Review

Gas Hydrate-Based CO$_2$ Capture: A Journey from Batch to Continuous

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Abstract: Future carbon dioxide capture and storage (CCS) will be impacted by the new scenario in which the energy supply rapidly shifts from oil-based to natural gas-based means, but this shift also presents an opportunity to utilize natural gas hydrates (NGHs). This review discusses the present state of CCS research and development, the advantages of the various approaches, and the barriers to commercialization that exist today. It also provides an evaluation of certain practical small- and large-scale CCS applications. The high initial investment, as well as ongoing maintenance costs, plague today's commercially accessible CO$_2$ capture technologies, including absorption, adsorption, membranes, and cryogenic separation. Gas hydrate-based capture has the potential to become the dominant method for CO$_2$ separation because of the high recovery rates and purity it provides. Hydrate-based technologies, including CO$_2$ capture, CO$_2$ separation, and transportation, can also be used to reduce greenhouse gas emissions and have excellent application potential. Despite this, the potential of technology based on gas hydrates to help reduce the effects of climate change in the future has received little attention. This study discusses cosmopolitan energy provision and environmental challenges and conversions, and the role of gas hydrates in the carbon cycle. This paper summarizes the state-of-the-art developments in hydrate-based reactors, thereby providing a perspective on the roles of NGHs in the future energy supply and climate change mitigation. In all these areas, we focus on identifying future CCS challenges and the technological development risk in gas hydrate-based systems, which should be highlighted in the next several decades.

Keywords: gas hydrates reactor; CO$_2$ capture; batch to continuous

1. Introduction

Increasing worldwide average air and ocean temperatures, widespread melting of ice and glaciers, notably at the North and South poles, and therefore rising global average sea levels are all clear indicators of a warming climate system. It is strongly believed that human-caused greenhouse gases (GHG) and aerosol emissions are the primary causes of these climatic shifts around the world [1,2]. Since the start of the Industrial Era, there has been a dramatic increase in the atmospheric concentration of greenhouse gases, such as carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O). The global carbon cycle is depicted in Figure 1, a simplified schematic. In this figure, the black figures and arrows represent data from before the Industrial Revolution, while the red numbers and arrows show how things have changed since then [3]. From 278 ppm in the year 1750, the atmospheric quantity of CO$_2$ rose by 40 percent to 390.5 ppm in 2011. Sea levels have risen 0.17 mm since 1861, and the average world temperature has risen 0.60 degrees since 1861 [4]. A recent analysis found that even if all human-caused carbon emissions stopped at the end of the 21st century, the world's average temperature would rise by 2 °C relative to pre-industrial levels [5]. However, this average temperature rise could pose serious problems for the planet as a whole [6]. Therefore, it is everyone's duty to

work together to slow global warming. An international accord called the United Nations Framework Convention on Climate Change was the first significant step taken to combat global warming in 1992 (UNFCCC). The Kyoto Protocol (KP) was ratified as part of this international pact [7]. Over the course of the first commitment period of KP, from 2008 to 2012, 37 industrialized countries and the European Community agreed to reduce their carbon emissions by an average of five percent from their 1990 levels [7].
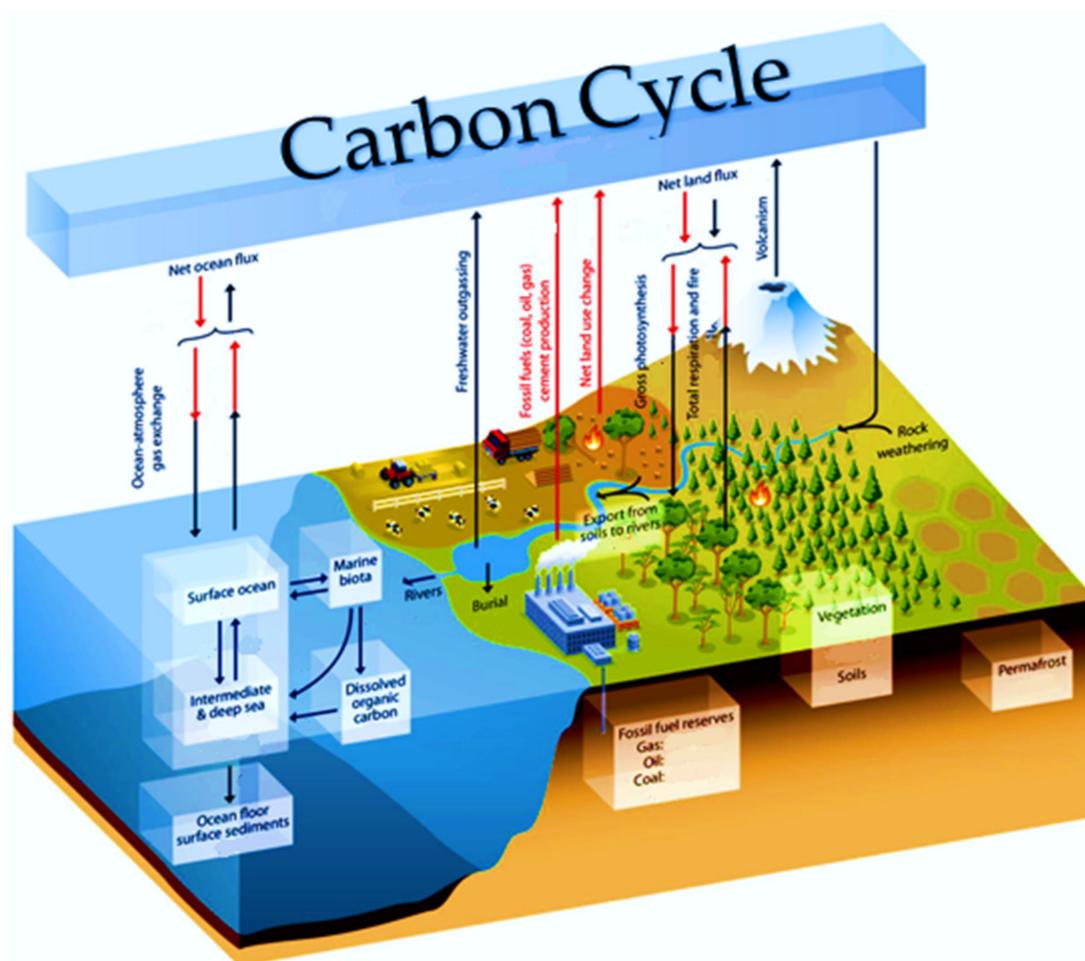

Figure 1. Diagrammatic representation of the international carbon cycle [3].

Human population growth and economic development in each country/region are two major contributors to the increase in atmospheric carbon release (as CO_2). Two major contributors to carbon dioxide emissions are the energy intensity of the economy and the carbon intensity of the energy system. However, there is a dearth of available CO_2 sinks. Carbon emissions from human-caused sources are highlighted in Figure 1, which depicts the global carbon cycle [8,9]. There are not many options for cutting down on CO_2 production. There is no political or technologically sound way to address the problem by reducing the population or lowering living standards; therefore, other alternatives are all that remain for cutting down on CO_2 emissions. UNFCCC has identified the following options as the most promising ones:

- Lifestyle changes that lower energy consumption [10–12].
- Switching from fossil fuels to renewables [13–17].
- Discovering and developing more sustainable energy resources [12,18–20].
- Cutting down on greenhouse gas output instantly. A number of outcomes are included in this, such as:
  - Increasing the effectiveness of energy generation and consumption [21–23].

○   Accelerating the rate at which CO_2 is absorbed by sinks [1].

○   Flue gas cleaning if concurrent with suitable storing [24–27].

The first approach takes a long time and is typically only used in developed nations. Altering one's lifestyle is not a simple or politically backed endeavor in other nations, particularly China and India, which are responsible for a sizeable portion of global CO_2 emissions [1]. Many advanced nations have begun the transition away from fossil fuels and toward other energy sources, particularly renewable energies; however, the significantly greater cost of renewable energy and technical/political issues are obstacles to a swift shift from fossil fuels to renewable fuels [28]. As a result, the growth in renewable energy use is not fast enough to counteract the worldwide rise in greenhouse gas emissions.

One of the most promising of these approaches is cleaning up flue emissions. Capturing and sequestering GHGs, especially CO_2, is a top priority for the KP since it is the quickest solution to reduce GHG emissions. Carbon capture and storage (CCS) is the only current technology that allows humanity to keep burning fossil fuels.

In addition, the generation of electricity is not the only factor in global warming. GHG emissions are impacted significantly by CO_2 emissions from the transportation sector, particularly long-distance/international commerce transportation channels such as international shipping [29]. In addition, the use of biogas, mostly landfill gas, as an alternative fuel gas resource [30] gas with a high concentration of carbon dioxide [30], in both gas treatment and CCS implementation, CO_2 capture is a crucial step. Landfill gas can contain as much as 50 mol% CO_2 [29]. As a result of releasing such a significant quantity of carbon dioxide, the fuel's heating capacity is diminished. The already high levels of carbon dioxide (CO_2) in these natural gas reserves have been found to rise. Massive energy demands, coupled with the security of fuel supply and the availability of large gas reserves around the world, have drawn significant attention to the production of such reservoirs. The amount of carbon dioxide (CO_2) stored in some of these reservoirs is extremely high. Natuna in Indonesia is the largest discovered field, with a carbon dioxide (CO_2) concentration of 15–80% [31]. CO_2 levels in Peninsular Malaysian fields such as Bujang, Sepat, and Noring average around 60%. In addition, the K5 Field off the coast of Sarawak has 25.65 quadrillion standard cubic feet of gas reserves, 70-mole percent of which is carbon dioxide [32].

