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Role of CO_2 Capture and Sequestration (CCS) Using Gas Hydrate Based Technology for Sustainable Energy

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ABSTRACT

Technology advancements and increasing energy demands has introduced the world to the major problem of climate change. The emission of greenhouse gases in the atmosphere due to combustion of fossil fuels has adversely affected biodiversity and ecosystem. For the remedial of this global issue, extensive studies come up with the hybrid approach of utilizing CO_2 Capture Technology for sequestrating CO_2 in hydrates. This paper aims to provide review of the current CO_2 capture techniques and the work done to study the CO_2 sequestration in porous medium using CCS technology. For the sequestration of CO_2, CO_2-CH_4 exchange technique is mainly focused. The water saturation and clay minerals showed inhibitive nature on CO_2 storage efficiency in natural hydrate bearing sediments. In addition, the gas chromatography provides evidence for the greater CO_2 storage capability in hydrates. Further, this technique showed the wider aspect of CCS technology for generating energy and reducing excess CO_2 from the atmosphere.

Keywords: Climate Change; Greenhouse Gas; CO_2 Capture; CO_2 Sequestration; Gas Hydrate; Sustainable Energy

NOMENCLATURE

Abbreviations

CCS	CO_2 Capture and Storage
IMH	Intercalated Methane Hydrate
HP-LT	High pressure-Low temperature
GC	Gas Chromatography

1. INTRODUCTION

Natural gas hydrates are ice like crystalline non-stoichiometric solid which are made from natural gas (primarily methane) and water molecules under low temperature and high-pressure conditions (Sloan and Koh, 2007; Pandey *et al.*, 2017b). They are widely available in the permafrost regions and mostly in continental margins of oceans (Lee *et al.*, 2017). They are considered as significant source of energy for future generation because of their rich source density, high density of energy, and global distribution (Pandey *et al.*, 2018, 2019). With increased demands of these natural gas hydrates, there is a huge challenge to exploit these hydrates safely and efficiently. Many techniques have been introduced based on shifting the thermodynamic stability of gas hydrates, including depressurization, thermal stimulation, and inhibitor injection as well as the combination of depressurization and thermal stimulation method. However these methods undergoes excessively energic dissipation, possibly environmental disasters like landslides, land collapse, and unfriendly effects like flow assurance issues in oil and gas industries (Mech et al., 2015a, 2015b; Pandey et al., 2017a; Pandey and Sangwai, 2020a, 2020b; Wang et al., 2021). Therefore, CO_2/CH_4 replacement from natural gas hydrates was proposed for energy exploitation and it has also been considered promising gateway for sustainable development and carbon sequestration. Besides from all other methods, comparing with hydrate exploitation methods, CO_2/CH_4 replacement have more advantages, such as recovery of methane gas, reducing water, maintaining reservoir stabilities, sand production and less energy in input (Wang *et al.*, 2021). Carbon dioxide (CO_2) gas hydrate is a clean, safe, non-toxic material as

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contrast to carbon sorbents (Wang *et al.*, 2021). Since the preindustrial era, organic evolution of carbon emissions has been rapidly increased. Due to combustion of fossil fuels and cement production, carbon emissions have increased by 97% from 5.0 Gt/year (1997) to 9.76 Gt/year (2017) (Zheng *et al.*, 2020). In recent years, Carbon capture and storage (CCS) technologies have been developed to mitigate these rising emissions. In addition, it has enabled oil and gas professional to capture CO_2 from effluent gases and ensure long-term storage. The CO_2 capture storage sites can be classified as either ocean storage sites or geological sites. The ocean storage can have two methods first which involve injection of CO_2 into seawater and second method involved as storage of CO_2 in marine sediments. The second method is relatively permanent and theoretically safe (Liu *et al.*, 2018).

Many researchers have achieved extensive constructive outcomes from CO_2/CH_4 exchange/replacement process experiments for the recovery of methane gas. The feasibility of gas production from this replacement mechanism was first presented in 1996 (Wang *et al.*, 2021). When carbon dioxide gas is injected in methane hydrate, due to large size of CO_2 molecules, large cages of methane hydrate are preferentially occupied by CO_2 molecules (Wang *et al.*, 2021).

