −79°C at atmospheric pressure. This extreme negative temperature makes solid CO₂ risky to be handled without proper protection as it could cause severe burns (frostbite). Research teams in Germany and Australia have come up with a technology to convert gaseous CO₂ directly into solid particles. However, this is still in research stage and its feasibility and safety is yet to be studied.

Fortunately, existence of hydrates technology provides potential alternative. CO₂ hydrates form at optimum conditions of pressure and temperature, around 20 bars and 4°C. This paper views gas hydrates as an attractive means to transport CO₂. In this work, mathematical comparisons are done on gas hydrate and liquefaction technology CO₂ transportation.

For hydrates, taking a basis of 1000 moles of CO₂, and density of 47.7 kg/m³ volume of CO₂ is calculated. Since water is 85% of the hydrates, moles of H₂O is calculated using simple ratio and percentage. Since hydrates is made up of water and gas, total volume of hydrates is found by adding the volume of water as well as carbon dioxide Then, volume of CO₂ in 1 m³ of hydrates is found and moles of CO₂ in 1 m³ of hydrates is recalculates using the idea gas law where PV= nRT. The density of CO₂ hydrate is 1199.8 kg/m³ when all the cages are enganged with gas molecules [22]. Based on the density, the mass of 1000 m³ hydrate is calculated and compared to the 1000 m³ Liquefied CO₂. For liquefaction, 1 mol of gas occupies 22.4 dm³/mol at Standard Temperature and Pressure (0°C and 1 atm) [23]. Starting from a basis of 1 mol, knowing the volume of CO₂ is reduced by about a 1/550 ratio by liquefaction, volume of CO₂ is found. Then, using the ratio method, moles of CO₂ in 1 m³ of liquid is found. Mass of CO₂ in 1000 m³ of volume is then by multiplying volume with density. The results are tabulated in Table 1 below.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Storage capacity in CO₂ as hydrates and liquefied</th>
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<tbody>
<tr>
<td>CO₂ parameters gas hydrate liquefaction</td>
<td></td>
</tr>
<tr>
<td>Volume of CO₂ occupied in 1m³ 0.7420 m³ 1 m³</td>
<td></td>
</tr>
<tr>
<td>Moles of CO₂ in 1m³ 867.97 mol 24553.74 moles</td>
<td></td>
</tr>
<tr>
<td>Mass of CO₂ in 1000 m³ 1,198,800 kg 1,030,000 kg</td>
<td></td>
</tr>
</tbody>
</table>

It is from the calculations; liquefied CO₂ takes lesser space then Gas hydrates. In terms of volume, the liquefied CO₂ utilises the full capacity while gas hydrates are compromised with the volume take up by water molecules. Storing significanly more moles of CO₂ and maintaining lower mass than gas hydrates, CO₂ transportation by liquefaction seems to be better option in the first glance. Gas hydrates were found to be economically less favorable than liquid form for the transportation of natural gas primarily.
due to the lower energy density of natural gas hydrates relative to liquefied gas [24]. However, it is found that CO\textsubscript{2} hydrates-based transportation is a viable and feasible option for sources with lower emissions which results to lower gas to be captured and transported. The return of investment for natural gas hydrates is better than for liquefied natural gas at lower capacities, resulting in gas hydrates chain to be much more feasible option when it comes to lower amount of CO\textsubscript{2} emissions [25].

Table 2 Ship based transport liquefaction energy study

<table>
<thead>
<tr>
<th>Source</th>
<th>Liquefaction Energy per tonne CO\textsubscript{2} (kWh/tonne CO\textsubscript{2})</th>
<th>Liquefaction Cost Per tonne CO\textsubscript{2} (RM/tonne CO\textsubscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrio et al., 2004</td>
<td>110</td>
<td>44</td>
</tr>
<tr>
<td>Aspelund &amp; Jordal, 2007</td>
<td>105</td>
<td>42</td>
</tr>
<tr>
<td>Yoo et al., 2013[26]</td>
<td>115</td>
<td>46</td>
</tr>
<tr>
<td>Lee et al., 2012 (Modified basic process proposed by Aspelund and Jordal)</td>
<td>98.9</td>
<td>39.56</td>
</tr>
</tbody>
</table>