Carbon capture and storage (CCS) is a method that involves capturing CO_2 from major sources (fuel-fired power stations), transporting it by pipeline, and then permanently burying it under the subsurface. Pre-combustion, post-combustion, and oxy-fuel combustion are the principal CO_2 collection technologies used in today's fuel-fired power plants [33]. Figure 2 depicts the block flow diagrams for all three technologies. In pre-combustion technology, carbon is removed from the fuel prior to combustion. Steam reforming and the partial oxidation method can be used for the pretreatment of fuel. In the earlier method, hydrogen is produced by reacting steam with fuel gas. By exposing the fuel to an abundance of oxygen, the partial oxidation process generates clean byproducts, such as a mixture of carbon monoxide and hydrogen (syngas) [34]. The post-combustion method captures the CO_2 from the flue gases generated during the combustion of fossil fuels. Pollutants, including carbon dioxide (CO_2), nitrogen dioxide (N_2), and others, are released into the environment along with the exhaust gases from power plants and industry. In comparison to pre-combustion and oxy-fuel combustion methods, post-combustion technology can be simply integrated into existing power plants, making it a more financially viable option [35]. Oxy-fuel combustion technology involves the use of pure oxygen combined with recovered fuel gas to burn low-nitrogen fuel. Oxy-fuel combustion technique produces ultra-clean fuel, but it is more expensive to process because it requires fuel compression and dehydration equipment [36]. Consequently, due to high operational costs, large-scale initiatives can fail quickly, which is detrimental to climate change mitigation efforts.
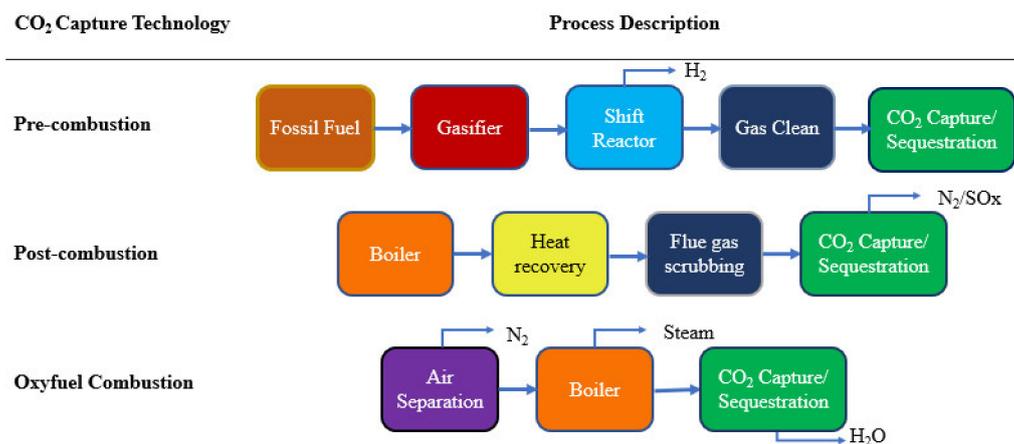
Figure 2. Carbon capture processes.

There are commercially available post-combustion CO_2 capture technologies that are being used in various industrial applications. The most common technologies are absorption, adsorption, membrane separation, and cryogenic distillation; the advantages and limitations are summarized in Table 1 [18].

1.1. Absorption

CO_2 can absorb either physically or chemically by coming into direct contact with the proper solvent. Physical absorption of CO_2 is based on Henry's law and its application is limited to low CO_2 concentrations. In chemical absorption, CO_2 reacts reversibly by treating solvent to make a weakly bonded intermediate compound. These week bonds can easily break by heating to regenerate the original solvent and CO_2 [37]. Chemical absorption has been used in natural gas treatment processes for several years. The alkanolamines are the most used and accepted solvent for capturing acid gas, i.e., CO_2 and H_2S. Monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), diisopropanolamine (DIPA), and methydiethanolamine (MDEA) are the most used chemicals in this category. These solvents are utilized in portions of 10 to 50 wt%. aqueous solutions. Utilization of amines solvent incorporates several operational problems that make them unfavorable for the treatment of high-CO_2 content gas mixtures. The most important one is corrosion. Amine solvents are not corrosive in nature. In fact, one of their applications is as an anti-corrosive agent; however, the presence of acid gasses is drastically changing this behavior in a way that one of the most challenging issues in the amine absorption process is corrosion [38]. In addition, a remarkably high circulation rate is required for capturing high concentrations of CO_2. MEA and DEA, as the most used amine solvents, have a loading of 0.33 and 0.5–0.7 mole gas/mole amine, respectively [39]. Therefore, the application of the amine process is limited to a maximum of 20 mol% of acid gas in the mixture [38]. Even for this low concentration of acid gas, the amine absorption process suffers from high CAPEX and OPEX. Estimations showed that the deployment of this technology could reduce the thermal efficiency of a modern power plant, with roughly 16 mol% CO_2 in flue gas, from approximately 45% to 35% [40]. New studies are targeting the amine solution process to overcome this shortcoming [41]. Hence, there is no solution now for very high CO_2 content natural gas.

1.2. Adsorption

Adsorption is a surface-based process where atoms, ions, or molecules from a gas, liquid, or dissolved solid bonding to a solid surface. From an industrial viewpoint, adsorption is a very important phenomenon that involves different aspects of chemical engineering. Adsorption is involved in various natural gas treatment processes and can be broken down into three different categories: chemisorption, physisorption, and size exclusion.

Chemisorption is normally happening in catalytic processes such as Fischer– Tropsch synthesis [42]. Physisorption is reversible adsorption on the surface of a material. Silica gel dehydration is the most famous physisorption adsorption [43]. In size exclusion, the target molecules fit into the pores of the adsorbent, and the rest passes by. CO_2, N_2, or O2 capturing is an example of this category of processes. In the physisorption and size exclusion categories, the process is almost the same. Pressure swing adsorption (PSA), vacuum swing adsorption (VSA), and temperature swing adsorption (TSA) are processes for the continuous capturing of target gases on industrial scales. PSA is the most practiced and studied process for capturing CO_2 from flue gas [44]. As the adsorption takes place in a fixed bed column of absorbent, for the continuous process, at least two parallel columns are required in the PSA process. One column should capture the gas and the second one should regenerate [43].

The key parameter in this process is the selection of absorbent. It should show good mechanical stability and especially resistance against corrosion and erosion, high adsorption capacity as well as proper selectivity, stable lifetime capacity, and adequate adsorption/desorption kinetics [44]. Adsorption technology for capturing CO_2 from fuel and flue gas has some advantages. For example, CO_2 and H_2S can be captured together and prevent this poisoning and corrosive gasses from entering the process/atmosphere. Pure CO_2 is produced via the adsorption process. In addition, the capturing capacity is higher than the absorption process, and heating is lesser than the absorption process; however, it has some drawbacks as well. The produced CO_2 has low pressure, and it requires compression duty. Furthermore, heat management in a solid material is difficult. In addition, the degradation of sorbent material after a few cycles can reduce the capacity. Aside from the mentioned limitations, capturing CO_2 as high as 70% in a mixture requires too many adsorbents and parallel product lines; therefore, utilization of adsorption for high CO_2-content gases requires high CAPEX and OPEX.

1.3. Membrane

The usage of membranes existed in nature long before humans began to understand and utilize the concept. From cell walls to peel, the membrane controls the transfer of materials [45]. In the industry, the desalination of water in the reverse osmosis process was the first usage of the membrane [46]. By using the difference in permeation of gases through a dense homogeneous membrane, CO_2 can be separated from other gases. The permeability of a gas depends on its solubility in the membrane and its diffusion through the membrane. Semipermeable membranes are currently used for CO_2 removal from natural gas [47]. The membrane separation does not require any chemicals, and thus, it is a cleaner process in terms of environmental concerns. Nevertheless, due to the required pressure difference as the driving force of diffusion, membranes suffer from the high cost of compression. Furthermore, in a membrane process, the high recovery rate and high purity of the product are not achievable at the same time. Therefore, proper pretreatment should normally accompany a membrane process. In addition, the most challenging step in membrane technology is scaling up [48].

Table 1. Pros and cons of most common CO_2 capture technologies.

Method	Advantages	Drawbacks	Ref.
Absorption	• CO_2 recovery does not require heat to reverse a chemical reaction. • Combined CO_2/H_2S removal. • Fast kinetics. • Best work with low CO_2 partial pressure. • Wet scrubbing allows good heat integration. • Ease of heat management. • More than 70 years of experience.	• Significant amount of energy (in the form of heat) required for regeneration. • Energy required to heat, cool, and pump nonreactive carrier liquid (usually water) is often significant. • Low capacity requires circulating large volumes of solvent, resulting in large pump loads. • Produced CO_2 pressure is low. • Not suitable for high CO_2 partial pressure.	[48–54]
Adsorption	• CO_2 recovery is primarily based on the pressure swing. • CO_2 and H_2S capture can be combined. • Large capacities. • Fast kinetics. • Best work with low CO_2 partial pressure.	• Produced CO_2 pressure is low. • Heat management in solid systems is difficult. • Produced large pressure drop. • Heat required to reverse chemical reaction. • Sorbent attrition. • Not suitable for high CO_2 partial pressure.	[55–58]
Membrane	• No steam load or chemical attrition. • Clean process. • Low maintenance cost. • Compact design. • Can deliver CO_2 at high pressure.	• High capital cost. • High operational cost. • Membranes may not keep out all unwanted contaminants. • Tradeoff between recovery rate and product purity. • Requires high selectivity. • Requires good pretreatment. • Bad economy of scale.	[54,59–61]
Cryogenic distillation	• Produced highly pure CO_2. • Favorable for high CO_2 content mixtures.	• Large cooling duty. • High operational cost. • Not suitable for small/medium scale applications.	[62–64]

1.4. Cryogenic Distillation

Cryogenic distillation uses the difference between phase behaviors of gases as a separation concept. CO_2 at atmospheric pressure has no melting point, and it converts to dry ice at -78.5 °C, while N_2 and CH_4's normal melting points are -210 °C and -182 °C, respectively. This difference in phase boundary is the basis of low-temperature processes for the separation of carbon dioxide from flue and fuel gas [62]. The cryogenic process consists of two steps. The process dries and cools the gas stream, either flue or fuel, and compresses it to a condition slightly above the CO_2 sublimation line. In this step, depending on accompanying components, a rich CO_2 liquid or a cold gas stream forms. Then in the second step, the stream expands, passing through a Joule–Thomson

valve to cool it further and converting the system into three phases: solid, liquid, and gas. Utilizing a proper separator along with further heat treatment, the result is highly pure liquid CO_2 [62]. This process is more favorable for the purification of high CO_2-content gas mixtures (>50) [63]. Nevertheless, the cryogenics process requires large cooling duties, which makes it less favorable for smaller plants such as LPG or offshore applications. Some researchers have suggested that if this technology combines with other capture techniques, the high operational cost and, consequently, the final product cost can be reduced to a reasonable level [64].

