



Journal of Applied Sciences

ISSN 1812-5654

science
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A Review on Carbon Dioxide Hydrate Potential in Technological Applications

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Abstract: The enticing characteristics of carbon dioxide hydrates initiate numerous research activities around the globe and in a wide variety of fields from carbon dioxide sequestration to cool storage applications. A general introduction to clathrate hydrates and carbon dioxide hydrates in particular has been discussed. The motivations behind carbon dioxide hydrate research and the general fields of interest for these compounds are briefly explained in this study.

Key words: Carbon dioxide emissions, clathrate hydrates, carbon dioxide hydrate, technological applications

INTRODUCTION

The increasing demand for energy to supply for the need of industrial developments and the escalating human population has led to accelerated mining and combustion of fossil fuels. These worldwide activities cause a continuing increase of the rates of anthropogenic carbon dioxide emissions, resulting in the increase of the level of atmospheric carbon dioxide. The atmospheric carbon dioxide level has increased 22% since 1958 and about 30% since 1880 (Robinson *et al.*, 2007). The alarmingly increase of carbon dioxide in the atmosphere is believed to have caused some significant climate changes. For instance, the worldwide temperature measurements, carefully screened for instrumental and experimental conditions such as effects of urbanization, show an increase in global mean annual surface temperatures of 0.3 to 0.6°C for the last 159 years (Nicholls and Leatherman, 1996). If the temperature continues to increase, devastating effects on world population will be unavoidable. Due to this concern, the increasing quantities of carbon dioxide and other greenhouse gases in the atmosphere has caused widespread global concerns and has attracted international action such as the Kyoto Protocol.

The main sources of carbon dioxide in the atmosphere are thermal power generation, oil and natural gas refining and processing, cement manufacturing, iron and steel making and petrochemical industries. As shown in Table 1, fossil-fuelled power combined with oil and gas refining and processing cover more than 87% of the industrial carbon dioxide emissions.

As the world's dependency on oil and gas as the main source of energy is foreseen to continue for years to

Table 1: Annual carbon dioxide emissions from major industrial sources*

Industry	CO ₂ emission in Mt CO ₂ year ⁻¹
Power	10,539
Cement manufacture	932
Iron and steel making	646
Oil refining	798
Petrochemical	379
Oil and natural gas processing	50
Other sources (including biomass)	124

*Source: http://www.ipcc.ch/pdf/special-reports/srccs/srccs_technical_summary.pdf

come, a new approach should be developed in order to reduce the increasing amount of carbon dioxide release as a by-product of energy production. A paradigm shift is required in order to successfully combat this environmental problem and the basis of this paradigm shift is to look at carbon dioxide not just as a polluting greenhouse gas but also as a valuable raw material. This approach requires the development of separation technologies to separate the carbon dioxide in bulk from the natural gas under different concentrations, techniques to sequester or store the carbon dioxide and processes to convert the bulk carbon dioxide to different added-value products like chemicals, temperate-farming-agro-products and refrigerants. The benefits from this approach are three-fold. Firstly, for the growth of the hydrocarbon based industries, new technologies suitable to cater for high carbon dioxide concentration have to be developed on a high priority basis. Secondly, from the large quantities of carbon dioxide that is produced, a variety of added-value products could be obtained, thus converting a polluting greenhouse gas into a valuable resource. Thirdly, carbon credit is gained under the Kyoto Protocol for utilizing the carbon dioxide which can be used to generate additional revenue.

CLATHRATE HYDRATES

Gas or clathrate hydrates were discovered almost two centuries ago by Davy (1814). In the early days, interest in gas hydrates was mainly focused on the discovery of new hydrate formers, mainly inorganic chemicals and the composition of these hydrates (Sloan, 1998). Only after the discovery of the occurrence of hydrates in oil production pipelines by Hammerschmidt (1934), a shift towards more industrial hydrate research focusing on hydrocarbons based hydrates was carried out to cater for the needs of oil and gas production. Since then, hydrate research has been intensified especially after the discovery of natural gas hydrate deposits in the Siberian permafrost regions by Makogon (1981).

