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New Technique Integrating Hydrate-Based Gas Separation and Chemical Absorption for the Sweetening of Natural Gas with High H_2S and CO_2 Contents

Gaihuan Liu, Lin Zhu,* Wenhao Cao, Huimin Liu, and Yangdong He

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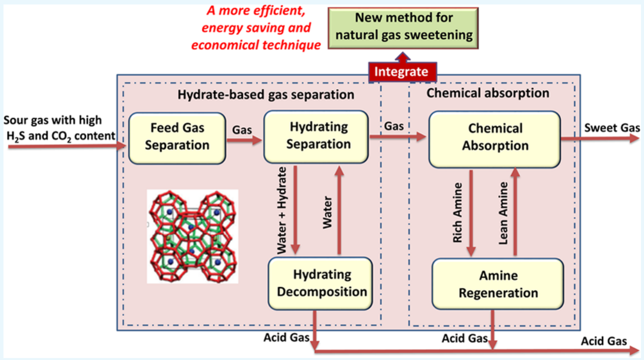
ABSTRACT: Given the drawbacks of the traditional MDEA absorption process, we introduced a hydrate-based gas separation approach. Then, to study the effectiveness of this method, we performed some hydrating experiments demonstrating that energy consumption could be remarkably reduced. However, the acid components (H_2S and CO_2) in the product gas failed to meet the specification requirements of the sales gas. Consequently, a new technique was developed that integrated hydrate-based gas separation and chemical absorption for the sweetening of natural gas with high H_2S and CO_2 contents. To evaluate the performance of this new integrated method, technical comparisons based on simulation and experimental data were conducted. The results showed that the new integrated method could effectively remove sour components, which resulted in the product gas being able to meet the sales gas specifications. Additionally, the integrated technique consumed much less energy than the traditional MDEA absorption process and its amine regeneration duty was only 42% that of the MDEA method. What is more, upon an economical evaluation being performed, it was shown that the integrated technique tremendously reduced the investment and operating cost.



1. INTRODUCTION

With the development of the global economy, environmental degradation has aroused great public concern. It has been world-recognized that raising the proportion of natural gas in the one-off energy structure can effectively improve the environment by ameliorating air pollution. As stipulated by the provisions of the Constitution of the International Labor Organization, an operational area's H_2S content must not exceed 300 ppm under the protection of a protective suit.[1] On the other hand, according to toxic gas leakage analysis results, natural gas with high H_2S and CO_2 contents should generally not be treated at a pressure higher than 2 MPa. Meanwhile, regarding the highly sour natural gas treatment process, gas sweetening comprises a key step because it consumes most of the energy used. It is thus of great significance to develop an effective and safe method applicable for acid component removal from natural gas with high H_2S and CO_2 contents under low pressures. A lot of focus has been aimed at optimizing the natural gas sweetening process and reducing energy consumption.[2−5]

Most popular methods for natural gas sweetening include chemical absorption and/or physical absorption,[6−8] and the former is by far the most common technique. However, the chemical absorption methods (such as the MDEA method) have limited desulfurization and decarbonization efficiency due to limitations posed by pressure conditions.[9] Besides, they require intensive energy expenditure majorly in the solvent regeneration process.[7,10] Abedini et al.[11] investigated the acid gas removal performance using an amine solvent with wet gas conditions of 220 and 750 psia. It was found that when MDEA was used to purify sour gas containing large amounts of CO_2 under low pressure, the product gas became unable to reach the requirements of the sales gas specification and the additives of other amine components could improve the plant performance. Mohamad et al.[12] conducted the integrated energy and exergy evaluation of an acid gas recovery plant and proposed an energy-saving strategy based on the investigation of the MDEA-DEA-PZ amine blend. Physical absorption methods (such as the Sulfinol method) are less restricted by pressure conditions than chemical absorption. In most cases, chemical and physical solvents are blended together.

