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Review

Hydrate capture CO_2 from shifted synthesis gas, flue gas and sour natural gas or biogas

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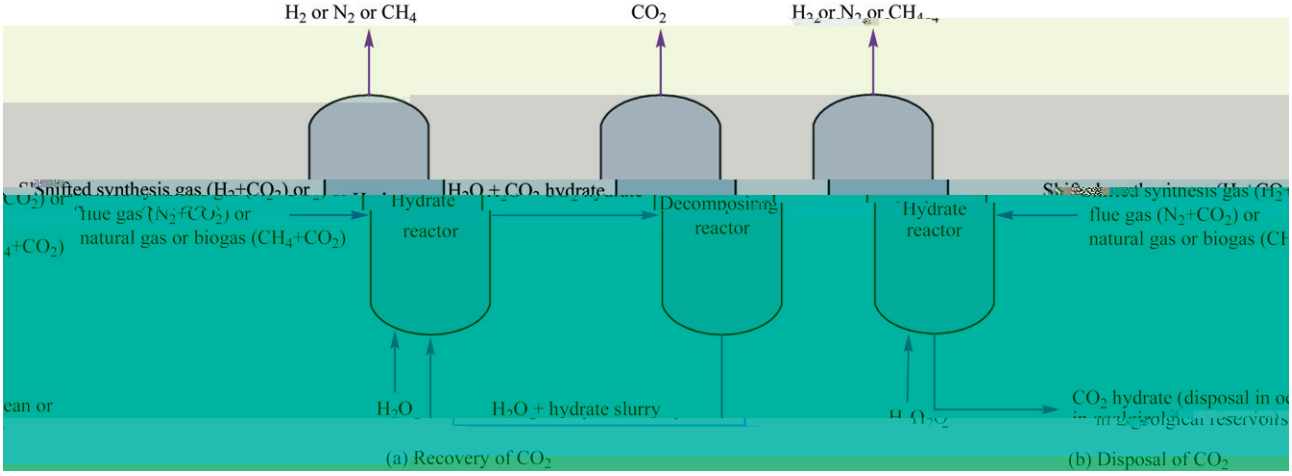
CO_2 capture by hydrate formation is a novel gas separation technology, by which CO_2 is selectively engaged in the cages of hydrate and is separated with other gases, based on the differences of phase equilibrium for CO_2 and other gases. However, rigorous temperature and pressure, high energy cost and industrialized hydration separator dragged the development of the hydrate based CO_2 capture. In this paper, the key problems in CO_2 capture from the different sources such as shifted synthesis gas, flue gas and sour natural gas or biogas were analyzed. For shifted synthesis gas and flue gas, its high energy consumption is the barrier, and for the sour natural gas or biogas (CO_2/CH_4 system), the bottleneck is how to enhance the selectivity of CO_2 hydration. For these gases, scale-up is the main difficulty. Also, this paper explored the possibility of separating different gases by selective hydrate formation and reviewed the progress of CO_2 separation from shifted synthesis gas, flue gas and sour natural gas or biogas.

clathrate hydrate; CO_2 capture; hydrogen; shifted synthesis gas; flue gas; sour natural gas or biogas

Carbon dioxide (CO_2), the most important greenhouse gas (GHG), is primarily responsible for the human-induced climate change. During the last century, the concentration of CO_2 in the atmosphere increased [1] from 275 to 387 ppm, and International Panel on Climate Change (IPCC) predicted [2] that by the year 2100, the atmosphere may contain up to 570 ppm CO_2, causing a rise of mean global temperature of around 1.9 K.

CO_2 emissions can be controlled from three ways. First is using non-carbon energy resources to replace fossil fuels, such as biomass, solar and wind energy. But besides high costs of renewable energies, there are some barriers for changing the technological systems. So, in the coming 20 years, the energy consumed will be mainly from fossil fuels. Second is improve energy efficiency to reduce the GHG emissions per unit energy consumption. Third is carbon capture and storage (CCS). It is the most imperative technology to stabilize CO_2 concentrations in the atmosphere, which has attracted considerable interests for countries and scientists. CCS involves CO_2 separation and capture, CO_2 transportation and CO_2