Clathrate hydrates or gas hydrates are crystalline solid compounds that are formed in mixtures of water and non-or slightly polar low molecular weight gases or volatile liquids and when subjected to appropriate temperature and pressure conditions. They are formed when hydrogen-bonded water molecules form cage-like structures, known as cavities in the crystalline lattice. These cavities have to be at least partially filled with the hydrate-forming molecules, also known as the ‘guest molecule’s, in order to stabilize the structure. Guest molecules are either non-polar or slightly polar in nature and the most common guest molecules are methane, ethane, propane, iso-butane, normal butane, nitrogen, carbon dioxide and hydrogen sulfide. Depending on the type and the size of guest molecule presents, different gas hydrate structures can be formed. The types of cavities that are formed and the distribution of those cavities in a unit cell are used to distinguish the clathrate hydrate structures. A numerous number of structures are known but there are three different structures have been well studied, namely, structure I (sI), structure II (sII) and structure H (sH) (Sloan, 1998).

The unit cell of structure I hydrate consists of 46 water molecules forming two small cavities and six large cavities. The small cavity has the shape of a pentagonal dodecahedron (5^{12}) while the large cavity has the shape of a tetradecehedron ($5^{12}6^2$). The unit cell of structure II hydrate consists of 136 water molecules forming sixteen small cavities and eight large cavities. Similar to the small cavity of sI, the small cavity of sII also has the shape of a pentagonal dodecahedron (5^{12}) but the large cavity has a shape of a hexadecahedron ($5^{12}6^4$). In structure H, the unit cell consists of three small cavities of 5^{12} , two medium cavities of $4^35^66^3$ and one large cavity of $5^{12}6^8$. The number of water molecules, cages and some geometry of the different hydrate structures are given in Table 2.

Table 2: Geometry of hydrate unit cells and cavities (Sloan and Koh, 2008)

Structure	I		II		H		
Crystal system	Cubic		Cubic		Hexagonal		
Space group	Pm3n		Fd3m		P6/mmm		
Lattice parameter (Å)	a =12.0		a = 17.3		a = 12.3, c = 10.17		
No. of H ₂ O molecules	46		136		34		
No. of cavities	8		24		6		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Number	2	6	16	8	3	2	1
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Average cavity radius (Å)	3.95	4.33	3.91	4.73	3.94	4.04	5.79
Variation in radius	3.4	14.4	5.5	1.73	4.0	8.5	15.1
Coordination No.	20	24	20	28	20	20	36

Table 3: Ratios of molecular diameter to cavity diameters for clathrate hydrate former (Sloan, 1998)

Cavity type	Dia. (Å)	(Molecular diameter)/(Cavity diameter)			
		Structure I		Structure II	
		5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$
H ₂	2.72	0.533	0.464	0.542	0.408
N ₂	4.10	0.804	0.700	0.817 ^z	0.616 ^z
CH ₄	4.36	0.855 ^z	0.744 ^z	0.868	0.655
H ₂ S	4.58	0.898 ^z	0.782 ^z	0.912	0.687
CO ₂	5.12	1.000	0.834 ^z	1.020	0.769
C ₂ H ₆	5.50	1.080	0.939 ^z	1.100	0.826
C ₃ H ₈	6.28	1.230	1.070	1.250	0.943 ^z
i-C ₄ H ₁₀	6.50	1.270	1.110	1.290	0.976 ^z
n-C ₄ H ₁₀	7.10	1.390	1.210	1.410	1.070

In order to form clathrate hydrate, the size of the guest molecules must not be too large or too small compared to the size of the cavities. A ratio of the molecular diameter to the cavity diameter of approximately 0.75 appears to be optimal (Christiansen and Sloan, 1994). Structures I and II can be formed with a single guest component while structure H requires at least two different guest molecules (large and small). Most components of natural gas (CH₄, C₂H₆, C₃H₈, CO₂, N₂ and H₂S etc.) form hydrates. Table 3 presents the diameter ratios of natural gas components and a few other components relative to the diameter of each cavity in structures I and II. In Table 3, size ratios denoted with a superscript ζ are those occupied by a simple hydrate former. On one hand, if the size ratio is less than 0.76, the molecular attractive forces cannot contribute to cavity stability. On the other hand, above the ratio value of about 1.0, the guest molecule does not fit into a cavity without lattice distortion (Sloan, 1998).