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Chukwugozie et al.[13] proposed a blending physical and chemical solvent to enhance the acid components removal performance for natural gas with an acid gas composition of 16.9% under a feed gas pressure of 2.5 MPa. It was found that more than 30−40% mercaptans along with sour gas were absorbed, requiring less than 25% regeneration energy, compared to using MDEA as a standalone solvent, researched by Ghanbarabadi and Khoshandam.[6] The outstanding advantage posed by physical absorption is its strong ability to remove organic sulfur, but nevertheless, it has no obvious superiority in H_2S and CO_2 removal compared to chemical absorption. Moreover, hydrocarbons C_{3+} are often coabsorbed by physical solvents, which results in a mass loss of natural gas. It will also hinder sulfur recovery and impair the quality of the sulfur product.[14] Sarker[15] conducted the research on gas sweetening performance of single amine solvents and mixed amine solvents DGA−MEA, DEA−MDEA, and sulfolane−MDEA. Results showed when only H_2S removal efficiency was considered, the performance of MDEA was better than that of sulfolane−MDEA. Rostami et al.[16] found that the addition of sulfolane led to the higher solubility of hydrocarbons, which they burn in the sulfur recovery unit, resulting in a higher temperature of the reaction furnace from 985 to 1015 °C. Despite a vast amount of research on chemical and physical absorption techniques, to the best of authors' knowledge, limited or no work was considered for highly sour gas sweetening under low-pressure conditions. In recent years, many new techniques have been developed to enhance natural gas sweetening performance. He et al.[17] used a hybrid membrane process for natural gas sweetening. The results showed that advanced membranes at high pressures should be pursued to promote the application of the designed membrane system. Wang et al.[18] published research on the use of pure ionic liquids in the selective absorption performance of $H_2S/CO_2/CH_4$ to optimize its acid gas removal efficiency. Haider et al.[19] presented the potential feasibility of ionic liquids and their use with membranes in the natural gas industry. Their investigation showed that ionic liquids had many advantages regarding their feasibility in terms of technical, economical, and environmental aspects; however, large-scale adaption of this process required detailed analysis and lots of experience in natural gas sweetening. It is clear that the application of these innovative approaches fails to consider the effect of feed gas pressure and acid component content on the gas sweetening performance. Moreover, no experimental or industrial data is provided to support their findings. Thus, it is crucial to develop an efficient technique suitable for sweetening of natural gas with high H_2S and CO_2 contents under low pressures.

Since the 1980s, gas hydrate technology has become a research topic of global interest due to its relatively low cost and environmental friendliness.[20] In recent years, there has been increasing interest in the new hydrate-based gas separation method for natural gas sweetening.[21−24] Gas hydrates are icelike crystalline compounds formed by water and small-size gas molecules (e.g., CH_4, C_2H_6, H_2S, CO_2, etc.) under suitable temperature and pressure conditions.[25,26] The formation/decomposition of gas hydrates has a wide usage and has been identified as a promising technology for various industrial applications, such as gas storage and transportation,[27,28] refrigeration and air conditioning,[29,30] desalination,[31−33] and gas separation.[34−37] In previous studies, it has been shown that hydrate-based gas separation is a technology with a great amount of potential.[38−41] Maria et al.[42] performed an experimental evaluation of a unique hybrid method based on gas hydrate crystallization and membrane gas separation and proposed an alternative approach for xenon recovery from natural gas. Ko and Seo[43] studied the formation and dissociation behavior of SF6 hydrates in the presence of a surfactant and an antifoaming agent to maximize the performance of SDS and AAC. Li et al.[44] performed experiments on the effect of graphene oxide nanofluids on low-concentration coalbed methane via gas hydrate formation. The addition of graphene oxide nanofluids enhanced the hydrate formation rates and the CH_4 separation efficiency. The hydrate-based gas separation process can be applied to acid gas removal as H_2S and CO_2 are inclined to form hydrates under rather low pressure in the presence of water.[21,22] Liu et al.[23] investigated the hydrate formation conditions of sour natural gas through modeling and experiments in different solutions. They proposed a new calculation method for predicting the hydrate formation conditions of $CH_4/CO_2/H_2S/N_2$ quaternary sour gas in methanol−water solutions in their work. Xia et al.[24] proposed using the hydrate formation process to simultaneously capture CO_2 and H_2S from simulated syngas. They found that the synergic additives could remarkably accelerate the hydrate formation rate and enhance the selectivity of CO_2 or H_2S in the hydrating process. Mesbah et al.[45] modeled the phase equilibria of semiclathrates of CH_4, CO_2, N_2, and H_2S in TBAB solution using a correlation based on a two-stage formation mechanism. Their findings demonstrated the reliability of the model. However, research on the hydrate-based gas separation method application in the natural gas sweetening field has still been relatively limited. Most of the studies on this topic are related to the thermodynamic model for hydrate formation conditions. Performance evaluations of the hydrate-based gas separation method for sweetening of natural gas with high H_2S and CO_2 contents have thus rarely been involved. With this in mind, this paper conducts a thorough analysis of the hydrate-based gas separation method for the sweetening of natural gas with high H_2S and CO_2 contents. The results of our study suggest that the newly emerging hydrate-based gas separation process is simple and has low energy consumption; however, it also has an obvious limitation: the product gas is not eligible for sale as the sour components such as H_2S and CO_2 cannot be completely removed.