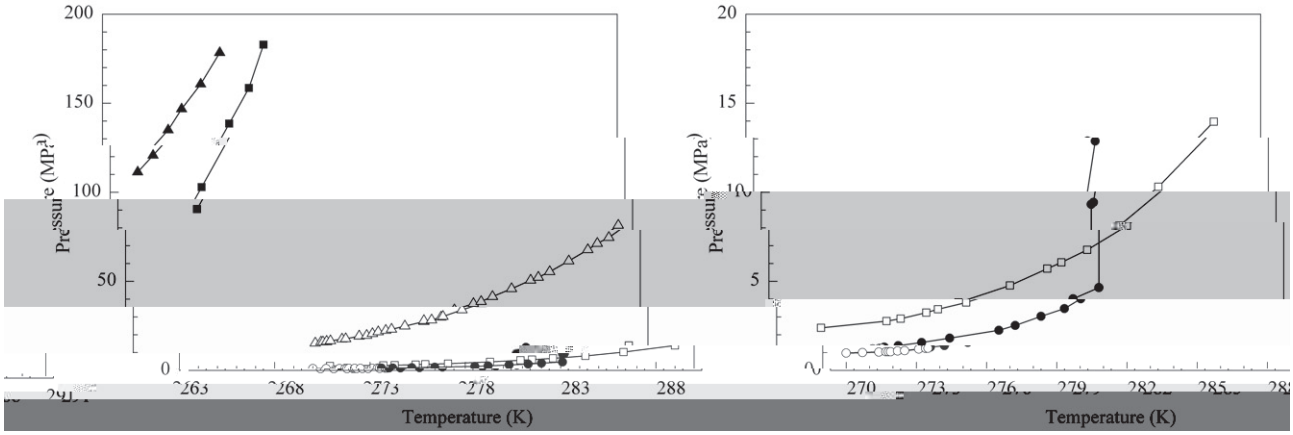
Process of CO_2 capture from shifted synthesis gas, flue gas, sour natural gas or biogas

Figure 2 shows the phase diagram of hydrate formation for H_2 [12−14], N_2 [15], methane [16] and CO_2 [16,17]. Seen from the phase diagram of hydrate, CO_2 hydrate formation pressure is the lowest among four gas hydrates. While for different gas mixture, the difficulty of HBCC is inverse proportion with the hydration pressure difference between CO_2 and objective gas. CO_2 capture is more easily in the case of greater pressure difference.

Thus, due to the huge pressure difference between CO_2 and H_2, it is easily to realize CO_2 capture from shifted synthesis gas (CO_2/H_2). But the enormous pressure difference brings new problems. The hydrate formation pressure of shifted synthesis gas (CO_2+H_2) in water is relevantly high, for example, the hydrate formation pressure for CO_2(39.2 mol%)+H_2 gas mixture is 5.75 MPa at 274.05 K [18]. Such high pressure leads to high energy consumption of gas compression. Therefore, the challenge of CO_2 capture from CO_2+H_2 gas mixture is to lower the hydrate formation pressure.

In the case of flue gas, a typical pre-treated flue gas contains 15–20 mol% CO_2, 5%–9% O_2, and the rest N_2. Since N_2 and O_2 form hydrate crystals under approximately same conditions, the treated flue gas is considered as a CO_2/N_2 mixture. Although the hydrate pressure difference between N_2 and CO_2 is much lower than that between H_2 and CO_2, there is still 15 MPa (273.15 K) between N_2 and CO_2 hydrate pressure. So, CO_2 capture from flue gas is relatively not difficult by hydrate theoretically. Similar to the shifted synthesis gas, the barrier of industrialization in HBCC from flue gas is that the operative cost is expensive if it has to compress the gas to the necessary hydrate formation pressure.

For CO_2 capture from CH_4+CO_2 gas mixture (such as sour natural gas, biogas, landfill gas etc.), it is more difficult than that from shifted synthesis or flue gas because there was a narrow region [19] (273−283 K and 1−6 MPa) between methane and CO_2 in phase diagram of hydrate formation (Figure 2b). Some researchers assumed CO_2 and CH_4 could form



Phase diagram of hydrate formation boundary. (a) For pure H_2, N_2, methane and CO_2 with water, (b) Enlarged view of methane and CO_2 hydrate phase diagram. (▲) H_2, Chapoy et al. [14]; (■) H_2, Dyadin et al. [12,13]; (△) N_2, Van Cleeff et al. [15]; (□) CH_4, Deaton et al. [16]; (○) CO_2, Deaton et al. [16]; (●) CO_2, Fan et al. [17]