2. CO_2 Capture Challenges and Outlooks

The first industrial-scale CCS project was launched at Boundary Dam SaskPower, Saskatchewan province, Canada, in October 2014; see Figure 3. The Boundary Dam Project is the integration of a rebuilt coal-fired generation unit with carbon capture technology as a post-combustion CCS project. The captured technology used in this project is amine solution absorption [65].

Figure 3. SaskPower carbon capture and storage project, Saskatchewan province, Canada. This project involves post-combustion capture of CO_2 accompanied with CO_2-EOR [65].

Aside from the big achievement of this CCS project, the Boundary Dam SaskPower practice has a very important message. The technology at the heart of efforts to avoid global warming will struggle to be economically viable in many places. Although SaskPower had a federal government subsidy of \$240 m, the project's long-term financial feasibility is only granted by a 10-year contract to sell all its captured carbon dioxide to the Canadian oil group, Cenovus Energy, for CO_2-EOR application. This opportunity is not granted to other power plants around the globe; the extreme reduction in crude oil prices during the last year proves that even having this option is not a long-term grantee for the feasibility of the CCS project. The energy required to operate CO_2 capture systems reduces the overall efficiency of power generation or any other processes. Therefore, the minimization of energy requirements for CO_2 capture is one of the highest priorities for future technology development to minimize overall environmental impacts and costs [66].

There are several ongoing studies on each of the mentioned capturing technologies to increase efficiency and reduce costs. Several publications summarized [67–74] this research. Nonetheless, there is room for novel and modern technologies to decrease the cost of capturing steps and reduce the environmental impacts. Electrochemical pumps, chemical

looping, and gas hydrate separation are a few examples of innovative technologies for the separation of CO_2 from other gases.

Gas Hydrate-Based Technology for Separation of CO2

Gas hydrate, which is known as clathrate hydrate, is a crystalline compound that consists of water molecules in the shape of hydrogen-bonded cages and entrapped gas/liquid molecules inside those cages. Gas hydrates are non-stoichiometric ice-like polyhedral structures. Gas hydrates are formed under low temperatures and high pressure. The water molecules encapsulate the guest (gas) molecules by H_2 bonding. Presently, there are three commonly known structures: sI, sII, and sH. Guest repulsion is more significant than attraction in maintaining cavity expansion in hydrates because the cavities are extended in comparison to ice and the presence of guest molecules prevents them from collapsing [75]. In structures I and II, the size of the guest significantly affects the occupancy of hydrate cavities and the hydrate structure. The shape and size of a guest molecule are both important in structure H. Crystal structures and cage occupancy can be approximated using the size ratio of the guest to the cavity. In turn, the equilibrium pressures and temperatures of the hydrate phase are established by the crystal structure. Hydrogen bonds and cavity occupation contribute to determining the heats of dissociation for all three configurations. Dissociation enthalpies are also consistent when similarly shaped cavities are occupied (regardless of the guest) [76]. Guest molecule sizes vary from 0.40 nm to 0.90 nm. sI encloses molecules of a size of 0.40 to 0.55 nm, while sII and sH can encapsulate molecules of a larger size, such as propane or iso-butane. The guest gas molecules tend to form stable hydrate crystals if the size ratio (gas molecule: cavity size) is approximately 0.9 [77]. The CO_2 molecule usually forms an sI hydrate structure as the size ratio of the CO_2 molecule for a small cage is one while it is 0.834 for the large cage of sI structure; therefore CO_2 molecule preferentially occupies the large cages [78]. Gas hydrate is normally stable at moderate to high pressures from a few kPa [79] to GPa [80] and low temperatures from 140 K to 330 K [81]. The formation of gas hydrate is a thermodynamic-driven process. Recently, gas hydrate has been nominated as a medium for CO_2 capturing, mostly from flue gas as a post-combustion CO_2 capturing scenario [82–84]. Hydrate-based separation is attracting attention as a new capturing technology due to its lower energy requirement compared to conventional capturing technology [85,86]. Furthermore, this technology uses water as the main chemical with a small portion of additives as a promoter [87,88]. Thus, it is considered a less environmentally harmful process. Selectivity is the most important parameter in any capturing method. CO_2 has a suitable size to form stable gas hydrate at a pressure of around two to six MPa, while N_2 is too small to stabilize hydrate structure at this pressure range. Therefore, CO_2 has a better chance of forming gas hydrate at moderate pressures compared to N_2. Consequently, the selectivity of CO_2 is high with a hydrate-based process [89]. Although the tendency of CO_2 and CH_4 to form hydrate is similar, CO2 still has a better chance to form hydrate at lower pressures compared to CH_4. Then, the separation of CO_2 from CH_4 is also possible under controlled conditions [90,91].

There are a few limitations to the industrial application of hydrate-based processes as a capturing technology. Hydrate formation is a crystallization process, and any other crystallization process requires proper super saturation conditions, enough contact area, and time. For example, in a study for the separation of CO_2 from CH_4 by hydrate study, the required time for nucleation is reported to be more than 6 h [92]. Moreover, hydrate formation is an exothermic process; therefore, as the hydrate formation rate increases, the heat generation will increase, and consequently, the reactor temperature will rise. As this process is a thermodynamically driven one, increasing the temperature can alter the condition from a hydrate's preferred to a non-hydrate's preferred condition [93]. The separation of gases by hydrate formation is not a new idea. This idea was first put into practice by Soviet scientists in the 1940s when Nikitin suggested the separation of argon from neon by utilization of SO_2 hydrates. Recently, the possible application of this process for CCS application encouraged scientists to look deeper into this process. Several research

groups are working on the utilization of gas hydrate technology for the separation of gases [94]. Table 2 shows a list of experimental studies on the separation of CO_2 from N_2, CH_4, or H_2 using a gas hydrate; however, the present studies are elementary and exploratory. Most of the reported processes are based on laboratory-scale setups, batch-type with low-capacity processes, which may not be applied on an industrial scale. In addition, the studies on the separation of CO_2 from CH_4 are very limited. However, as mentioned before, this mixture has existed in many locations, from very large scales, such as non-conventional natural gas reservoirs [95], to small scales, such as biogas produced in farms [96]. The fundamental studies, as well as semi-industrial information, are required before judging the capability of hydrate-based processes in the separation of CO_2 from CH_4. Most importantly, as CO_2 and CH_4 molecules share similar properties for hydrate formation, separation from them using the hydrate process is more challenging; therefore, more attention is required for the selection of additives to enhance the separation efficiency. This requires extensive information on the thermodynamic equilibrium and kinetic behavior of the CO_2/CH_4 mixture in the presence of additives. Unfortunately, these data are not available in the open literature. Most kinetic studies are focused on simple hydrates and recent thermodynamic investigations consist of CO_2/N_2 and CO_2/H_2 systems [97–99].

Methane (CH_4) and carbon dioxide (CO_2) hydrates have been the subject of molecular dynamic (MD) simulations in recent advances. The temperature dependence of the lattice constant and the thermal expansion coefficient were determined. At higher temperatures, the most relevant case for practical applications of hydrates is as an energy source or CO_2 sequestration medium; there is consistency between the lattice constants and the isobaric thermal expansion coefficients obtained from MD simulations [100]. Through analyzing sites of intersection, researchers were able to find new, precise quadruple points. For equilibrium below the quadruple point, the enthalpies of clathrate formation and dissociation are interpreted in a manner similar to both the Clapeyron and Clausius–Clapeyron approaches, based on flash calculations using high-accuracy equations of states. New hydration numbers were determined based on the assumption of equilibrium equality at the quadruple point [101].

Besides the insufficient fundamental and operation knowledge on CO_2/CH_4 hydrate mixture, most investigations on gas hydrate are limited to laboratory scale studies. Poor reactor performance is one of the barriers in the development path of this technology. Table 3 compares the common reactors used in gas hydrate studies. Stirrer-tank reactors (STR) are the most common reactor for the batch process, and the majority of the gas hydrate data are produced by this type of reactor. STRs are the best choice for closed systems and small-scale batch processes due to the simplicity of operation. However, STRs are not recommended for large-scale hydrate formation, as many technical challenges may arise during the scale-up, fabrication, and operation of this type of reactor. The use of a stirrer to agitate the gas and water phases is the first and most important issue in utilizing STRs [102]. The effective viscosity of the gas hydrate slurry would increase with an increase in the volume fraction of the hydrate phase, especially in batch or semi-batch processes; therefore, the stirrer shaft must provide enough variable torque during the complete hydrate formation process. Although the mixing of gas and liquid phases are necessary for hydrate formation during the kinetic phase, very fast mixing will prevent the accumulation of hydrate nucleus during the effective induction, which is essential for the nucleation part. Hence, STRs suffer from long induction time [103,104]. On the other hand, at the final stage of hydrate formation, the slurry will be very viscous and mixing needs more power. Recently, in a study, multi-walled carbon nanotubes (MWCNT) were employed and gave a very good viscosity-reducing surface effect [105]. The finding in this study may assist in the designing of hydrate formation reactors on a commercial scale. Additionally, in another study, a phase transition stage was identified as characterized by the behavior of the system's viscosity as hydrate formation occurred. The results of this study suggest that temperature is an important parameter for controlling viscosity in new hydrate technologies involving gas hydrates from pure water [106].

Table 2. Gas hydrate studies on gas separation.