CARBON DIOXIDE HYDRATE

As previously mentioned, carbon dioxide has been known to be among a number of molecules that can form clathrate hydrate. The first evidence for the existence of CO₂ hydrates probably dates back to the year 1882, when Wroblewski reported the clathrate hydrate formation in a

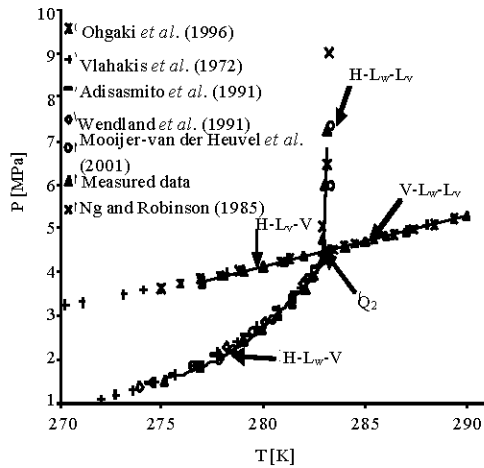


Fig. 1: Three-phase equilibrium data of simple hydrates of carbon dioxide (Sabil *et al.*, 2010)

system of carbonic acid and water (Wroblewski, 1882). The hydrate dissociation curve in the range 267 to 283 K is first published by Villard in 1897 (Villard, 1897). Later on, Tamman and Krige measured the hydrate decomposition curve from 230 to 250 K (Tamman and Krige, 1925). Frost and Deaton determined the dissociation pressure between 273 and 283 K (Frost and Deaton, 1946). Takenouchi and Kennedy (1965) measured the decomposition curve from 4.5 to 200 MPa. Carbon dioxide hydrate was classified as a structure I clathrate for the first time by Von Stackelberg and Muller (1954).

As a simple hydrate, carbon dioxide forms structure I hydrate under appropriate pressure and temperature conditions. If all the hydrate cavities are occupied, the chemical formula is $8 \text{CO}_2 \cdot 46 \text{H}_2\text{O}$ or $\text{CO}_2 \cdot 5.75 \text{H}_2\text{O}$. Extended compilations of published hydrate equilibrium conditions of carbon dioxide in pure water can be found in Sloan and Koh (2008). The phase behaviour of carbon dioxide and water in the hydrate forming region is measured by Sabil *et al.* (2010) in the temperature and pressure ranges of 271-292 K and 1.0-7.5 MPa, respectively as presented in Fig. 1. There are four different phases are observed namely: hydrate phase (H), vapour phase (V), liquid water phase (L_w) and condensed gas or liquid organics phases (L_v).

As shown in this figure, the hydrate stability region is bounded by the $\text{H-L}_w\text{-V}$ and $\text{H-L}_w\text{-L}_v$. As such, at any specified temperature, carbon dioxide hydrate will be stable as long as the pressure of the system is higher or equal to the equilibrium pressure of the system. The upper quadruple point, Q_2 (Fig. 1) at which hydrate, vapour, condensed carbon dioxide and liquid water phases exist in equilibrium is measured at 283.0 K and 4.47 MPa.

Carbon dioxide itself has a triple point at $T = 216.58 \text{ K}$ and $P = 0.5185 \text{ MPa}$ and a critical point at $T = 304.2 \text{ K}$ and $P = 7.3858 \text{ MPa}$. In literature, the lowest measured equilibrium pressure for carbon dioxide hydrate is at 0.535 kPa and 151.5 K for I-H-V equilibrium point and its value is reported by Miller and Smythe (1970).

INTERESTS ON CARBON DIOXIDE HYDRATE

Like other fields of research with a focus on carbon dioxide, the interest of carbon dioxide hydrates is mainly based on the possibilities of using the formation of carbon dioxide hydrates for carbon dioxide separation, capture and storage (CCS). Any technique that prevents or reverses the release of carbon dioxide to the atmosphere and diverts the carbon to a viable carbon sink can be considered carbon capture. Currently, there are a few techniques available for carbon dioxide capture and separation with some degree of success such as chemical solvents, physical absorption, physical adsorption, chemisorptions and chemical bonding through mineralization. However, the main concerns of these techniques are the amount of chemicals to be used in these processes, the energy penalties and the costs associated with these processes in their present form make these processes becoming less attractive for large-scale carbon capture (GCEP) carbon capture technology assessment, (Anonymous, 2005). The global climate and energy project (GCEP) lead by Stanford University is a major on-going research project with a long-term aim of the development of global energy systems with significantly lower greenhouse gas emissions. In this retrospect, clathrate hydrate technique offers a couple of advantages.