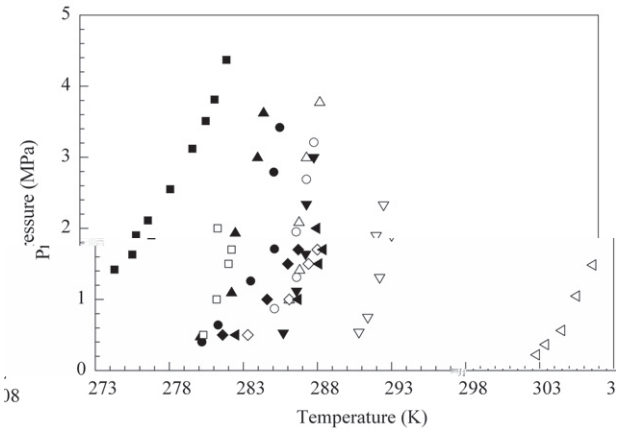
a CO_2 and CH_4 mixed hydrate. They deemed that there were interstices in CO_2 hydrate structure that could be filled by methane molecules and similarly CO_2 molecules could stabilize "holes" in methane structure [20]. If it is truth, separation of CO_2 and methane by hydrate is nonfeasible. However, more recent works indicate that pure hydrate would be formed [21] in CO_2 and CH_4 mixed gas. It makes HBCC from CO_2 and CH_4 mixed gas become true. But the separation efficiency is still the shortcoming of HBCC from CO_2 and CH_4 gas mixture.

The other trouble of hydrate based on separation industrialization is kinetic problem, such as hydrate formation rate, energy efficiency and enlargement of hydrate separator. The hydrate formation rate decides energy efficiency, scale of hydrate reaction tower and whether it is feasible in economy.

Many researchers studied the hydrate formation kinetics. At lab-scale, stirring, bubbling, spraying and adding promoters are the effective methods to improve the hydrate formation rate [22−24]. But when hydrate reactor scale-up, it might face complicated problems. To compare the hydrate formation rate data from difference sources on a common basis, Fan et al. [25] defined the gas hourly space velocity (GHSV) to compare the capacity of the hydrate separation processing. GHSV means gas volume of hydration in unit time per unit reactor volume. In Li's research [26], the highest GHSV for CO_2 from flue gas is 25.96 h^{-1} in lab-scale, which means that it needs a 3.9×10^4 m^3 volume hydrate react tower for a 1000 MW powder (the flow rate of flue gas from 1000 MW powder is about 1.0×10^6 Nm^3/h). Such GHSV is far away from industrialization.

To realize rapid CO_2 separation from gas mixture with low energy cost, additives usage to moderate the CO_2 hydrate formation conditions is a recognized feasible method. Kang and Seo et al. [9,27,28] experimentally measured CO_2 hydrate phase equilibrium in the presence of tetrahydrofuran (THF), propylene oxide and 1,4-dioxane. The equilibrium pressure of hydrates in the presence of THF is considerably lower than the case without the additive. Latter, researchers found the promoter effect of quaternary ammonium salt is better than THF. To selective the additives, researchers measured CO_2 hydrate formation conditions with low-concentration quaternary ammonium salt, such as, tetrabutylammonium tribromide (TBAB) [29–31], tetrabutyl ammonium fluoride (TBAF) [29], tetrabutyl ammonium chloride (TBAC) [29,32], tetra-iso-amyl ammonium bromide (TiAAB) [33], tetra- -butylphosphonium bromide (TBPB) [34,35] and tetra- -butylammonium nitrate ($TBANO_3$) [34].