3.2 Cost Estimation for CO\textsubscript{2} Transportation via Hydrates and Liquefaction

Cost estimation for CO\textsubscript{2} transportation as hydrate is based entirely on literature and experiments as there are no industrial scale CO\textsubscript{2} hydrates transportation being done currently. According to Matsuo et. al., [27], CO\textsubscript{2} hydrate formation consumes 154.22kWh/tonne CO\textsubscript{2} which costs MYR 61.69/tonne CO\textsubscript{2} setting the tariff to be RM0.40 cents per kWh [28]. For the CO\textsubscript{2} transportation via liquefaction, a eco-friendly technique, self-refrigeration is considered. The process flow for CO\textsubscript{2} liquefaction using self-refrigeration is available in literature. Energy required for liquefaction processes are tabulated in Table 2 from various sources. Observing the results of calculations discussed above, it can be stated that liquefaction is better than gas hydrates. Liquefaction consumes lower energy and costs lesser in average 107.22kWh/tonne and MYR 42.89, compared to gas hydrate technology which consumes 154.22kWh/tonne CO\textsubscript{2} and costs MYR 61.69/tonne CO\textsubscript{2}. However, the energy consumed to maintain the operating conditions for liquefaction and gas hydrate technology plays a major role in the technical feasibility of the technology for a particular source of emissions.

In this work, the cost for maintaining the optimum operating/storage conditions for liquefaction and gas hydrate technology, is estimated by calculating the cost of heat exchangers and compressors involved. Compressor is used to transfer and compress gases from one process unit to another to carry out chemical reactions, separation and to liquefy gases. A positive displacement compressor will usually be used to compress essentially the same volume of gas in a chamber regardless of the discharge pressure. The type of this compressor will be a multistage centrifugal compressor. According to [29], there are many advantages of a centrifugal compressor over a reciprocating machine. Hence, a centrifugal compressor is used as a base of calculation. Initial temperature and pressure is assumed to be at NTP which is 20°C and 1 atm.

“Shell and tube heat exchangers are comprised of multiple tubes through which liquid flows”. “The tubes are divided into two sets; the first set contains the liquid to be heated or cooled”. “The second set contains the liquid responsible for triggering the heat exchange, and either removes heat from the first set of tubes by absorbing and transmitting heat away in essence, cooling the liquid or warms the set by transmitting its own heat to the liquid inside. [30] After considering all the factors, Heat Exchanger was designed in shell-and-tube type. Advantages of shell-and-tube heat exchanger are discussed in [31]. Refrigerant considered in this study and calculations is ammonia.
3.3 Risk Analysis of CO2 Transportation

CO2 transportation via gas hydrates is a relatively new technological approach. New health, safety and environmental risks come hand in hand with the introduction of new methods or technologies. As for innovations of already available technologies or methods, higher risks compared to conventional ones comes associated. Risk analysis method is applied for the evaluations of involved risks. The risk analysis consists of the steps such as Identification of Hazards (HazId), Hazards Ranking, Risk Model Development, Risks Evaluation (quantitative risk evaluation).

Table 3 Hazards and preventive measures for CO2 transportation via hydrates

<table>
<thead>
<tr>
<th>Hazards</th>
<th>Preventive measures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fire hazards should be considered</td>
<td>The cargo tank should be filled with natural gas and inert gas system, which may be located onshore, is necessary for gas-free operation</td>
</tr>
<tr>
<td>Toxicity of the pellets are negligible</td>
<td>Source of ignition should be eliminated and all electrical equipment should be of approved safe type</td>
</tr>
<tr>
<td>Corrosivity of the pellets are negligible</td>
<td>Spaces adjacent to cargo tanks should be filled with inert gas such as nitrogen or continuously ventilated</td>
</tr>
<tr>
<td>Low temperature hazards should be considered</td>
<td>“Integral tanks” should not be applied for cargo tanks for hydrate pellets owing to their low temperature</td>
</tr>
<tr>
<td>Reactivity of the pellets are insignificant</td>
<td>Pellet carriers should be “Type 2G”* ships as described in the IGC Code[32]</td>
</tr>
<tr>
<td>Pressure control devices should be considered</td>
<td>A type 2G ship is a gas carrier intended to transport the products indicated, that require significant preventive measures to preclude their escape*. It is more than 150m in length and assumed to be able to handle damage anywhere along the length[33]</td>
</tr>
</tbody>
</table>

A risk analysis has already been carried out by SUGAR (Submarine Gas Hydrates Reservoirs) at the early development stage to detect “showstoppers” for the new CO2 hydrates transportation at sea technology. This technology is already at a conceptual design stage and risk analysis is carried out to determine any risks that may interfere with the introduction and development of this technology. Cargo handling of CO2 hydrates are assumed to be solid bulk cargoes as the hydrates are in the form of pellets. According to Penca, 2009[34], the hazards involved in hydrates carriers are considered and the preventive measures are tabulated in Table 3. In terms of liquefied technology, the associated risks are tabulated in Table 4 below.