Ref. No.	Authors	Gas Mixture	Additive	Reactor Type/Volume	Year
[107]	Kang and Lee	CO_2/N_2	THF [1]	Stirrer/70 cm^3	2000
[44]	Seo et al.	CO_2/N_2 CO_2/CH_4	N/A	Stirrer/50 cm^3	2000
[10]	Seo et al.	CO_2/N_2	Silica gel	Stirrer, 50 cm^3	2005
[108]	Duc et al.	CO_2/N_2	TBAB [2]	Stirrer/1820 cm^3	2007
[109]	Linga et al.	CO_2/N_2 CO_2/H_2	THF	Stirrer/323 cm^3	2007
[110]	Linga et al.	CO_2/N_2	THF	Stirrer/323 cm^3	2008
[111]	Li et al.	CO_2/N_2	TBAB	Stirrer/1000 cm^3	2009
[112]	Seo and Kang	CO_2/H_2	Silica gel	Stirrer or fluidized bed/500 cm^3	2010
[12]	Li et al.	CO_2/N_2	TBAB, DTAC [3]	Stirrer/1350 cm^3	2010
[15]	Li et al.	CO_2/H_2	TBAB, CP [4]	Stirrer/1350 cm^3	2011
[113]	Gholinezhad et al.	CO_2/H_2	TBAB	Stirrer/570 cm^3	2011
[114]	Kim et al.	CO_2/H_2	TBAB	Stirrer/N/A	2011
[115]	Xu et al.	CO_2/H_2	TBAB	Bubble reactor/40 L	2012
[116]	Xu et al.	CO_2/H_2	TBAB	Stirrer/336 cm^3	2012
[117]	Babu et al.	CO_2/H_2	Silica gel	Fixed bed/1240 cm^3	2013
[118]	Sun et al.	CO_2/N_2 CH_4/N_2 CH_4/H_2	THF	Stirrer/1500 cm^3	2014
[119]	Zhou et al.	CO_2/CH_4	N/A	Stirrer/5.7 L	2014

[1] Tetrahydrofuran. [2] Tetra-n-butyl ammonium bromide. [3] Dodecyl trimethyl ammonium chloride. [4] Cyclopentane.

The second common type is bubble column reactors. Similar to stirrer tank reactors, the dominant phase is liquid water, which has a high heat capacity. Therefore, the heat of hydrate formation can be removed more efficiently from reactor walls, and a stable thermal profile can be provided in this type of reactor. Furthermore, the movement of bubbles in the water phase will agitate the system. However, providing tiny, uniform bubbles in the entire column cross-section and length is not a simple task; therefore, bubble columns cannot provide enough contact area for the continuous production of gas hydrate unless it is equipped with a stirrer system, which has their own drawbacks, as mentioned above [120]. However, some hydrate reactor is designed and reported in the literature based on bubble column technology [121–123].

The third common type of gas hydrate reactor is a spray tower. By spraying water into a continuous gas phase region, the gas/water interfacial area can readily be increased. Furthermore, as the tiny water droplets have large velocities in the gas phase of the reactor, the necessity of a mechanical stirring system is eliminated from this type of reactor. Thus, the design of the reactor is simple, and scaling up can be achieved easily; however, as the heating capacity of the gas phase is small, and a large portion of the spray tower is occupied by the gas phase, the heat of the hydrate formation may not be removed throughout the reactor walls efficiently—this will easily increase the reactor temperature. By increasing the temperature, the system super-saturation condition, which is essential for crystallization, would be decreased, and this would result in decreasing the rate of hydrate formation or even stopping it [120].

Table 3. Comparison of common reactors used in gas hydrate studies [120].

Reactor Type	Advantages	Drawbacks
Stirred-tank reactors	Suitable for lab-scale Simple operation Design is well established	High torque power for mixer High fabrication cost Risk of leakage is high Difficult scaling up
Bubble column	Effective heat removal Capability for internal cooling Heat and mass transfer can increase with addition of mixer Can convert all water to hydrate	Requires high-pressure compatible compressor to recycle extra gas Use of stirrer to bring up the stirrer-tank disadvantages
Spray Tower	Fast hydrate formation of a large contact area Can eliminate induction time Simple design No mechanical stirrer is needed Easy scaling up	Non-effective heat removal Hydrate slurry is inevitable

There are a few research groups working on the development of gas hydrate-based processes. However, as all studies are in the development stage, so far, very limited technical data have been reported in the open literature. Most of the reported processes are based on laboratory-scale setups in which stirred vessels, bubble columns, or spray towers are employed as the crystallizers, and the batched process is used in their experiments. This resulted in a lack of information on the impact of hydrodynamic parameters during continuous or semi-batch hydrate processes.

The principal aim of the present study is to investigate a gas hydrate-based separation process for the separation of CO_2 from natural gas mixture with high CO_2-content. Considering the wide application of capturing technology from small-scale to large-scale systems, this is a step towards continuous gas hydrate formation to reduce CO_2 footprints.

3. Economic Limitations to Hydrate-Based CCS

Several research articles detailed technical improvements in hydrate-based CO_2 capture methods, but very few addressed economic considerations [124]. In a study conducted by Babu et al. [125], a comparison was made on the basis of 500 MW of electricity produced by a coal gasifier. In this study, the hydrate-based CO_2 capture is compared with SELEXOL and SIMTECHE processes. The estimated cost of electricity was 6.13 and 6.24 cents/kWh for a twin-stage Tetrahydrofuran (THF) promotor system.

However, there is a lack of data for the economic analysis of CO_2 sequestration as hydrates in geological settings due to the relatively low level of technological maturity in this area. This section covers the topic of estimating the price of various parts of the hydrate-based CCS. The cost of a hydrate-based CO_2 capture technology employing TBAB as a promoter was estimated by Duc et al. [108]. This method captures CO_2 from the flue gases of the steel-producing industry. The costs of reducing CO_2 emissions were found to range from $20 to $40 per metric ton of CO_2, depending on operational parameters and feed gas quality. It was reported that the customer acquisition cost values were lower than the standard absorption-based CO_2 capture approach, which costs between $40 and $100 per ton of CO_2 captured [126]. The hydrate-based CO_2 capture method is more amenable to syngas applications, as reported by Spencer et al. [127]. According to their research, the energy cost of using hydrates to capture carbon dioxide is reduced by 50–75% compared to using absorption. Therefore, hydrate-based capture proves to be a sustainable and cost-effective alternative to absorption-based capture. As a relatively new field of study, hydrate-based CO_2 sequestration necessitates extensive study to refine existing methods and ensure its continued deployment to the government and industry.

4. Gas Hydrate Crystallizers

Ever since gas hydrates were first discovered, scientists have developed a wide variety of equipment to study them. Typical gas hydrate crystallizers and reactors were reviewed by Mori et al. [120]. Normally, stirrer-tank, bubble columns, or spray towers are used for gas hydrate crystallizers in both thermodynamics and kinetics studies. In addition, the rocking cells are used for thermodynamic studies [128,129] and the pipeline condition is simulated by means of the flow loops [130,131]. Moreover, there are a few unique crystallizers, the vast majority of which are currently protected by patents. In this section, we provide a review of these reactors and analyze the pros and cons of using them in an industrial setting. This analysis excludes rocking cells and flow loops since these types of reactors are not applicable to gas hydrates production on an industrial scale.

### 4.1. Stirrer-Tank Reactors (STRs)

The stirrer-tank reactor (STR) is a common equipment in gas hydrate lab-scale installations [132–136]. Due to its ease of use, this type of reactor is ideal for closed-system, low-throughput batch applications. A liquid phase predominates in these reactors. The stirrer is used to combine the gas and liquid phases.

Large-scale hydrate production is not advised in stirred-tank reactors due to the high probability of encountering technical difficulties during scale-up, manufacture, and operation. The first and most crucial problem with STRs is the stirrer itself, which is used to agitate the gas and water phases [120]. Increases in the volume fraction of the hydrate phase would result in increases in the effective viscosity of the gas hydrate slurry, particularly in batch or semi-batch processes. Therefore, an adequate and varying force from the stirrer shaft is required throughout the entire hydrate formation process. Hydrogen hydrates can only form when the gas and liquid phases are mixed; however, rapid mixing can ruin the nucleation process by dispersing the hydrate nucleus too quickly [137]. When the hydrate has fully formed, the slurry will be extremely viscous, necessitating increased mixing force. In addition, since the hydrate reactor needs to be run under high pressure, properly sealing the stirrer shaft is not a simple task. While this is feasible from a technical standpoint, doing so would significantly increase the price of the reactor. Current stirrer-tank configurations often use magnetic stirrers in place of impellers to solve the sealing issue under pressure. These two lab-scale stirrers-tank reactor designs are shown in Figure 4. When the viscosity of the slurry increases, however, a magnetic stirrer cannot deliver adequate thrust and will simply jam.
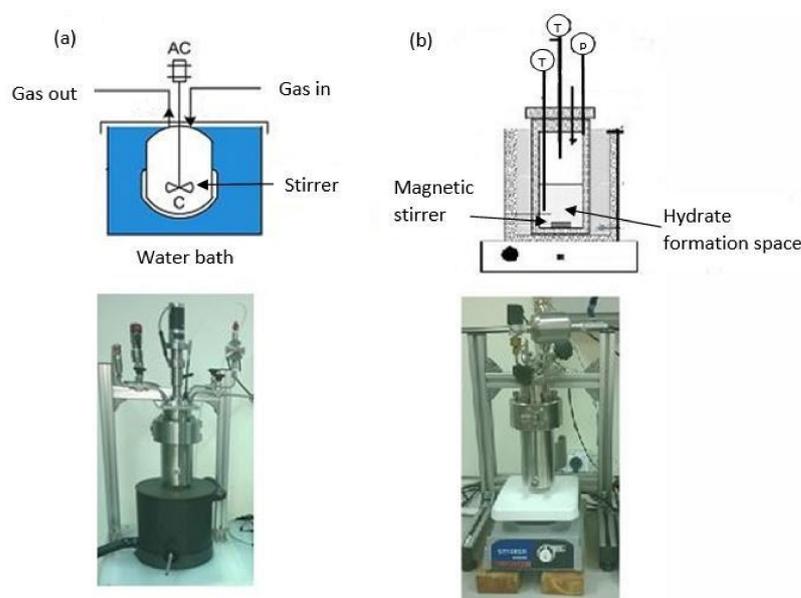
Figure 4. Lab-scale stirrer-tank reactors. (**a**) Impeller and external motor. (**b**) Magnet bar and magnet stirrer. Pictures are from Phase Separation Laboratory, RCCO$_2$C, Universiti Teknologi PETRONAS.

