A Proposed Workflow for Disposal of Carbon Dioxide using Carbon Dioxide Hydrate

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Abstract: *Carbon dioxide (CO_2) is an important greenhouse gas because it transmits visible light but absorbs strongly in the infrared. It is mainly generated from the combustion of fossil fuels or vegetable matter, among other industrial processes such as cement production and ammonia plants. CO_2 emitted from burning fossil fuels is believed to be a major contributor to the amount of CO_2 levels in the atmosphere contributing to global warming. Hydrate technology can be used to capture CO_2 gas in the form of hydrates. In this technology, CO_2 and water are combined at certain conditions of temperature and pressure to form a hydrate, and then transported and released at great depths into the ocean. Disposal of CO_2 in the form of hydrates in the sea is a great potential as the ocean is vast and occupies 70% of the earth's surface. Numerous power plants and petrochemical plants are located near the coastline and hence there is easy access to the ocean. The CO_2 hydrate formation as a CO_2 disposal method may potentially offer significant savings in CO_2 disposal because of minimal cost of CO_2 capture. This paper proposes a workflow for disposing of CO_2. The model describes the sequence of operations for CO_2 capture and disposal using CO_2 hydrate. A typical example would be used to describe the workflow from CO_2 emitted to CO_2 hydrate disposal. CO_2 hydrate is denser than seawater and therefore CO_2 hydrate deposited in the ocean will sink to the seabed as long as the disposal site is within the hydrate formation envelope.*

Keywords: *Carbon Dioxide, Disposal, Hydrate*

1. Introduction

Capture and disposal of CO_2 is actively being sought as a means to avoid release of greenhouse gases to the atmosphere. This must be aggressively pursued with the impetus of increasingly stringent carbon restrictions and problems associated with global warming. In today's world, global warming has become one of the most critical topics urgently needed to be addressed. Carbon dioxide is considered to be the major contributor (i.e., 60%) of greenhouse gas emissions which are major factors in global warming (Masemore et al., 1999).

2. CO_2 Hydrate Technology

Hydrates are ice-like crystalline solids formed from a mixture of water and gas subjected to high pressure and suitable low-temperature conditions. These conditions are found in the permafrost and under the ocean floor. Hydrates consist of geometric lattices of water molecules containing cavities occupied by light hydrocarbons and other types of gaseous components such as nitrogen, carbon dioxide, and hydrogen sulfide. PVTSim, a computer program (Calsep, 2008) was used to analyse the CO_2 hydrate potential for CO_2 disposal. Hydrate equilibrium lines for different samples were estimated.

The PVTSim program was used to estimate the conditions at which gas hydrates may form and in what quantities. Figure 1 compares the equilibrium curves of a dry gas sample (99% methane), 100% CO_2 in fresh water, and 100% CO_2 sample in sea water.

Above 37°F, the pressure required for 100% CO_2 to form hydrates increases drastically. Therefore it is important to form hydrate in sea water below 37°F. The sea water composition used in the analysis was 96.5% water and 3.5% NaCl. On the average, sea water in the region is about 3.5% salinity.
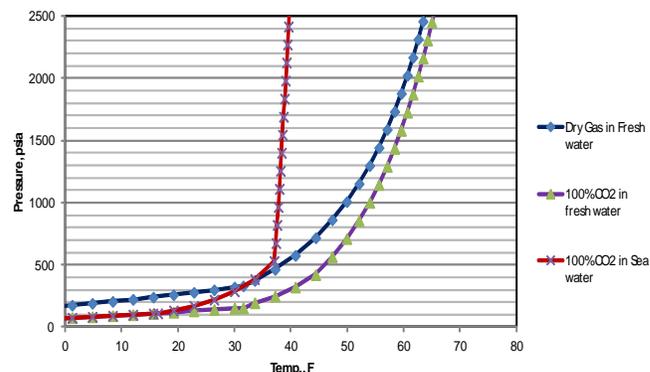

Figure. 1 Hydrate equilibrium curves for dry gas, 100% CO_2, and 100% CO_2 using seawater composition (3.5% NaCl)
(**Note:** Curves were generated from results using the computer program PVTSim)

Hydrate technology can be used to capture CO_2 gas in the form of hydrates. CO_2 hydrates can be transported by tankers and released at suitable depths in the ocean. The mole ratio between water to CO_2 gas is approximately 6:1, thus large amounts of water are required for the process. A 6:1 mole ratio gives 100% volume of hydrate, however, if a smaller ratio is used, some free CO_2 gas would remain.