Firstly, the main chemical required for carbon dioxide hydrate formation is water which provides the process with abundant (cheap) and green raw chemical. Secondly, reduction of energy requirements for hydrate formation can be obtained by including certain organic chemicals in low concentrations, known as hydrate promoter in the hydrate forming system (Mooijer-van den Heuvel, 2004). The inclusion of one of these hydrate promoters will reduce the pressure requirement or increase the temperature at which the clathrate hydrates are stable. This leads to a reduction in the energy required for pressurization or cooling the targeted systems. Moreover, the interest in carbon dioxide hydrates is not limited to carbon capture and sequestration. As mentioned earlier, a paradigm shift is required to look into carbon dioxide also as a material to be used in industrial processes. The various areas of interest of carbon dioxide hydrates in accordance with their respective possibilities to be

developed as tools to overcome the ever increasing carbon dioxide concentration in the atmosphere are summarized in the following sections.

Marine carbon dioxide sequestration: Due to the pressures and temperatures at ocean depths which are suitable for carbon dioxide hydrates formation (Aya *et al.*, 1997; Brewer *et al.*, 1999); sequestration of carbon dioxide as clathrate hydrates has been thoroughly investigated. Between 1000 and 2000 m (deep water), carbon dioxide in the liquid state diffuses and also dissolves in the ocean (Liro *et al.*, 1992). In addition, carbon dioxide hydrates can appear from 500 to 900 m in CO₂-rich seawater (Kojima *et al.*, 2002). Due to their densities (Holder *et al.*, 1995), these hydrate sink towards the deep sea bottom where they stabilize in the long term (Lee *et al.*, 2003; Harrison *et al.*, 1995). Additionally, it has been proposed to replace the natural gas in naturally occurring hydrate fields by replacement with carbon dioxide (Komai *et al.*, 2000). In bulk, these carbon dioxide hydrates can be transported as slurries in pipelines or in pressurized and chilled vessels from the points of carbon dioxide captured to the points of carbon dioxide sequestered. Currently, marine carbon dioxide sequestration is presently at an experimental stage implying that on-going research activities on carbon dioxide solubility (Aya *et al.*, 1997; Yang *et al.*, 2000); carbon dioxide hydrate formation and dissociation kinetics (Englezos, 1992; Circone *et al.*, 2003); carbon dioxide hydrate stability (Harrison *et al.*, 1995), hydrodynamics conditions (Yamasaki *et al.*, 2000) and other related fields are required to ensure the success of this sequestration method. However, the possible negative environmental impacts of acidification of seawater (Widdicombe and Spicer, 2008) and elevated carbon dioxide concentration in the ocean (Ishimatsu *et al.*, 2004) to marine life should also be thoroughly investigated.

Separation process: In the 1960s and early 1970s, desalination of seawater using gas hydrate formation was thoroughly studied. Knox *et al.* (1961) proposed a process for the desalination of seawater to produce potable water and to setup a pilot plant to study this process. The feasibility of seawater desalination via hydrates was demonstrated (Colten *et al.*, 1972) but the process was not developed industrially since it was not economically viable (Englezos, 1993). However, Javanmardi and Moshfeghian (2003) showed that with the inclusion of a hydrate promoter, the total cost of the hydrate process is comparable with other process such as multistage-flash distillation (MSF), multi-effect distillation (ME) and Reverse Osmosis (RO) for water desalination.