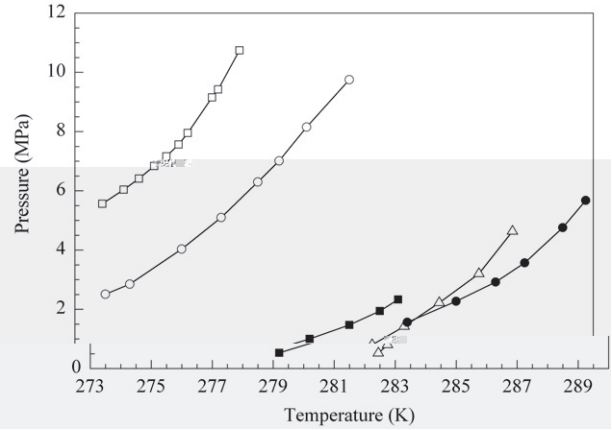
The phase equilibrium conditions of CO_2 hydrate with additives in water is showed in Figure 3. All of these additives can decrease the hydrate equilibrium pressures of CO_2 hydrate, especially TBAF and TiAAB. They can drop the hydrate pressure of CO_2 to near room temperature and atmospheric pressure, TBAF to 290.8 K and 0.54 MPa, TiAAB to 302.8 K and 220 KPa.



Phase equilibrium conditions for CO_2+additives (TBAB, TBAC, TBAF, TBPB, $TBANO_3$, TiAAB) systems. (■) CO_2, Fan et al. [17]; (●) CO_2+0.293 mol% TBAB, Li et al. [29]; (○) CO_2+0.617 mol% TBAB, Li et al. [29]; (▲) CO_2+0.293 mol% TBAC, Li et al. [29]; (△) CO_2+0.617 mol% TBAC, Li et al. [29]; (▼) CO_2+0.293 mol% TBAF, Li et al. [29]; (▽) CO_2+0.617 mol% TBAF, Li et al. [29]; (□) CO_2+3.68 mol% $TBANO_3$, Mayoufi et al. [34]; (◆) CO_2+0.580 mol% TBPB, Mayoufi et al. [35]; (◇) CO_2+0.918 mol% TBPB, Mayoufi et al. [35]; (◀) CO_2+3.03 mol% TBPB, Mayoufi et al. [34]; (◁) CO_2+0.769 mol% TiAAB, Majumdar et al. [33]

Pre-combustion CO_2 capture approach is that CO_2 capture from shifted synthesis gas, which was obtained by water-gas shift of fossil fuel. The typical shifted gas is a mixture of H_2 (60 mol%) and CO_2 (40 mol%) with traces of CO and H_2S coming out from an integrated gasification combined cycle (IGCC) at a pressure of 2.5−7 MPa [36].

At early research, researchers devoted to how to reduce the hydrate pressure of CO_2+H_2 mixture gas. Kumar et al. [37] reported that few C_3H_8 can lower the equilibrium pressure of CO_2+H_2 hydrate. Then Hashimoto et al. [38] and Lee et al. [39] reported the equilibrium pressure of CO_2+H_2+THF hydrate is much lower than that of CO_2+H_2 hydrate. Zhang et al. [40] and Li et al. [18] found that CO_2+H_2+cyclopentane(CP) hydrate system and CO_2+H_2+TBAB hydrate system have lower equilibrium pressures at the same temperatures compared with CO_2+H_2+THF system. Figure 4 collects the effects of additives on the phase equilibrium of CO_2(40 mol%)+H_2(60 mol%) hydrate. These additives can not only drop the formation pressure of CO_2+H_2 hydrate system, but also accelerate the hydrate formation and shorten the induction time through enhancing the driving force relatively [41,42]. However, the driving force should not be too high. When the driving force is more than 2.5 MPa [41], H_2 prefers to going to the hydrate phase, which would decrease the selectivity to CO_2 capture.



Phase equilibrium conditions for CO_2(40 mol%)+H_2(60 mol%) +additives (C_3H_8, CP, THF, TBAB) systems. (□)CO_2+H_2+H_2O, Kumar et al. [37]; (○) CO_2+H_2+3 mol% C_3H_8, Kumar et al. [37]; (■) CO_2+H_2+3 mol% THF, Lee et al. [39]; (△) CO_2+H_2+1 mol% TBAB, Li et al. [18]; (●) CO_2+H_2+CP, Zhang et al. [40]

Based on the above studies, Linga et al. [43] presented a two-stage hydrate/membrane process for CO_2 capture from shifted synthesis gas, and at the same time they defined a metrics, separation factor to evaluate the hydrate based separation process. Then, Kumar et al. [6] and Li et al. [44] designed the analogous two-stage and one-stage hydrate/membrane process with C_3H_8 and TBAB, respectively. In Table 2, we summarized the operation conditions and separation factors for multi-stage hydrate/membrane process for CO_2/H_2 separation with additives. The best result shows the separation factor of CO_2 reaches 136.08 with TBAB by a single stage hydrate/membrane process under a moderate condition. But only about 60% CO_2 is captured from feed gas.