According to Figure 5, Linga et al. employ a stirrer-tank reactor fitted with an impeller designed in a way in which gas is induced from the impeller [138]. Consequently, the crystallizer can increase the agitation of the gas and liquid phases and reduce the agglomeration of hydrate crystals at the interface. The gas in the liquid phase is circulated internally by this impeller. A stream of gas flows toward the shaft from top to bottom and enters the propeller blades, and flies to the liquid phase as little bubbles when the stirrer is operating under pressure. Although the crystallizer's efficiency is improved in this approach, the impeller can still become stuck if a dense hydrate slurry forms inside the reactor.
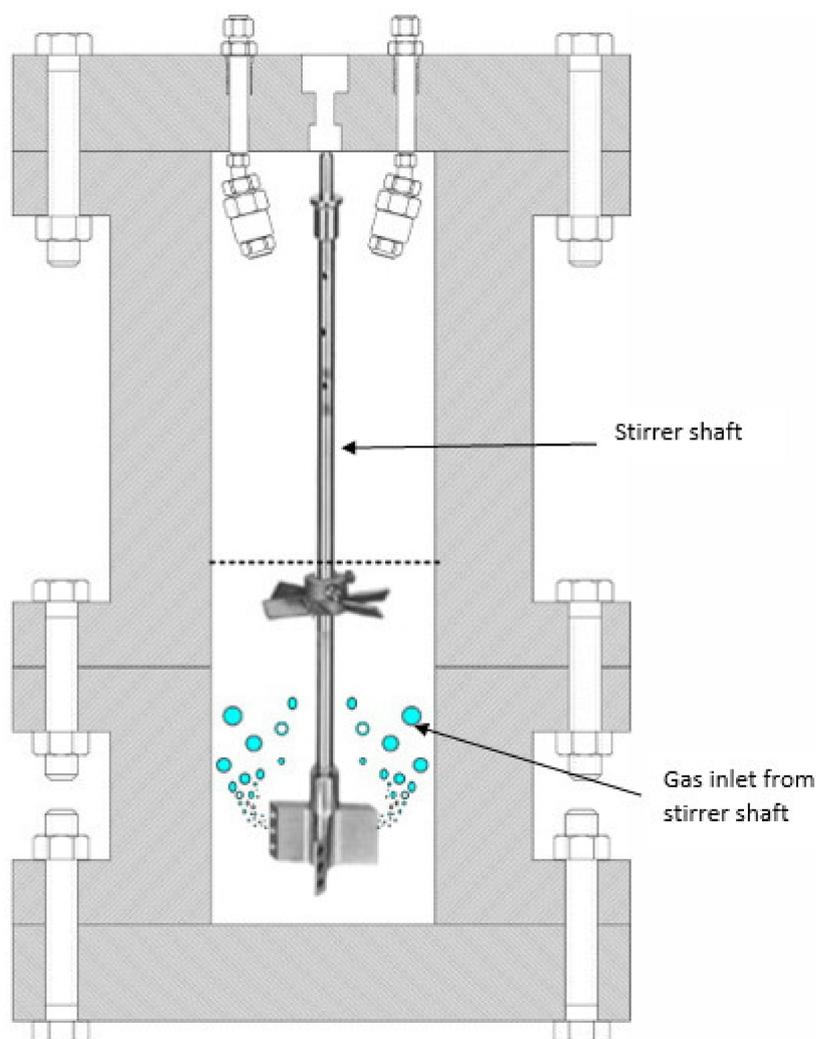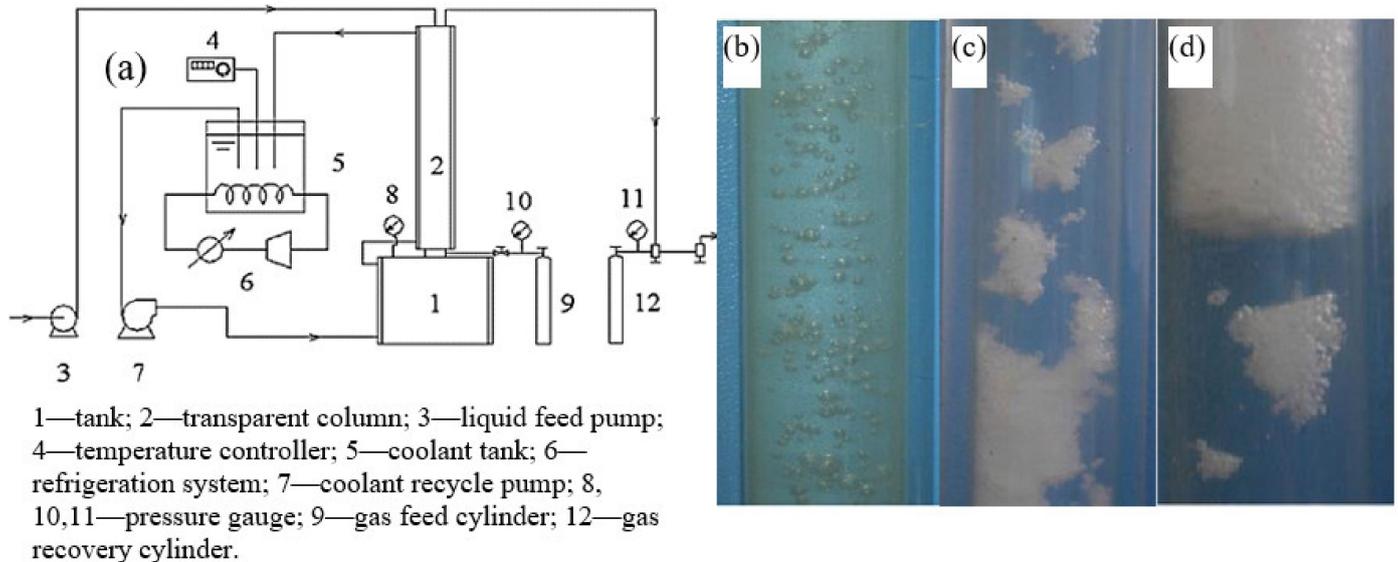

Figure 5. Cross-sectional diagram of the gas-inducing reactor proposed by Linga et al. [138].

4.2. Bubble Reactors

Liquid water, with its enormous heat capacity, is the main phase in bubble column reactors, which are similar to stirrer-tank types. As a result, a steady thermal profile may be given in this type of reactor, and the heat of hydrate formation can be removed from the reactor walls more efficiently. In addition, the system will be disturbed by the motion of bubbles in the water phase; however, it is not easy to provide tiny bubbles that are uniform in size over the whole cross-section and length of the column. For this reason, continuous gas hydrate generation is impossible in bubble columns without the use of a stirrer system, which has its own set of problems [120].

However, there are reports of bubble column-based hydrate reactors in the literature. Figure 6 depicts a new setup for producing gas hydrate and studying its dynamics, developed by Luo et al. [122]. In this system, gas bubbles are released from the bottom of the reactor and travel up the length of a transparent column until these bubbles reach the gas/liquid interface. Gas distribution is uniform throughout the column due to the narrow diameter, as seen in Figure 6b. Bubbles are shown in Figure 6c,d to be encasing themselves in a hydrate shell and then rising to the gas/liquid interface due to their buoyancy, where hydrates eventually agglomerate and block the whole column diameter.

1—tank; 2—transparent column; 3—liquid feed pump; 4—temperature controller; 5—coolant tank; 6—refrigeration system; 7—coolant recycle pump; 8, 10,11—pressure gauge; 9—gas feed cylinder; 12—gas recovery cylinder.

Figure 6. (**a**) Schematic drawing of the experimental setup employed by Luo et al. [122]. (**b**) Bubbles without hydrate. (**c**) Bubbles with hydrate cover. (**d**) Hydrate blockage in the reactor.

It should be noted that Hashemi et al. also presented a bubbler crystallizer to produce gas hydrates. This crystallizer was used to investigate the interfacial mass transfer between the gas and liquid phases during gas hydrate formation [123]. A schematic drawing of this apparatus is shown in Figure 7. The bubbler had a square design with 34 holes and the diameter of the columns was 0.1 m. The O_2/N_2 combination and tap water were used to measure the mass transfer between the gas and liquid phases, as hydrate formation was not possible under experimental conditions [123]. According to Xu et al., a new bubble column-based reactor has been developed for gas hydrate synthesis [139]. As shown in Figure 8, their main reactor had a total volume of 40 L, was built of stainless steel, and had transparent Plexiglas for visual viewing.

This reactor's size and retention duration allowed them to analyze how gas flow rate affected the kinetics of hydrate formation. The CO_2 was captured from the integrated gasification combined cycle (IGCC) synthesis gas using this apparatus.
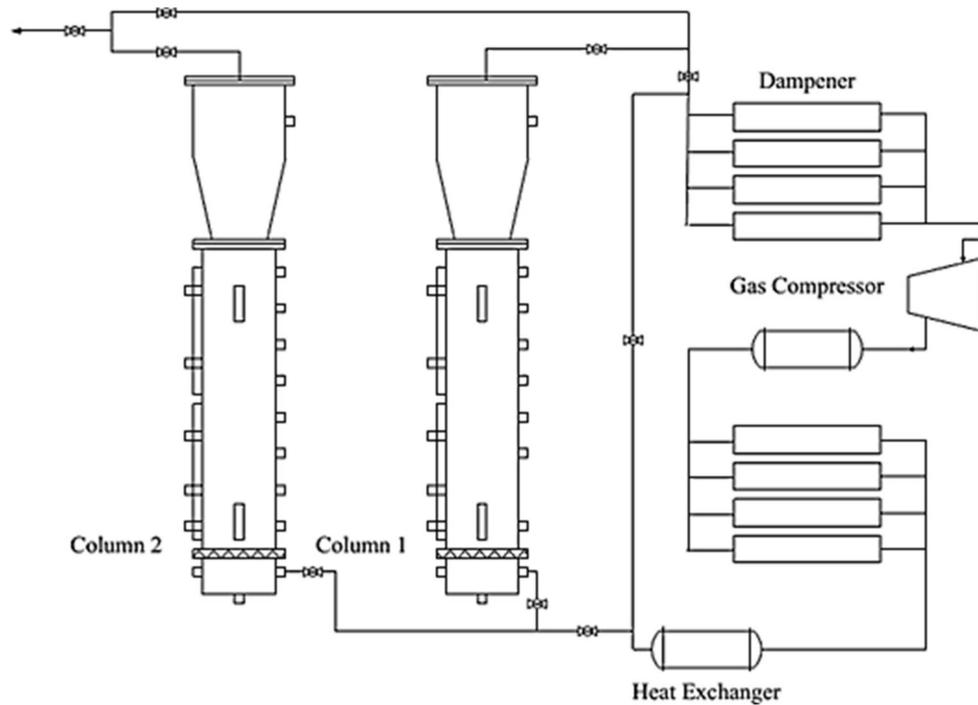
Figure 7. Slurry bubble column setup used by Hashemi et al. [123].