Using a 6:1 mole ratio a linear relationship can be obtained which provides the amount of water required in bbl/d per MMscf/d of gas feed. This is shown in the equation below.

$$V_{water} = 811.6 \; x \; V_{gas}$$

where V_{water} = amount of water in bbls/d and V_{gas} = CO_2 gas feed in MMscf/d

For example for a 50 MMscf/d CO_2 gas feed as much as 40,580 bbls/d of water is required. Excess water may be used to ensure all gas is captured. Likewise the mass of CO_2 hydrate (tonnes/d) formed as a function of CO_2 gas feed in MMscf/d is given by the following equation:

$$M_{hydrate} = 180.1 \times V_{gas}$$

For a typical plant capacity of 50 MMscf/d gas feed, $1.985 \; x \; 10^7$ lbs/d of hydrate is produced. The total weight of hydrate can be split into water and CO_2 as follows:

$$M_{water} = \frac{6M_{hydrate}}{7} \quad \text{and} \quad M_{CO_2} = \frac{M_{hydrate}}{7}$$

The proposed workflow for disposal of CO_2 using hydrate technology will be described using Trinidad as an example and the slurry form of the hydrate is assumed in this analysis. A conversion table is given in Annex 1.

3. CO_2 Emissions in Trinidad

Carbon dioxide net emissions in Trinidad and Tobago (T&T) have been steadily increasing over the past few years. Figure 2 shows the rank in emissions per capita for some main carbon dioxide producers. Trinidad is ranked no. 2 in these 2009 rankings (UN, 2009). Although T&T has a high emission per capita the total CO_2 emissions from Trinidad is less than 1% of the CO_2 emitted worldwide.

The high emissions per capita results mainly from the growth of the industrial sector with the majority being in the petrochemical sector, followed by power generation then the transportation sector and finally the combined manufacturing and domestic sectors (Boodlal and Furlonge, 2008). This is shown in Figure 3.

Trinidad and Tobago's major source of carbon dioxide emissions has been identified as the petrochemical sector. Trinidad is one of the largest traders of ammonia in the world with eleven ammonia plants in operation. In the manufacture of ammonia, large amounts of CO_2 are produced as a by-product when nitrogen from the atmosphere is combined with hydrogen produced by steam reforming of natural gas. Also the concentration of CO_2 emitted from ammonia plants is highest compared to other facilities in T&T. Figure 4 shows the CO_2 emissions

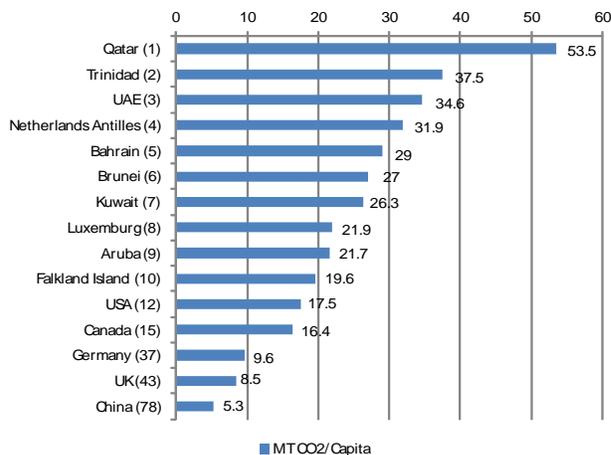in the petrochemical sector and it can be seen that production of ammonia produces the largest amount of carbon dioxide.
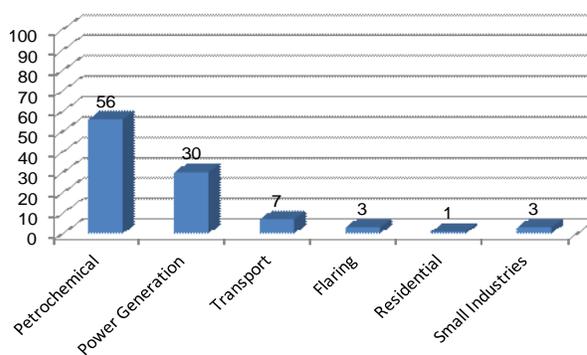