To improve CO_2 capture rate, Surovtseva et al. [45] design a integrated cryogenic and hydrate CO_2 capture process. The shifted synthesis gas first enters cryogenic condensation, in which above 70% CO_2 can be captured at pressure of 5−6 MPa and 223 K. The liquefied CO_2 is high purity of 95%−97%. Then, the hydrogen-enriched gas stream is directly fed to the hydrate reactor, where further reduction of CO_2 down to 6%−7%.

Besides additives, hydrate reactor is a key factor to decide whether HBCC could industrialization. Xu et al. [46,47] built a scale-up equipment consisting of a 40 L cuboid bubble reactor (10.0 cm in side length and 4.0 m in height) in this year. Their job opened the chapter of hydrate-based CO_2 capture from laboratory to the industrialization. The future research should be focus on the design and optimization of scale-up continuous hydrate reactor.

Additives	Feed pressure (MPa)		Temperature (K)	Stage	Separation factor		Ref.
	1	2			1	2	
No	7.5	3.8	273.75	2	98.70	94.70	[43]
C_3H_8	3.8	3.5	273.70	2	27.84	91.19	[6]
TBAB	3.0		278.15	1	136.08		[44]

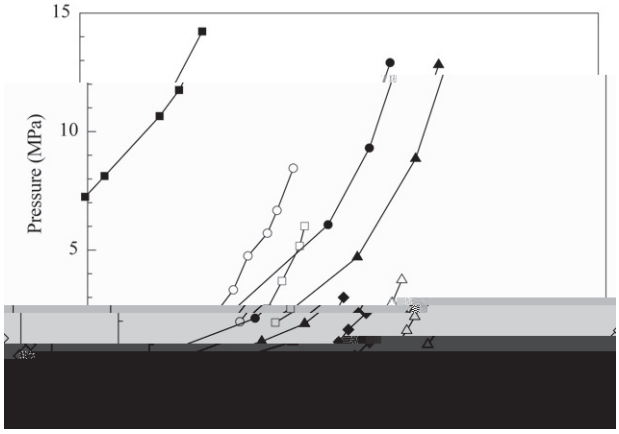
Post-combustion CO_2 points to CO_2 capture from large scale power-plants emissions, which is one of the major sources of carbon emissions to the atmosphere. The main components of power plants emissions, namely flue gas, are CO_2 and N_2.

Kang and Seo et al. [9,27] measured the phase equilibrium condition of CO_2/N_2 at different CO_2 concentrations. Through phase equilibrium experiments and computation, it was firmly verified that HBCC was possible to recover more than 99 mol% of CO_2 from the flue gas. Their jobs provided the theoretical basis for this technology.

Although separated CO_2 from flue gas is possible, it is far away from industrialization for its low energy efficiency and high cost.

Linga et al. [43] designed a three-stage CO_2/N_2 separation process without additives, in which CO_2 content in hydrate can reach to 98%. But CO_2 recovery was less than 10% in hydrate and the operation pressures were 10 MPa, 5 MPa and 2.5 MPa in three stages at 273.75K, respectively. This meant that the emitted flue gas has to be compressed and cooled before entered hydrate reactor, which needed enormous energy. To reduce the energy consumption, lower the pressure and promote the temperature are two routes.

Similar to the pre-combustion capture, additives could decrease the hydration pressure of flue gas (Figure 5).