Enlighted by the above study results, a new method for purifying high-sour natural gas was proposed and studied. This new technique integrates hydrate-based separation with chemical absorption, aiming at effectively removing sour components from the feed gas. The performance of this new method was evaluated through both simulations and hydrating experiments. The technical evaluation results of this new method were compared with those from traditional MDEA absorption and hydrate-based gas separation. Additionally, comparisons in the aspect of energy consumption and cost between the three methods were performed to illustrate the feasibility of the new integrated method. Our study results indicated that the new proposed integrated method could effectively remove the sour components from feed and were able to well meet the sales gas specifications. Furthermore, it could reduce the energy consumption as well as the cost remarkably, compared to chemical absorption. This study provides a new concept for the sweetening of high-sour natural gas and promotes development of natural gas hydrate technology.

2. BASIC DATA, SIMULATIONS, AND EXPERIMENTAL METHODS

The performances of the three different methods for sweetening of natural gas with high H_2S and CO_2 contents were investigated. These three methods consist of the traditional chemical absorption method, the hydrate-based gas separation method, and the new method combining the former two processes. Five types of natural gas with different compositions were used as feed gas and the feed flow rate was 280 MMscfd (1 MMscfd is equal to 2.8317×10^4 m^3/d). The parameters, including product gas specification, energy consumption, and cost, were compared. The commonly used solvent MDEA[46,47] was adopted for the chemical absorption process in this study.

2.1. Basic Data. The feed gas condition, lean MDEA condition, and sweet gas specification are shown in Table 1.

Table 1. Parameters of Feed Gas and Lean MDEA and Specifications of Sales Gas

items	parameters	units	value
feed gas condition	molar flow rate	kmol/h	14 118
	volume flow rate	MMscfd	280
	pressure	MPa	2.0
	temperature	°C	30
lean MDEA condition	concentration	wt %	45
	temperature	°C	35
sales gas specification	H_2S content	mg/m^3	≤6 mg/m^3 (Class I) <20 mg/m^3 (Class II)
	CO_2 content	%	≤3% (Class I) ≤4% (Class II)

From an industrial application perspective, the feed sour natural gas pressure was determined to be 2.0 MPa, as it could be compared with that in actual practice. For sales gas specification, government regulations have made it compulsory for the existing sweet gas to be below a certain content of H_2S. This value varies from country to country and is generally in the 3−5 ppm (equals to 4.23−7.05 mg/m^3) H_2S range, and the CO_2 content is often limited to 2−5%.[9] In this study, the sales gas specification in Table 1 refers to China's GB 17820-2018 standard and Class I is required generally in China. Since the hydrate-based gas separation process is a relatively new method for acid gas removal, five types of natural gas with different compositions were selected for carrying out a complete performance evaluation, as shown in Table 2.