Figure 2. Carbon dioxide emissions per Capita, 2009

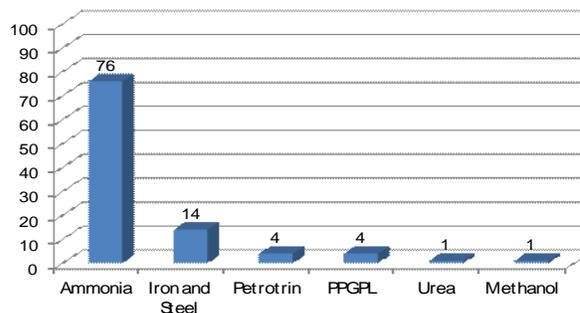**Figure 3.** Carbon dioxide Emissions by Sector (%) in Trinidad and Tobago

Figure 4. Carbon Dioxide Emissions by Chemical Sector (%) in Trinidad and Tobago

Dependent on the source, captured raw CO_2 feed may contain 98-99.5% dry CO_2 and 0.5-2% inerts (non-condensable gases such as H_2, N_2, O_2, and CH_4) together with traces of absorption liquid from capture process and most importantly, 0-3% water vapor (Hegerland et al.,

2002). These compositions are most prevalent in the ammonia plants in T&T due to high efficiency of CO_2 capture process via liquid absorption using a solution of potassium carbonate known as the Benefield Solution (Ramlakhan, 2007). Some of the 250 MMscf of CO_2 produced daily is presently being used in methanol production and some is expected to be used in EOR processes while the remainder has to be disposed (estimated at 50MMscf/d).

4. CO_2 Capture and Disposal

Figure 5 shows the general concept of capturing and disposing of CO_2. The workflow involves compression of the CO_2 captured from an ammonia plant into a hydrate formation vessel with cooled sea water. For 50 MMscf/d of carbon dioxide, about 40,580 bbls/d of water is needed for hydrate formation. Since a large amount of water is required, the preference will be to use available sea water rather than pure water. Carbon Dioxide and sea water combine to give CO_2 hydrate which is transferred to an insulated storage vessel and then to a tanker for disposal.
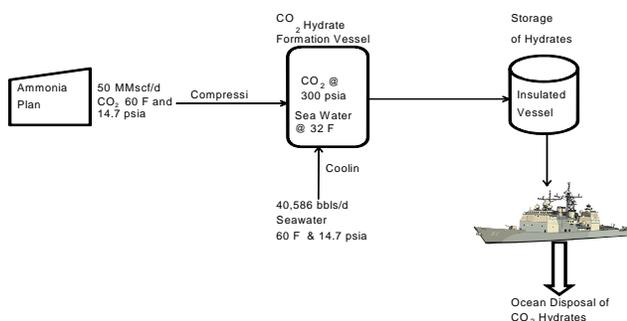
Figure 5. Carbon dioxide disposal workflow using hydrate formation

5. CO_2 Hydrate Formation Process

The carbon dioxide hydrate formation process is illustrated in Figure 6. The energy requirements for the process are also shown in the figure. Sea water is cooled to 32°F and pumped into the hydrate formation vessel. The cooling requirement estimated for 40,580 bbls/d of water is 7.34×10^8 btu/d. This was estimated using water enthalpies before and after cooling obtained from NIST (2008).

The energy requirement for water cooling can be obtained from waste heat from power generation using a heat recovery steam generator. In T&T, the power generation plant is in the same industrial complex as the ammonia plants and close proximity to the Pt. Lisas port. During the formation of the hydrate, large amounts of heat are given out which must be removed. This heat of formation is estimated to be 3.75×10^9 btu/d and can be removed using heat exchange tubes extending the full length of the formation vessel.
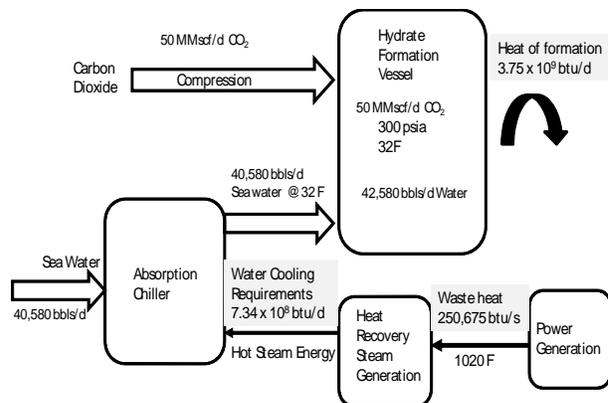
Figure 6. Carbon Dioxide Hydrate Formation with Energy Requirements