The emission of CO_2 in the atmosphere is restricted by injecting liquid CO_2 on the ocean subsurface with an intent to form CO_2 hydrate (Oya *et al.*, 2017). Hydrate-based carbon capture (HBCC) have also been a topic of interest for many researchers as it enables a net depletion in carbon dioxide emissions from pre-combustion and post-combustion mixtures of gas, including shale gas, biogas, fuel gas. HBCC is credible for pre-emissions capture at steel mills, power plants and in manufacturing sectors because it has vast scale cyclic capacity and large CO_2 capture capacity (Wang *et al.*, 2020).

In this paper, current situation of CO_2 capture and its sequestration as hydrate at techno-economic level has been discussed. Further, the carbon capturing techniques and their technologies applied in the power and industrial sector are highlighted and carbon dioxide sequestration process in the form of CO_2 hydrate have been discussed.

2. CO₂ CAPTURE TECHNIQUES

Many subsiding technologies affect the work of fossils fuels or their emissions in the surrounding (e.g. carbon utilization, capture, and storage, replacement of coal by methane, use of nuclear power) (Cannone et al., 2021). The first step of CCS technology is developing awareness about separation and sequestration of carbon dioxide which can be adopted in various commercial sectors. The following are some types of carbon capturing techniques:

2.1 Oxy-Fuel Combustion CO₂ Capture Technique

This is one of the most efficient technology for capturing carbon dioxide from power plants. In this technique, near-pure oxygen is use to burn fuel as an oxidant. The main constituent of oxy-fuel combustion power generation are: a) to produce near pure oxygen - ASU (air separation unit); b) to purify flue gas and maintain its quality- FGP (Flue gas processing unit); c) to generate power heat and burn fuel-Gas and boiler turbine; d) for final purification of CO_2-carbon dioxide processing unit (CPU) (Cannone et al., 2021). The important requirement for any oxy-fuel combustion process is production of oxygen gas. Presently, the most cost-effective and efficient technology for production of oxygen in large scale is conventional cryogenic multi-column distillation. The standard method with high-low pressure column comprises of a double column distillation cycle. The gases which are coming into high pressure column are separated into an overhead nitrogen vapor and bottom liquid enriched in oxygen (Sun *et al.*, 2021).

Oxy-fuel combustion capture technique is used in both gas-turbine power plant and coal-fired power plant. Oxy-fuel combustion technique capture mainly integrates ultra-super critical (USC) and super critical pulverized coal (SCPC) power plants with lignite and sub-bituminous like low-rank coal. Oxy-fuel combustion capture techniques with critical CO_2 combined with Allam cycle applied as working fluid at very high temperature (around 1423 K at the inlet of the turbine) and pressure (around 29.9 MPa). The Allam cycle plant fuel by methane gets 50% lower heating value (LHV) efficiency which means it can capture 100% of carbon dioxide (Jadhawar *et al.*, 2021).

2.2 Pre-Combustion CO₂ Capture Technique

This technique covers decarbonization by gasification or steam natural gas reforming of primary fuel such as coal, methane, biomass respectively, and separation of carbon dioxide. Hence, outcome of this technology produces the purest form of hydrogen. The natural gas which is primary in nature flows with the water and air into the gasifier reactor, usually pressurized. When the gasification process ends, the mixture of hydrogen, carbon monoxide (syngas), carbon dioxide, and methane is obtained. The pressure and temperature conditions strongly govern the gas composition of the gas hydrate. At high temperature, the amount of carbon monoxide increases while the amount of natural gas decreases. With increasing gasification pressure, the mole fractions of carbon monoxide and natural gas increases (Cannone et al., 2021).

The gasification operation does not confiscate the molecules of carbon, but it changes carbonaceous solids into useful product of gas used in heating chemicals and removing the contaminant products. The most common technique is the integrated gasification combined cycle technique (IGCC). The CO_2 content of pre-combustion capture is greater than post-combustion processes, and hence lower energy is required for separation of CO_2. The CO_2 concentration can be in the range 30-40% mol for IGCC after water removal and water gas shift (WGS). The Vacuum Pressure Swing Absorption (VPSA) and physical solvent are technologies that are mainly used for capturing carbon di-oxide gas in IGCC power plants (Sun *et al.*, 2021).