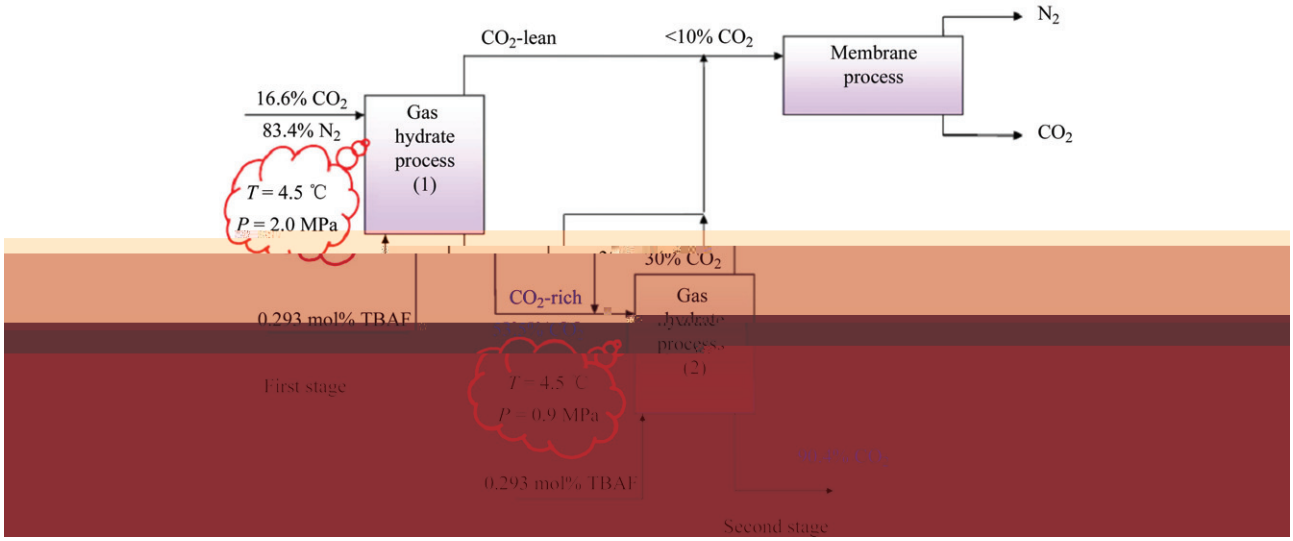


Phase equilibrium conditions for CO_2+N_2+additives (THF, TBAB, TBAF, TiAAB) systems. (■) CO_2(17 mol%)+N_2+H_2O, Kang et al. [48]; (●) CO_2(17 mol%)+N_2+1 mol%THF, Kang et al. [48]; (▲) CO_2(17 mol%)+N_2+3 mol%THF, Kang et al. [48]; (○) CO_2(15.3 mol%)+N_2+0.293 mol%TBAB, Li et al. [26]; (□) CO_2(15.3 mol%)+N_2+0.617 mol%TBAB, Li et al. [26]; (♦) CO_2(15.3 mol%)+N_2+0.293 mol%TBAF, Li et al. [26]; (△) CO_2(15.3 mol%)+N_2+0.617 mol%TBAF, Li et al. [26]; (◇) CO_2(20.9 mol%)+N_2+0.763 mol%TiAAB, Majumdar et al. [33]

Base on the above phase equilibrium studies, Linga et al. [49] modified their process. They used THF as additive. The process is still three-stage separation, while the pressure decreases to 2.5 MPa at three stages. This change can reduce at least 50% energy cost.

Subsequently, Li et al. [25,26,50] further modified the process in order to save energy. Li et al. [26,51] enhanced the three-stage hydrate separation temperature to 277.65 K used TBAB as additive. Also they [50] combined dodecyl trimethyl ammonium chloride (DTAC) and TBAB as additives and changed three-stage to two-stage separation. Fan et al. [25] designed the two-stage hydrate separation process (Figure 6), which decreased the hydrate pressure to 0.9 MPa at 277.65 K through adding TBAF. Table 3 summarizes the separation efficiency of multi-stage CO_2/N_2 separation process with various additives.

Additives	Feed pressure (MPa)			Temperature (K)	Stage	Separation factor			Ref.
	1	2	3			1	2	3	
No	10	5	2.5	273.75	3	13.2	7.3	36.7	[43]
THF	2.5	2.5	2.5	273.75	3	7.60	6.8	7.7	[48]
TBAB	3.7	2.5	2.5	277.65	3	9.47	14.41	8.9	[26]
DTAC+TBAB	1.66	1.66		274.95	2	9.60	62.25		[50]
TBAF	2.0	0.9		277.65	2	36.98	19.12		[25]