Heat from the surrounding can transfer into the formation vessel and increase its temperature, causing dissociation of the hydrate as it forms. Insulation is therefore necessary to minimise heat transfer with the surroundings. NanoPore thermal insulation provides exceptional performance with a very low overall thermal conductivity of 0.004 btu.in/ft^2.h.F (NanoPore, 2010). About 240 Btu/hr of heat gained from the surroundings must be removed when using 1" thickness NanoPore material, compared to 4.35×10^7 btu/hr without any insulation.

6. CO_2 Hydrate Disposal

Figure 7 illustrates the concept of CO_2 hydrate disposal in deep water using a tanker. Carbon dioxide hydrate in storage is loaded onto the tanker which moves to a selected deep sea disposal site and injects the hydrate to the ocean floor using a freely dangling pipe as shown.
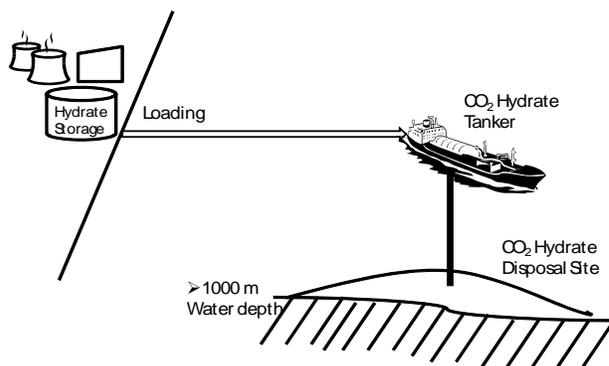
Figure 7. Deep sea disposal of CO_2 hydrate

Use of commercial insulated multi-tank design vessels for carrying 22,000 m^3 of CO_2 is within the current state of shipbuilding technology. This is so because similar vessels are presently used to transport liquefied petroleum gas. These vessels sail at a service

speed of 17 to 20 knots (31-37 km/hr). A single 22,000 m^3 refrigerated tanker can transport the equivalent of 200 x10^6 tonnes CO_2/year (Coleman et al, 2005).

The estimated depth range for CO_2 hydrate disposal is 800 to 1,000m. Figure 8 shows the CO_2 hydrate equilibrium line with the seawater temperature gradient. The point where seawater gradient crosses the equilibrium line indicates the region of hydrate formation or hydrate disposal in seawater. This region starts at about 800 m and corresponds to about 1,160 psia and 35°F.
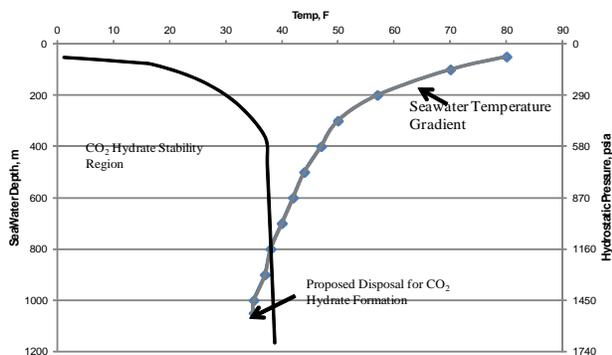

Figure 8. Seawater Temperature Gradient with pure CO2 hydrate equilibrium line
(***Note:*** Salinity of 3.5% NaCl) with corresponding Depth and Hydrostatic Pressure