1. Gas Cylinder
2. Relief Valve
3. Liquid container
4. Flow meter
5. volume controller pump
6. chiller system
7. heat exchanger
8. coolant
9. Mixer
10. water bath
11. distributor
12. reactor
13. coolant recycle pump
14. visual windows
15. safety valve
16. vacuum pump
17. PID controller
18. gas-liquid separator
19. gas collection
20. data logging
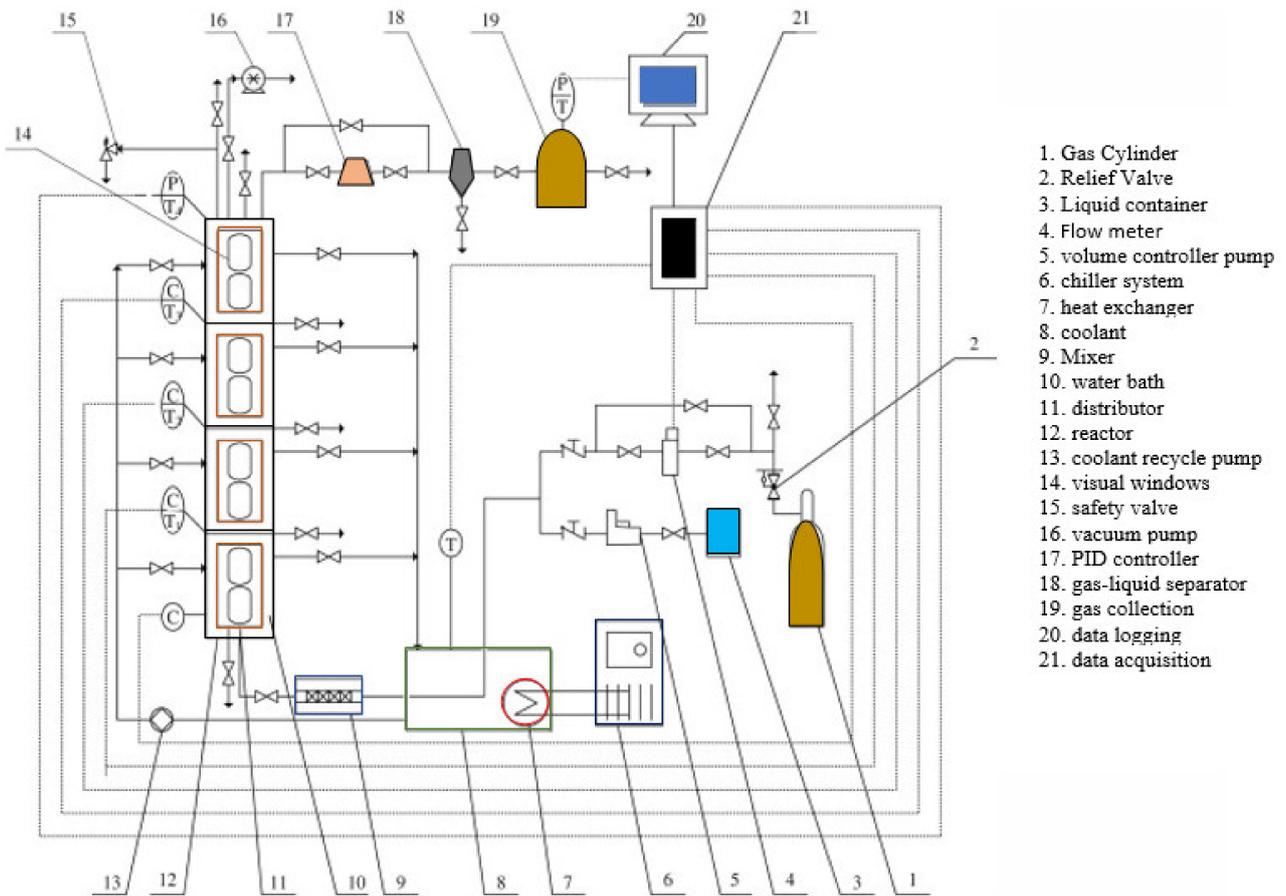21. data acquisition

Figure 8. Schematic of experimental apparatuses used by Xu et al. [139].
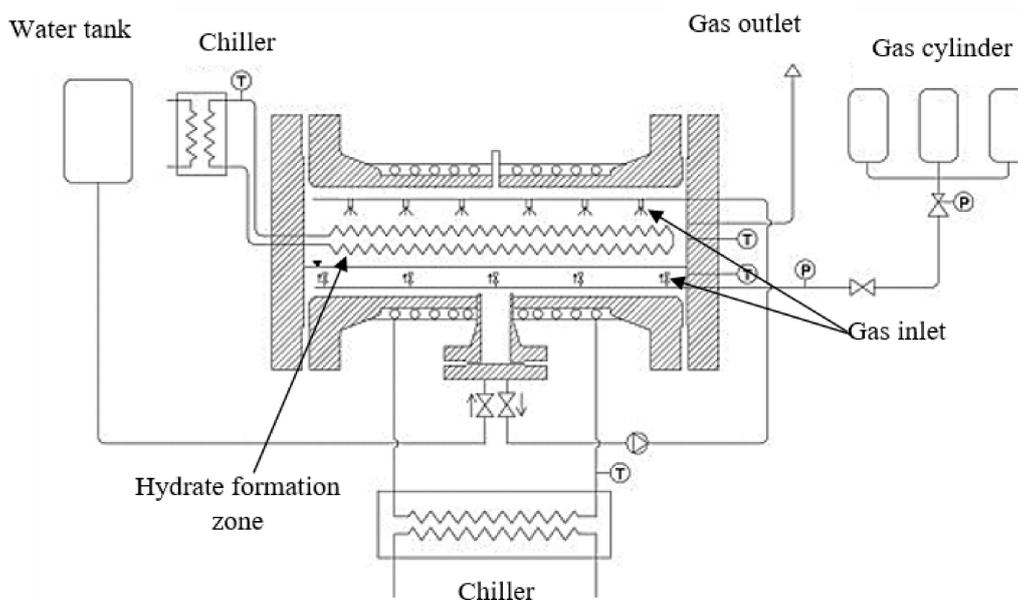
4.3. Spray Reactors

Spray tower reactors are the third most frequent design for processing gas hydrates. The gas/water interfacial area can be easily increased by spraying water to a continuous gas phase region. Because the tiny water droplets are moving at such high speeds in the gas phase of the reactor, the mechanical stirring system can be removed. As a result, the reactor's design is straightforward, making expansion a breeze; however, since the gas phase has a low heat capacity and occupies a sizable amount of the spray tower, it is possible that the heat generated by hydrate formation will not be dissipated effectively over the reactor's walls, leading to a rapid rise in temperature. When the temperature is raised, the super-saturation condition in the system, which is necessary for crystallization, is reduced, and the rate of hydrate production slows down or stops altogether [120]. For the first time, Rogers et al. showed that the spray process could be used to create hydrates [140]. Fukumoto conducted an initial study on the potential benefits of using water spraying to accelerate the hydrate formation process. A spray nozzle was used to direct water vapor toward a cold plate within a cylinder containing HFC-32 gas during the experiment. Figure 9a depicts the reactor's schematic. According to their findings, an intimidating water spray system has the potential to serve as a practical tool for the continuous generation of gas hydrate. The spray chamber's shape, thermal stability, and design, as well as the spray nozzle chosen, all play critical roles in the effective implementation of this technology at greater sizes [141]. Subsequently, Ohmura et al. from the same team unveiled a spray-mechanism-based hydrate crystallizer suitable for use in the laboratory [142]. A high-pressure spray chamber, into which a small amount of water was to be introduced, formed the basis of the experimental setup. As can be seen in Figure 9b, this scheme has been rigged up with a plunger pump to move water from the chamber's base to a spray nozzle located at the chamber's top. With this setup, water is sprayed and recycled in tandem, allowing for continuous gas hydrate formation. The total process was a batch system, nevertheless, because the generated hydrate cannot discharge from the reactor chamber. There is also the possibility of pipeline blockage from hydrate particles passing through due to the pump's negative pressure in the output line, as the water circulation system was primarily installed in the thermos-stated bath. Several experiments conducted by Prof. Mori's group used this setup [143,144].
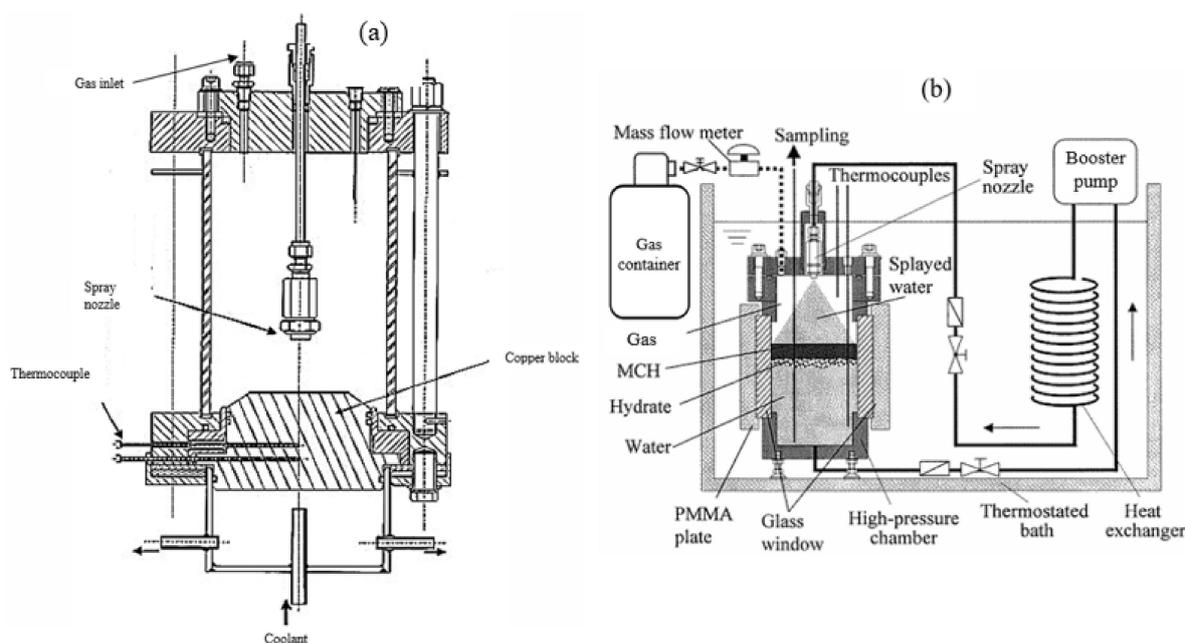
Figure 9. (**a**) The spray chamber employed by Fukumoto et al. [141]. (**b**) Spray reactor used Prof. Mori [142].