Extensive studies have been focused on the removal or separation of carbon dioxide from industrial gases through the formation of carbon dioxide hydrate. Seo *et al.* (2000) reported the proof-of-concept to carbon dioxide separation from multicomponent gas stream by the formation of carbon dioxide hydrate. A Hydrate Based Gas Separation (HBGS) for the separation of carbon dioxide from flue gas with tetrahydrofuran chosen as a promoter had been proposed by Kang and Lee (2000). According to the authors, the HBGS process makes it possible to recover more than 99 mol% of CO₂ from the flue gas. This process also has several other advantages, such as moderate operational temperatures in the range of 273-283 K and continuous operations, making it possible to treat a large amount of gaseous stream. Rice (2003, 2006); proposed a system for hydrogen production from methane hydrate with sequestering of carbon dioxide hydrate. The author claimed that through this process, the production of hydrogen is made available without the release of carbon dioxide to the atmosphere. In this case, the carbon dioxide is separated from the process stream and injected back in the natural gas hydrates reservoir as clathrate hydrate. Chatti *et al.* (2005) made a review on the benefits of clathrate hydrate based processes. The post and pre-combustion capture of carbon dioxide by using carbon dioxide formation is extensively studied in University of British Columbia (Kumar *et al.*, 2006; Linga *et al.*, 2007, 2008). Moreover, the US Department of Energy (DOE) is developing a high pressure process for carbon dioxide separation (Tam *et al.*, 2001). It focuses on the low temperature SIMTECHE process, where a shifted synthesis gas stream (carbon dioxide, hydrogen and other gases) is combined with pre-cooled nucleated water in a carbon dioxide hydrate slurry reactor. The outlet mixture (carbon dioxide hydrate slurry, hydrogen and other gases) flows into a hydrate slurry gas separator which divides the flow into two streams: carbon dioxide hydrate slurry and hydrogen-rich product gas. Initial economic findings show that in comparison with absorption process with either amine or Selexol, the SIMTECHE process requires less additional capital cost of USD\$ 23.9 millions (USD\$ 56.9 millions for amine and USD\$ 85. One millions for Selexol) for the integration of carbon capture system (CCS) in an Integrated Gasification Combined Cycle (IGCC) plant (Tam *et al.*, 2001). The authors also stated that the cost of carbon dioxide removal for the SIMTECHE process is also found to be the cheapest among the studied processes at USD\$ 8 per ton of CO₂ (USD\$ 21 per ton CO₂ and USD\$ 14 per ton CO₂ for amine and Selexol absorption processes). These initial findings show that carbon dioxide separation process based on hydrate formation may be more economical compared to conventional processes.

Cool storage application: Following the discovery of the ozone layer depletion by chlorofluorocarbons (CFCs) which leads to the phasing out of CFCs as working fluid in refrigeration systems, the interest in CO₂ as a working fluid in refrigeration systems has been revived. Large-scale usage of CO₂ based refrigerants will eliminate the need of using conventional refrigerants such as CFC and HFC. One way of using CO₂ in refrigeration process is in the form of clathrate hydrate slurries, as a two-phase (solid-liquid) refrigerant. Due to the latent heat of fusion of the solid, two-phase refrigerants, sometimes also known as phase-change materials are more energy-efficient than single-phase refrigerants (Darbouret *et al.*, 2005). CO₂ hydrate slurries are promising systems in the field of cold distribution and storage as phase-change materials due to several factors. Firstly, the melting temperatures of some clathrate hydrates are consistent with the temperature need in applications such as air conditioning (Liang *et al.*, 2001). Moreover, the heat of dissociation of CO₂ hydrates has been found to be suitable for refrigeration application and it can be generated by direct gas injection into an aqueous solution instead of using mechanical methods, as in the case of ice slurries (Martinez *et al.*, 2008).

Others: A hydrate based process can also be a good alternative to freeze-crystallisation processes to concentrate water-rich streams which require relatively low temperatures (Huang *et al.*, 1966). Similarly, it might also be a good alternative for processes that use evaporative techniques which require higher temperature, typically higher than the atmospheric boiling point of water (Gaarder and Englezos, 1995). Vaessen *et al.* (2000) has shown the feasibility of using eutectic freeze crystallization with carbon dioxide hydrates for the separation of highly soluble salts from aqueous solutions. In these cases, the development of carbon dioxide hydrate applications is not only relevant to the reduction of energy consumption but also for conservation and transport of temperature-sensitive materials that might be degraded at the conditions applied with freeze crystallisation or evaporative processes such as some vaccines and antibiotics (Zweig, 2006).

CONCLUSION

In conclusion, it has been shown that there are a lot of technological applications that can be developed based on CO₂ hydrates to simultaneously overcome the ever increasing carbon dioxide concentration in the atmosphere and increasing the usage of carbon dioxide in industrial processes.

ACKNOWLEDGMENTS

The authors would like to express their appreciations to Institute Technology PETRONAS (Ltd.), Malaysia for the financial assistance of the work.

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