Table 4 Hazards of CO2 transportation via liquids

<table>
<thead>
<tr>
<th>Risks associated with liquefied CO2 transportation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ship or truck accidents might cause the explosion of liquefied CO2. That is why liquefied CO2 is regarded as extremely dangerous with container ships called floating bombs.[35]</td>
</tr>
<tr>
<td>If there are leaks in the storage tanks of liquefied CO2 some of liquefied CO2 might return to gaseous state and at certain concentration, there is a risk of flammability and explosion.[36]</td>
</tr>
<tr>
<td>Liquefied CO2 is stored at approximately -56.6oC and it should be kept at this temperature during transportation. If there are problems related to keep temperature constant at this extreme condition, it might cause explosions.</td>
</tr>
<tr>
<td>Liquefied CO2 are non-toxic and insoluble in water so compared other oil spills, there are minimum risks of it for the environment but extremely dangerous for people since it is toxic and explosive.[37]</td>
</tr>
</tbody>
</table>

Transport of liquefied CO2 comes with various health, safety and environmental risks. Hence, it is necessary to develop an alternative to it which would be transportation of natural gases as natural gas hydrates. Transportation via this method is not only safer but much more economical as well based on various parameters. This method is safest, cleanest and might be the most feasible one if necessary development in the gas technology is completed [38][39].

3.4 Accomplishment from this Project

The idea of transporting CO2 as gas hydrates was proposed based on the foreseen advantageous potential of the transportation of natural gas as hydrates. The pilot plant for the transportation of natural gas as natural gas hydrates has been done in Japan [40]. Some cost estimations show that the cost of transportation in form of natural gas hydrates is approximately 18-24% lower compared to liquefied transportation [41][42]. 14% of the total formation energy is consumed back for the transportation of natural gas hydrates [43]. The costs of transportation and concluded based on conceptual design shows that hydrates carriers could economically competitive to liquefied carriers if the distance of transportation was less than 3000 nautical miles (5556 km) [41]. Natural gas hydrate transportation can be considered cheaper than liquefaction [44]. To establish a prospective CO2 hydrates process chain, a pellet carrier designs are vastly explored. More research and development are also being carried out to make this method a possibility with least cost. Based on the work done in this technical feasibility comparison, study, the gas hydrate...
study seems to be better option when the amount of CO\(_2\) to be transported is lesser. The transportation holds a major role in the CCUS chain and due to the high cost of transportation especially for small amount of emissions, releasing the CO\(_2\) to the atmosphere has been a common practice currently. This finding can encourage the industries with small amount of CO\(_2\) emissions to consider CCUS instead of releasing the CO\(_2\) to atmosphere.

4. CONCLUSION

This work analyses and compares the feasibility of CO\(_2\) transportation via gas hydrates and liquefaction. Calculations has shown that in a 1m\(^3\) volume capacity, 867.97 moles of CO\(_2\) can be transported as hydrates, while 24,553.73 moles of CO\(_2\) can be transported as liquefied CO\(_2\). In terms of volume it is considered not feasible to transport CO\(_2\) as hydrates. However, considering other factors, it is found that CO\(_2\) transportation via hydrates is a viable and feasible option for sources with lower emissions which results to lower gas to be captured and transported. This finding agrees with the literature where it is stated transportation of CO\(_2\) as gas hydrates is much more economical for transportation distances between 1000 km to 6000 km. As for transportation cost, transportation of CO\(_2\) hydrates is can be approximately 18-24% lower compared to liquefied transportation. Hence, it is safe to conclude that transportation of CO\(_2\) hydrates is more economically feasible for short distances and/or lesser amount of CO\(_2\) as compared. Further studies on technical feasibility of utilizing gas hydrate technology in Carbon Capture, Utilisation and Storage (CCUS) is highly recommended. Gas hydrate technology presents a huge unforeseen potential in leading to most efficient CCUS chain.

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