The prior design of Prof. Mori was scaled up by Li et al. to a 13-L reactor [145]. The fast formation of CO_2 hydrate was the subject of the experiment. The findings validated gas hydrate's rapid generation. The temperature of the reactor, however, was raised gradually [145]. Kikuo, using a Japanese patent, presented an additional example of a spray-based hydrate reactor [146]. The crystallizer in this design has a single spray nozzle located at its highest point. Furthermore, many gas inlets were allotted within the length of the reactor to provide internal circulation of the gas phase and improve the heat transfer rate, thereby compensating for the reactor's thermal instability; however, there was no evidence of this work's findings being published in the open literature.

In a recent study, Lucia et al. proposed a 25-L liquid spray mechanism-based reactor [147]. Figure 2.15 depicts a schematic of this reactor. The reactor requires a steady supply of water to function properly. The hydrate formation heat was dissipated via internal cooling. The generated hydrate is difficult to remove from the reactor chamber because the hydrate particles are attracted to the reactor's cool surfaces. It is unclear how Lucia et al. removed the hydrate from the reactor, as their experiment also planned to convert full liquid water to the hydrate [147]. In addition, when the cooling coils are covered with hydrate crystals, the reactor's thermal stability still is a concern with this design in Figure 10. Because gas hydrate has a thermal conductivity almost five times lower than ice, a larger layer of hydrate on the cooling coils reduces the efficiency of cooling. The graphs presented in their study confirmed this, as the temperature profile shows a cumulative rise over time [147].


Figure 10. Spray reactor for gas hydrate production presented by Lucia et al. [147].

Miscellaneous Types

In addition to these three varieties of reactors, some novel designs have been described in the public literature and patent records. Surface continuous crystallizer principles provide the basis of a sophisticated hydrate reactor recently introduced by Heinemann et al. [148]. Figure 11 depicts the construction of a scraped surface crystallizer in the form of a twin-pipe element. The crystallization process occurs within the inner pipe, and the space between the inner and outside pipes is filled with a cooling fluid. There is a scraper component that spins inside the pipe as well. Paraxylene is purified using this type of crystallizer [148]. This idea was adapted by Heinemann et al. for use in the gas hydrate process. The space between the inner and outer pipes is where crystallization occurs in their setup. The inner pipe is a moving surface, similar to a conveyor belt, a revolving drum, or a reciprocating surface. Spray nozzles are employed to atomize the water before it enters the

reaction zone. Nonetheless, as the creators themselves pointed out, the hydrates stick to the moveable surface, and it adds complexity to the reactor to remove these hydrates [148]. As with stirrer-tank reactors, the complexity and number of moving parts in this setup make it difficult to scale up.
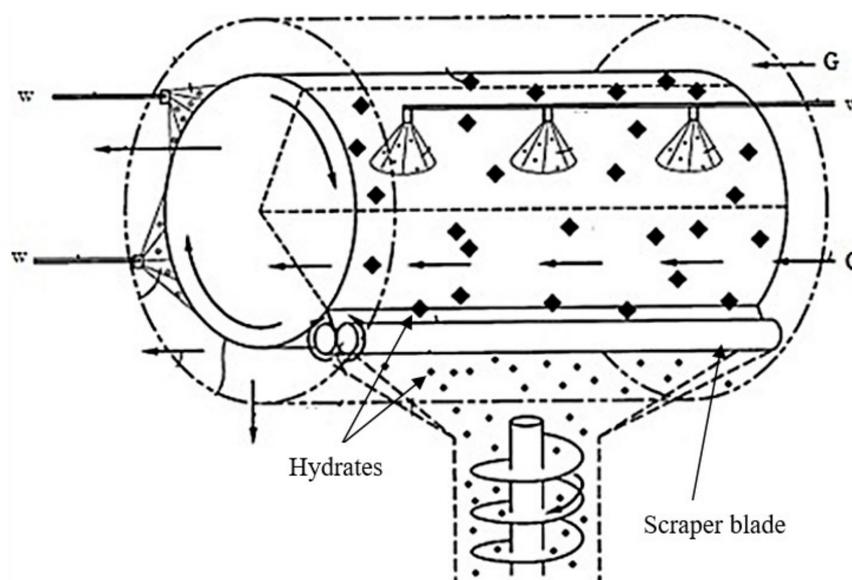

Figure 11. Hydrate production reactor by Heinemann et al. [148]. Where, G: gas, and w: water.

In 2003, Oak Ridge National Laboratory developed the Continuous-Jet Hydrate Reactor (CJHR) for making carbon dioxide hydrate from liquid carbon dioxide [149]. The same basic ideas behind the CJHR's design were implemented in a pilot version four years later [150,151]. The design's primary focus was on using CO_2 hydrate for seafloor CO_2 storage. As can be seen in Figure 12, the reactor included both a continuous phase liquid stream and a dispersed phase, the latter of which was forced through a series of capillary plates to form tiny bulbs that were then introduced into the continuous phase. The CO_2 hydrate crystals are submerged at the bottom of the reactor, which can be the sea floor for commercial use [150].
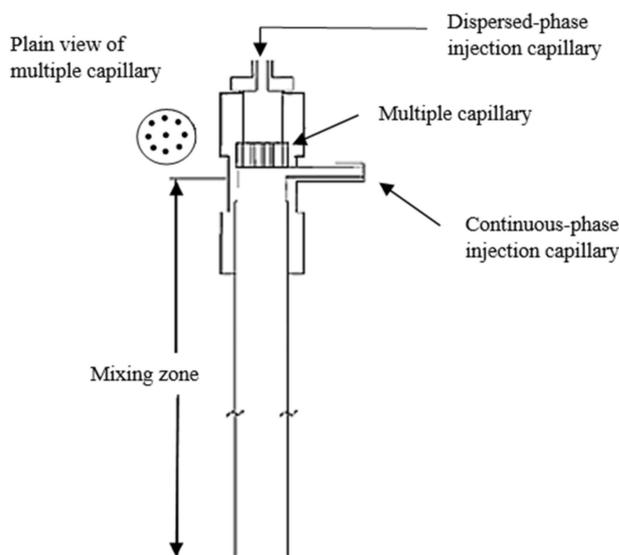

Figure 12. Schematic drawing of the continuous-jet hydrate reactor from Oak Ridge National Laboratory [150].

More recently, another innovative setup for creating gas hydrates has been developed by Nagamori et al. from Mitsui Engineering and Shipbuilding Co. (MES), Tokyo, Japan [121]. According to Figure 13, this reactor used an ejector-mixer system followed by a shell and tube generator. The ejector-mixer system in this reactor eliminates the requirement for agitation inside the reactor. The slurry is made to rotate inside the shell and tube generator by use of dividing walls located at either end of the device [121]. Mitsui Engineering & Shipbuilding Co., Ltd., Tokyo (JP) invented a gas hydrate production apparatus shown in Figure 14, capable of reacting a raw gas with a raw water to thereby form a slurry gas hydrate and capable of removing water from the slurry gas hydrate by means of a gravitational dewatering unit. In this invention, the gas hydrates are separated from the the raw water by overflow, while the water is continuously recycled with the fresh gas to make more hydrates. [152].
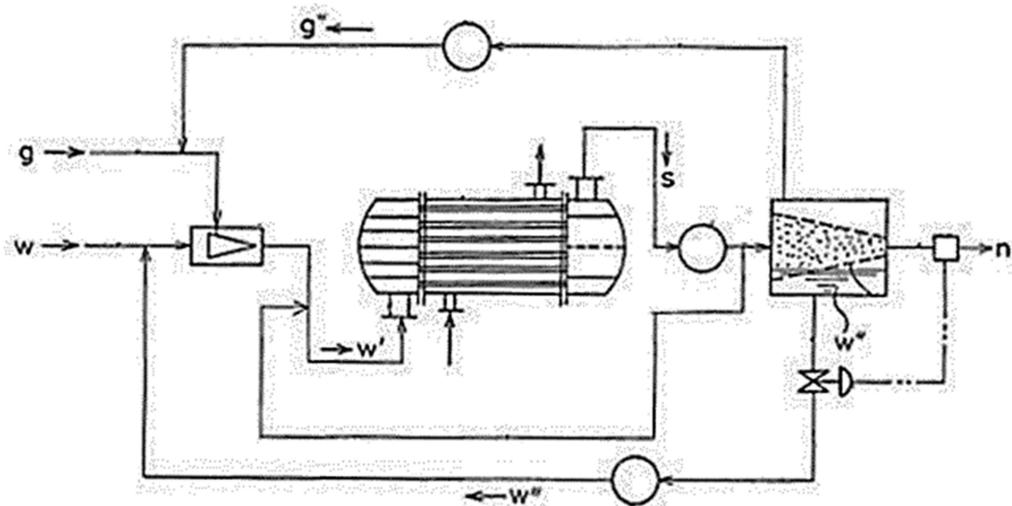
Figure 13. Hydrate plug reactor by Nagamori et al. [121]. Where, g: gas, w: water, s: hydrate slurry and n: gas separated.
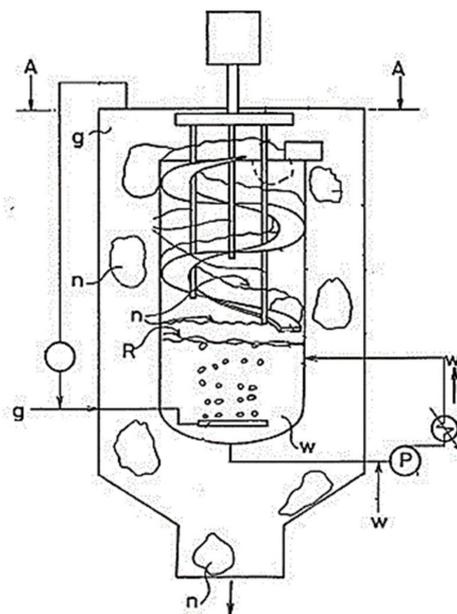

Figure 14. MES gas hydrate formation equipment [152]. Where, g: Gas supplied, w: water, n: hydrate sulray, R: Liquid-gas interface.