2.3 Post-Combustion CO_2 Capture Technique

Post-combustion techniques enables the separation of carbon dioxide from exhaust gases. The carbon dioxide produced by the numerous industrial processes or combustion of fossils fuels, is concentrated, purified and dispatched to a storage unit. Technically, post combustion capture technique is the most effortless and straightforward techniques, and it can be used in sustainable plants without any consequent changes (Ors and Sinayuc, 2014).

The post-combustion capture technique are divided into physical and chemical absorption process (Cannone et al., 2021). The chemical absorption process is widely used post-combustion capturing technique. In chemical process, blend of aqueous amines which consists of amino acids salts, ionic liquids and ammonia are utilized, while in the scenario of solid sorbents they utilize calcium looping and others.

3. CO_2 SEQUESTRATION IN HYDRATES BY USING CO_2-CH_4 EXCHANGE TECHNIQUE

CO_2 gas is known to be a potential gas which can participate in the hydrate formation and forms the clathrate/hydrate crystals (Sabil et al., 2011). In marine sediments, CO_2 hydrates can be synthesized in high pressure-low temperature (HP-LT) conditions, which enhances the kinetics/sequestration capacity of reservoirs (Liu *et al.*, 2018). CO_2-CH_4 exchange technique serves dual purpose by extracting CH_4 gas and ensuring long-term storage and sequestration of CO_2 gas as hydrates (Ning *et al.*, 2014). This has been an area of interest for many researchers and investigators as it has uplifted the role of CCS technology for the development of clean energy in the form of CH_4 gas with the mitigation of excess anthropogenic CO_2 gas from atmosphere (Jia *et al.*, 2020).

In the CO_2-CH_4 exchange process, the stability of methane hydrate is disturbed by the action of CO_2 molecule on the surface of gas hydrate. This results in the disintegration of hydrate cage structure which further release CH_4 gas. Further, CO_2 gas injection led CO_2 molecules to acquire in larger cages due to comparative larger molecular size which led to the synthesis of either CO_2 hydrate or hybrid CO_2-CH_4 hydrate (Cui *et al.*, 2018).

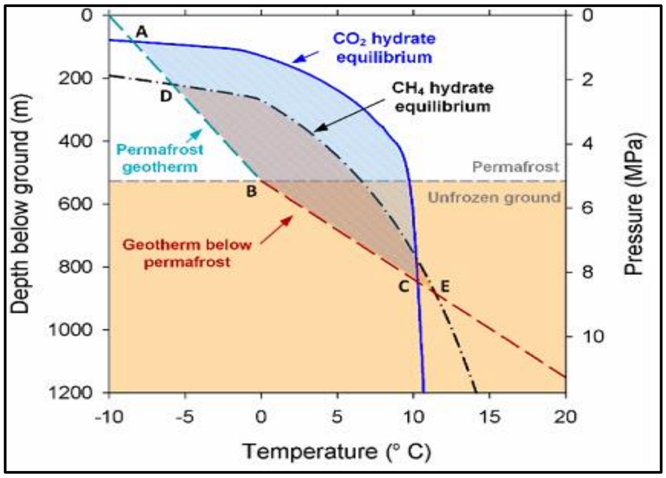

Figure 1. Phase equilibrium diagram of CO_2 and CH_4 hydrates for theoretical permafrost regions (Zheng *et al.*, 2020).

The pressure and temperature conditions contribute a major role in the formation and dissociation process of CO_2 and CH_4 gas exchange process using hydrate based technology (Jadhawar *et al.*, 2021). The combined phase equilibrium curve of CO_2 and CH_4 gas hydrates with their Hydrate Stability Zone (HSZ) or theoretical permafrost regions is shown in **Figure 1**. The equilibrium pressure of CO_2 hydrates in some regions is observed higher than CH_4 hydrates. This provides evidence of greater compatibility of CO_2 hydrates than CH_4 hydrates which makes CO_2-CH_4 exchange techniques more feasible (Zheng *et al.*, 2020).

3.1 Extensive Research

CO_2-CH_4 exchange technique is considered as the eco-friendlier approach for exploitation of methane from gas hydrates. The feasibility of this process was first

Table 1: Extensive research in CO_2-CH_4 exchange technique for CO_2 sequestration (Wang *et al.*, 2021).