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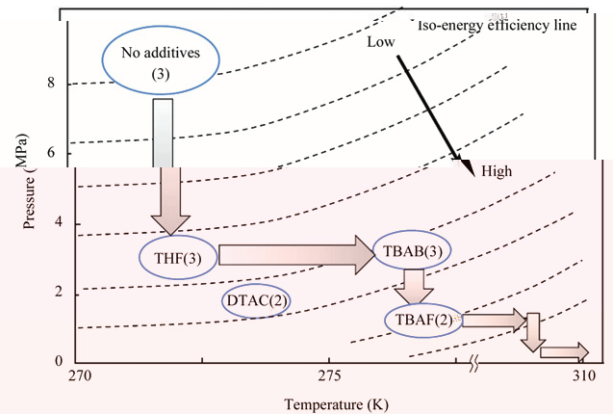
	First stage	Second stage
Compressed energy consumption (MW)	79 89	6
Recovery compression work (MW)	−60	
Recovery heat (MW)	−83	−38
Cooling energy consumption (MW)	4/3	7/3
Hydrate energy consumption (MW)	83	79
Cycle-water energy consumption (MW)	6.7	6.3
Total energy consumption (MW)	172	
CO_2 recycling (t/h)	303	
Energy consumption per unit	0.57 kW·h/kg$_{CO_2}$ (2.05 MJ/kg$_{CO_2}$)	

So far, CO_2 capture from flue gas has developed through three stages (Figure 8). The first generation is without any additives. In this stage, the separation efficiency and energy efficiency are very low. In the second stage, HBCC from flue gas undergoes the first breakthrough. The hydrate pressure decreases from 10 MPa to 2.5 MPa by adding THF, then increases hydrate temperature to 277.65 K. The third stage begins after the second breakthrough. The hydrate process changes from three-stage to two-stage and further decreases hydrate pressure to 0.9 MPa. The separation efficiency and energy efficiency are also improved. In this stage, HBCC from flue gas can competitive with membrane separation [26]. In the future, the condition of CO_2 capture from flue gas by hydrate would be continuing near or above room temperature and atmospheric pressure.



The development of CO_2 capture from flue gas

CH_4+CO_2 gas mixture contain sour natural gas, biogas, landfill gas, replaced-extracted gas etc. These gas sources are the promising energy. But raw gas contains large amount of CO_2, for example biogas contains approximately 55%−75% CH_4, 20%−45% CO_2, 5%−10% N_2 and 3000−5000 ppm H_2S [52]. It limited the usage of the gas mixture. If these sour methane wants to enlarge its range of usage and enter the existing natural gas distribution system, it must be purified to meet the qualification of pipeline natural gas (CO_2 contents<3%). Therefore, CO_2 capture is very essential for increasing the utilization of CH_4+CO_2 gas mixture.

Compared with shifted synthesis gas and flue gas, CO_2 separation from natural gas is more difficult due to CO_2 and CH_4 might form hydrate at the same time.

Gaudette et al. [53–56] measured the phase equilibrium of CO_2+CH_4 mixture hydrate and they found that the equilibrium pressure of CO_2+CH_4 mixture hydrate is between that of pure CO_2 hydrate and CH_4 hydrate, and the equilibrium pressure of CO_2+CH_4+H_2O hydrate decreases with the increase of the composition of CO_2 in the mixture gas. The additives, such as TBAB, TBAC, TBAF, THF can further reduce the equilibrium pressure of CO_2+CH_4 mixture hydrate. Thus, energy consumption is not a problem of CO_2 capture from CO_2+CH_4 mixture gas by hydrate. While low separation efficiency and the resulting low energy efficiency from CO_2+CH_4 mixture gas are the key problems.

Denderen et al. [20] studied CO_2 removal from contaminated natural gas by experiment. They employed 50/50 and 75/25 methane/CO_2 gas mixture as subject. Although gas hydrate can be used to purified natural gas by equilibrium separation, separation effect was not good, as 50% CO_2 can be reduced to 39% and 25% CO_2 to 16% at 275 K.

Nie [56] studied 33 mol%CO_2/CH_4 mixture gas separation with and without additives. They found that 90% hydrate reaction can complete within 30 min, the operating pressure should far away from the boundary line of methane, and the

They found the kinetic rate constant for CO_2 is greater than that for methane, but it is not under all conditions.

Latter, Golombok et al. [59] demonstrated that CO_2 hydrates form much faster than methane hydrate in some pressure regime. Beeskow-Strauch et al. [60] and Horvat et al.

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