4.4. Recent Development in the Gas Hydrate-Based CO$_2$ Capture and Sequestration

Behzad et al. [153] proposed a pilot-scale reactor scheme for the separation of CO$_2$ gas by hydrate process in Figure 4. Forming a gas hydrate involved the introduction of two gas and liquid streams into a spray reactor. The hydrate and any leftover gases are then allowed to leave the reactor. Once the gas hydrate slurry stream has been extracted from the reactor, heated, and sent to the separator, the hydrate will dissociate, and the trapped gas will be released. The settler tank receives the liquid stream, cools it to the ideal temperature, and sprays it back into the reactor. The hydrate reactor is the central part of this procedure. To manufacture gas hydrate, scientists have developed a novel spray tower-based reactor. This reactor is specially designed for continuous or semi-continuous gas hydrate production. Several scenarios are included in the design of this reactor.

Using spray tower technology, the quick hydrate formation process is enabled, and the heat transfer rate inside the reactor is increased to stabilize the reactor temperature, both of which are presented modification concepts in this work, as shown in Figure 15.
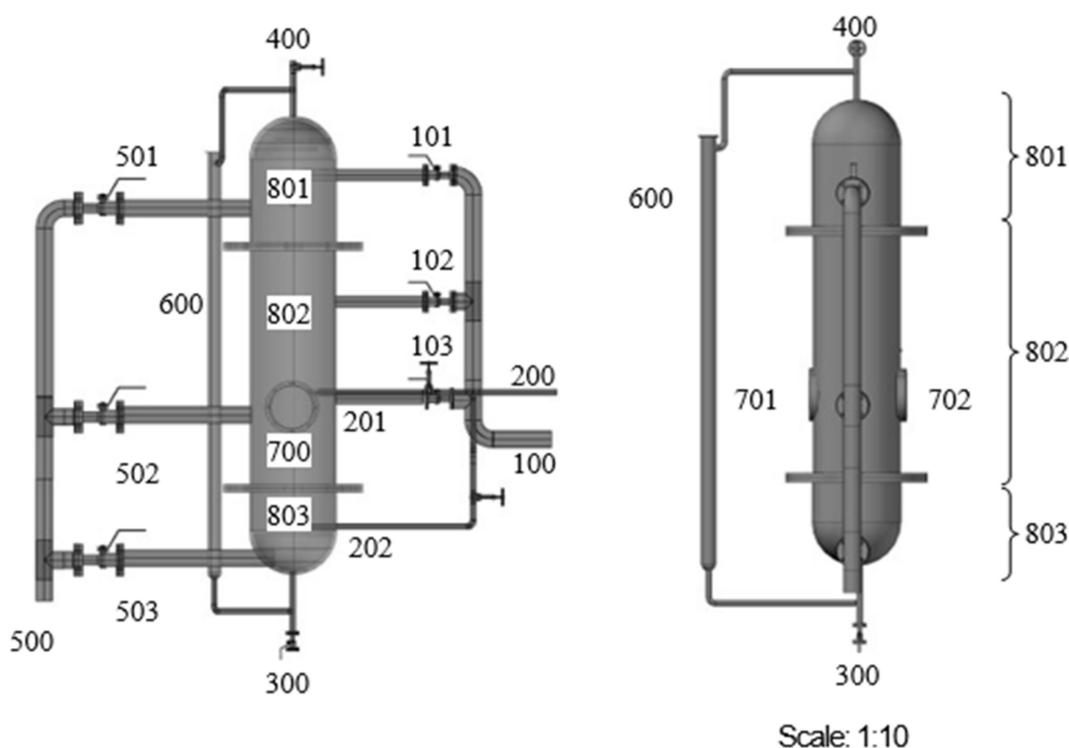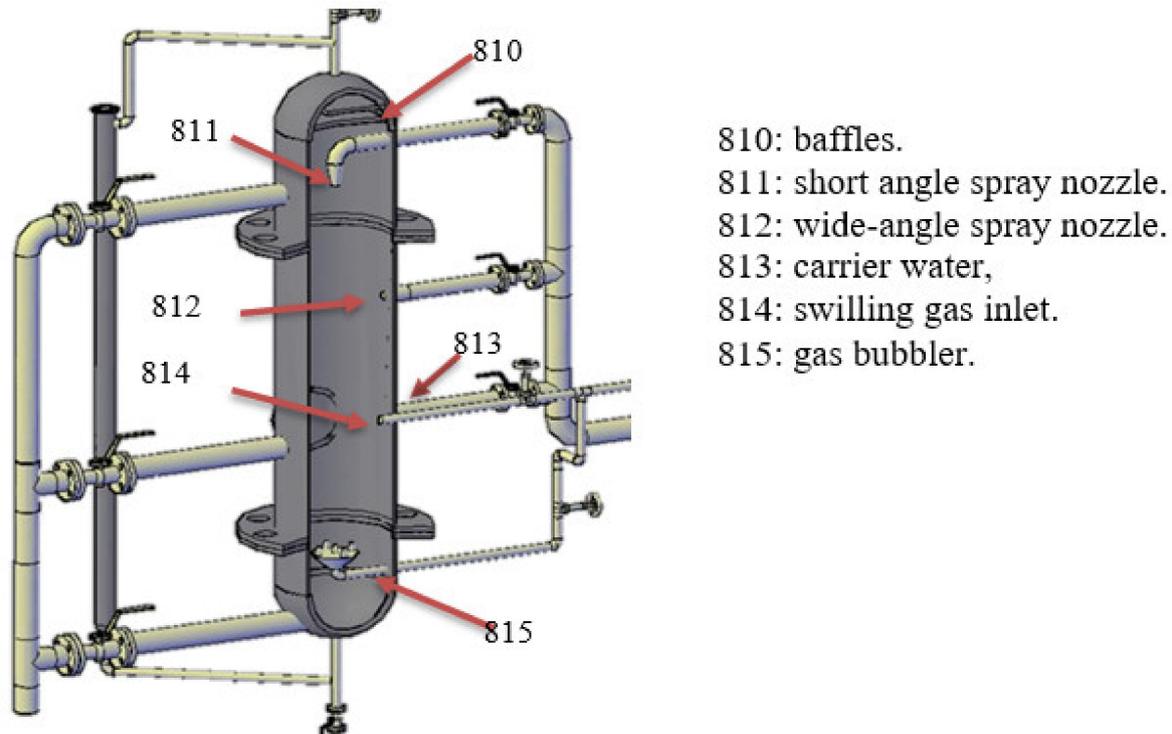

Figure 15. New hydrate crystallizer overview (100: Liquid inlets consisted of 101: Main spray, 102: Quench line, 103: Carrier water. 200: Gas inlets consisted of 201: Swirling gas inlet, 202: gas bubbling inlet. 300: Liquid return line. 400: Gas outlet. 500: Slurry outlets consisted of 501: Bubble column outlet, 502: Main outlet, 503: Heavy hydrate outlet. 600: Level meter tank. 700: Side windows consisted of 701: Front window, 702: Back window. 801: Spray section, 802: Active section, 803: Bubbler section).

The spray nozzle and its associated pipes, which make up the main spray system, are housed in the uppermost compartment. Additionally, the product gas is removed from the reactor's top, and mist-eliminating baffles stop any stray water droplets from being carried over. Most of the generated heat is released in the middle part, where most of the water and gas are transformed to hydrate. This part houses the primary gas intake. This means the hydrate may just float on top of the liquid water already there. The base has a collection chamber and a bubbler to collect hydrated substances. The reactor base also features an additional slurry outflow. It is possible that the hydrate phase may become denser than water if the reactor used to produce CO$_2$ hydrate or heavier gases also produce a solid

hydrate. Then, the hydrate crystals would settle to the bottom of the reactor. For a denser slurry, this is the appropriate output.

While hydrates form slowly, the pace at which hydrates are formed can be accelerated by increasing the mass transfer rate. Since this is an exothermic reaction, a great deal of heat is being produced within the reactor. As shown in Figure 16, these situations need the incorporation of additional streams into the reactor.

810: baffles.
811: short angle spray nozzle.
812: wide-angle spray nozzle.
813: carrier water,
814: swilling gas inlet.
815: gas bubbler.

Figure 16. Conceptual design of new gas hydrate reactor.

The result is a stable temperature in the reactor, no blockage in the upstream pipeline or vessels, and simple removal of hydrate slurry from the reactor. After several productive experiments, various flaws in the setup's design became apparent. However, these limitations can be overcome with better research and planning.

5. Conclusions

Extensive studies have been conducted to reduce carbon emissions and achieve net-zero goals. Consequently, with additional capital investments and significant operational and maintenance costs associated with CCS technology, scientists are looking into more long-term and budget-friendly options for climate change mitigation. Hydrate-based CO_2 capture technology has progressed as a viable variant among current conventional technologies such as adsorption, absorption, membrane, cryogenic distillation, etc. Since the hydrate-based CCS is a newly emerging technology for CO_2 capture, extensive research investigating the thermodynamic/kinetic behavior and effects of different inhibitor/promotors media is being widely conducted. In this study, the mechanical design and operational limitations of the hydrate formation reactors have been discussed. From the different patent and research studies, it has been found that the reactors with more moving parts, such as stirred tank reactors, are more difficult to operate and harder to shift the process of hydrate formation from a batch to a continuous production. At the same time, appropriate designs with spray columns are more viable and can handle limitations, such as proper mixing, less gas-to-liquid contact area, bulk, and continuous production of gas hydrates. Stagewise production can increase the efficiency of the reactor. The withdrawal of viscous hydrate slurry from the reactor is another bottleneck in the phase of shifting the operation towards

continuous hydrate production. These shortcomings can be overcome by more intensive studies to produce a better design. Hence, it is concluded that a considerable amount of CO_2 can be extracted from the gas stream with the suitable design of a multi-stage hydrate process. Still, more in-depth research considering a wider range of operational parameters and heat integration situations is necessary to identify the best hydrate process and upstream process. Even though a hydrate-based process might be seen as less energy demanding, it still requires a sizable CAPEX and OPEX to capture a meaningful amount of CO_2 from a gas combination with a high CO_2 content.

Conflicts of Interest: The authors declare no conflict of interest.

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