S. No	Extensive Research	Samples Used for Study	Gas Injected	Pressure (MPa)	Temperature (K)	Time (hr)	Methane (CH_4) Recovery (%)
1	(Ors and Sinayuc, 2014)	Medium grained sand pack system comprising 30% CH_4 hydrate saturation	CO_2	8.52	293	6	86.26
2	(Wang *et al.*, 2021)	Marine sediments derived from South China Sea bearing CH_4 hydrates	CO_2	2.30	273.65	50	14
3	(Pan *et al.*, 2020a)	Silica sand with 10% clay sediments (montmorillonite, (MMT))	$CO_2 + N_2$	8.19	274.20	280	24.40
4	(Pan *et al.*, 2020a)	Silica sand with 30% clay sediments (MMT)	$CO_2 + N_2$	8.25	274.20	280	26.80
5	(Pan *et al.*, 2020a)	Silica sand with 50% clay sediments (MMT)	$CO_2 + N_2$	8.34	274.20	280	30.30
6	(Koh *et al.*, 2012)	Clay sediments (MMT)	CO_2	3.50	273.20	120	64
7	(Pan *et al.*, 2020b)	Sand with 10% clay sediments (MMT)	$CO_2 + N_2$	9.98	274.20	280	16.50
8	(Pan *et al.*, 2020b)	Sand with 30% clay sediments (MMT)	$CO_2 + N_2$	10.03	274.20	280	24.50

observed in 1996 by Ohgaki *et al.* (1996). Further, some experiments and investigations were conducted by researchers to study the kinetics of CO_2-CH_4 as listed in **Table 1**. This method is observed to have a potential to sequester around 1,00,000 Gt of CO_2 gas which can create a significant positive impact on environment and promote use of CCS technology (Zheng *et al.*, 2020).

3.2 Results and Discussion

For the detailed analysis of the studies mentioned in **Table 1**, it is necessary to compare the outcomes of the studies to understand the effect of CO_2-CH_4 exchange process in porous media. **Figure 2** shows the comparison on the basis of CH_4 gas replacement efficiency for each study listed. Certain factors like permeability, porosity, secondary hydrate formation and heat and mass transfer are found to govern the CO_2-CH_4 exchange process in *in-situ* oceanic and permafrost reservoirs.

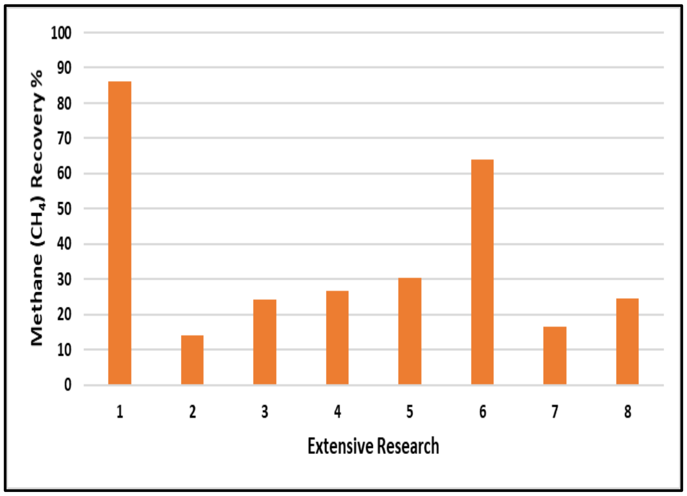

Figure 2. Comparison on the basis of CH_4 replacement % obtained in different studies.

Ors et al. (2014) studied the effect of CO_2 gas injection in medium grained sand pack system. The CO_2-CH_4 exchange process is confirmed using gas chromatography (GC). **Figure 3** represents the mole fractions of CO_2 and CH_4 gas at the beginning and at the

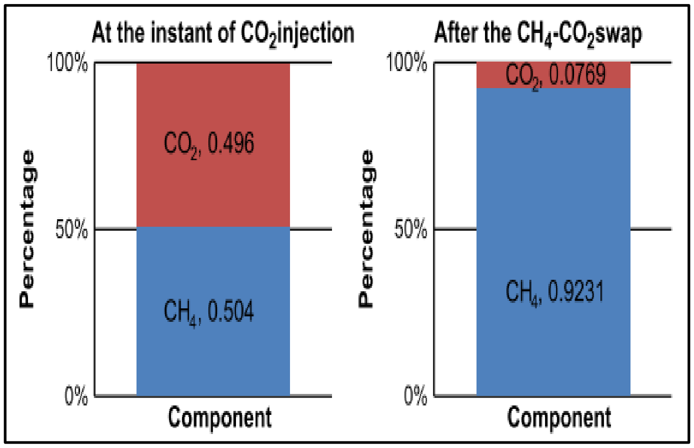

Figure 3. Mole fractions of CO_2 and CH_4 at the beginning and at the end of CO_2- CH_4 exchange process (Ors and Sinayuc, 2014).