The estimated distance to transport the carbon dioxide hydrate to the deep sea region is approximately 250 km. Figure 9 shows a map of Trinidad illustrating the distance the tanker has to travel to dispose the CO_2 hydrate from the Pt. Lisas Industrial port (circle on map) to a deep water disposal site. The diagram shows the water depth lines and it is expected that the disposal site would be in the area beyond 1,000 m line. It is estimated to take about 8 hours from the Pt. Lisas Industrial port to the deep sea disposal site. This is assuming tanker speed of about 35 km/hr.
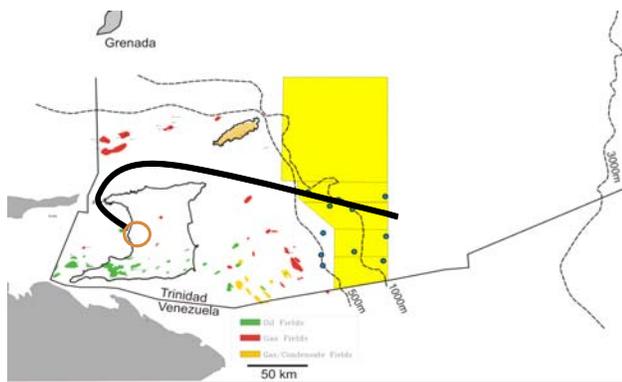

Figure 9. Map showing the disposal route for CO_2 Hydrate from the Pt. Lisas Industrial Port

7. Discussions and Conclusion

With high emissions per capita, Trinidad needs to find ways of disposing of CO_2. While still in its embryonic stages, CO_2 hydrate technology offers possibilities for disposing of carbon dioxide at deep sea. Seawater is the preferred choice of water since the formation of carbon dioxide hydrate requires a large volume of water. A large latent heat of formation must be removed during the hydrate formation process and can be removed using heat exchange tubes.

Cooling of water can be done using an absorption chiller with waste heat from a nearby power plant. Insulation is required for formation and storage vessels. NanoPore (2010) provides exceptional performance with a very low overall thermal conductivity. Vessels similar to those presently used to transport liquefied petroleum gas can be used to transport CO_2 hydrate to deepwater regions. Based on the seawater temperature gradient used in this analysis, CO_2 can be disposed at a depth of 1000m to form hydrate.

Annex 1: Conversion Table

Variable	Oilfield Unit	SI Unit	Conversion (Multiply SI Unit)
Energy	Btu	kJ	0.9478
Length	ft	m	3.28
Pressure	psi	Pa	1.45×10^{-4}
Rate (gas)	Mscf/d	m^3/s	3049
Speed	knots	km/hr	0.53995
Temperature	F	K	9/5(° K - 273) + 32
Volume	bbls	m^3	0.1589873
Weight	lbs	tonnes	2204.64

References:

Masemore, S. and Kirchgessner, D.A. (1999), "Greenhouse gas mitigation and monitoring technology performance: Activities of the GHG Technology Verification Centre", Society of Petroleum Engineers (SPE 52676)

Calsep (2008), *PVTSim Software*, Version 18, Calsep, Copenhagen, Denmark

UN (2009), *United Nations Statistics: Emissions per Capita 2009 by Countries*, United Nations

Boodlal, D. and Furlonge, H. (2008), "Trinidad and Tobago's CO_2 inventory and techno-economic evaluation of carbon capture options for emissions mitigation", *Proceedings of the Tobago Gas Technology Conference*, Tobago, 7-10 October

Hegerland G, Jorgensen, T. and Pande J.O. (2002), *Gas conditioning – The Interface between CO_2 Capture and Transport*, Norwegian University of Science and Technology, NTNU, NO-7465 Trondheim, Norway

Ramlakhan M. (2007), *Project Investment as, Norway Liquefaction and Handling of Large amounts of CO_2 for EOR*, YARA International ASA

NIST (2008), *NIST Chemistry Web Book*, available at: http://webbook.nist.gov/chemistry/fluid

NanoPore (2010), *NanoPore Thermal Insulation*, NanoPore Incorporated, available at: www.nanopore.com/products. <Assessed March 2010>

Coleman, D., Davidson, J., Hendriks, C., Kaarstad, O., and Ozaki, M. (2005), *Transport CO₂: IPPCC Special Report on Carbon Dioxide Capture and Storage*, Intergovernmental Panel on Climate Change, World Bank.

Author's Biographical Notes:

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