end of CO_2-CH_4 exchange process. They reported that the mole fraction of CO_2 and CH_4 gas was 0.504 and 0.496 at the time of CO_2 gas injection. Further, after 6 hrs, only 0.06708 g/mol of free CO_2 and 0.80518 g/mol of free CH_4 gas was found in the hydrate structure.

Wang et al. (2021) utilized fine sediments of 5.482 µm size which consist of clay minerals from South China Sea (montmorillonite (MMT), illite, etc.). As per their study, higher water saturation in the sediment, will form more hydrates. In addition, in the CO_2 gas storage, the free water produced after the disintegration of CH_4 hydrates also have significant impact represented in **Figure 4**.

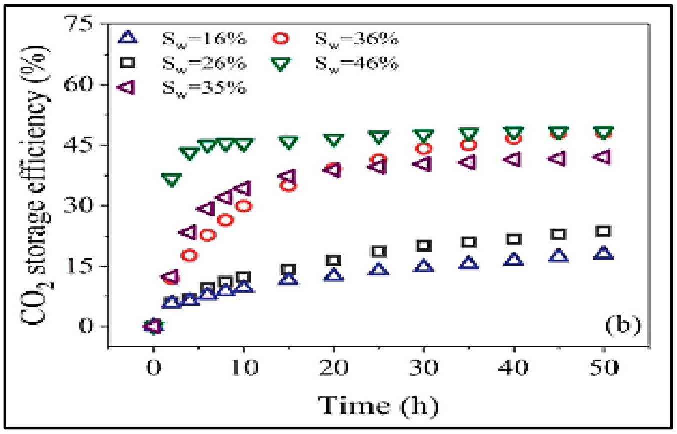

Figure 4. Effect of variations in water saturations in marine sediments on CO_2 storage efficiency (Wang *et al.*, 2021).

On the basis of size of sediments, the water is grouped as capillary bound, free mobile water and clay-bound water. The mobility of water in capillary bound and free mobile water is comparatively higher than strongly bound water. It is observed that the strongly bound water restricts the contact of CO_2 gas with hydrate which further decrease CH_4 gas replacement in hydrate.

Pan et al. (2020a) studied the effect of clay minerals in different proportion in hydrate bearing sediments when CO_2/N_2 gas is injected. Four concentrations of MMT in silica sand (0%, 10%, 30% and 50%) was studied in four stages. The inverse relation of the replacement efficiency increases with concentration of clay minerals present in sediment was observed. Later, the inhibitive nature of clay sediments against the CO_2-CH_4 replacement process by using 10% and 30% MMT in sand was reported (Pan *et al.*, 2020b). Further, Koh et al. (2012) performed a study of CO_2-CH_4 exchange process in Intercalated Methane Hydrate (IMH) reservoirs by injecting CO_2 gas. They reported a CH_4 gas replacement efficiency of 64% and observed a slower recovery in comparison to bulk natural gas hydrate.

4. CONCLUSION

This manuscript has reviewed the work done to study the hybrid process of sequestrating CO_2 gas as hydrates in porous media using CCS technology by CO_2-CH_4 exchange techniques. The CO_2 gas molecule due to comparatively large size was found to occupy large size cages leaving the CH_4 in the small cages. To enhance the exchange process, a mixture of CO_2 and N_2 was utilized which enables the replacement of CH_4 from small cages and improved the CO_2 storage capacity. Comparison on the basis of CH_4 gas replacement efficiency facilitate better understanding of the factors governing the long-term CO_2 gas sequestration. Certain factors like water saturation, percentage of clay sediments etc. is observed to have significant effect on sequestration capability. In addition, the availability of the optimum environment also plays major role in ensuring successful completion. This technology is believed to be the near-term technology with less field data in comparison to laboratory data and is constantly studied for building safer and cost-effective solutions for large-scale implementation.

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