2.2. Simulations and Experimental Methods. The performance of the traditional MDEA absorption process was evaluated by simulation software Promax 5.0. Promax is widely used in the gas sweetening field and is confirmed by practical operation data of gas processing plants (GPPs).

Table 2. Dry Basis Composition of Sour Natural Gas with High H_2S and CO_2 Contents

composition	CH_4 (vol %)	H_2S (vol %)	CO_2 (vol %)
No. 1	85	10	5
No. 2	79	15	6
No. 3	73	20	7
No. 4	67	25	8
No. 5	60	30	10

Hydrate-based gas separation is a new process for acid gas removal. Its performance evaluation and verification for the specific feed gas composition in a specific solution could therefore only rely on hydrating experiments, which is shown in Figure 1. Thus, a series of hydrating experiments were conducted to fully assess the desulfurization performance of the hydrate-based gas separation process.

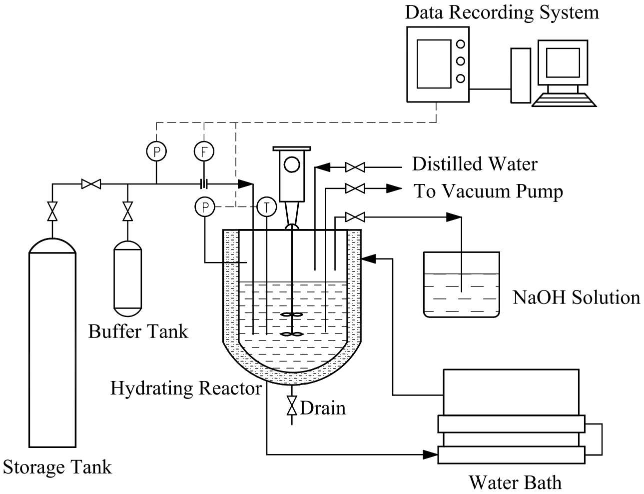

Figure 1. Schematic diagram of the stirring experiment apparatus for hydrate formation.

Figure 1 illustrates the experimental apparatus for hydrate-based gas separation. Briefly, it consists of a cylindrical stirring stainless steel reactor with a maximum operating pressure of 10 MPa. The volume of the vessel was 500 cm^3.[48] A magnetic stir bar was employed to agitate the vessel contents, which was coupled with an electromagnetic plate on top of the vessel. The temperature in the vessel was controlled by a water bath. A copper−constantan thermocouple with an uncertainty of ±0.1 K was inserted into the vessel to measure the liquid temperature. Two pressure transducers with an uncertainty of 0.04% in the range of 0−16 MPa were used to measure the pressure inside the vessel and piping, respectively. A flowmeter with an uncertainty of 0.05% was inserted into the piping to measure the gas flow rate. The temperature, pressure, and flow rate data were collected by a data acquisition unit and recorded in a computer every 10 s. A gas chromatograph with an uncertainty of 0.1 mol % was used to analyze the composition of the gas mixture in the vessel.[49]

The experiment in this study has been conducted under constant pressure (2.0 MPa) and constant volume. Distilled water is used as the solution for the hydrate reaction. According to the theoretical calculation results for hydrate formation conditions set out by the CPA-SRK + Chen-Guo model,[50] the optimal temperature for hydrate formation of $CH_4/H_2S/CO_2$ sour gas in distilled water solutions is 0−9 °C. Thus, the initial temperature of the reactor is determined to be 4 °C. Hydrate formation and decomposition are achieved through increasing and decreasing the temperature of the reactor, respectively. The pressure of the reactor is maintained by controlling the gas amount, which is achieved through manipulating the control valve at the inlet and outlet gas lines.

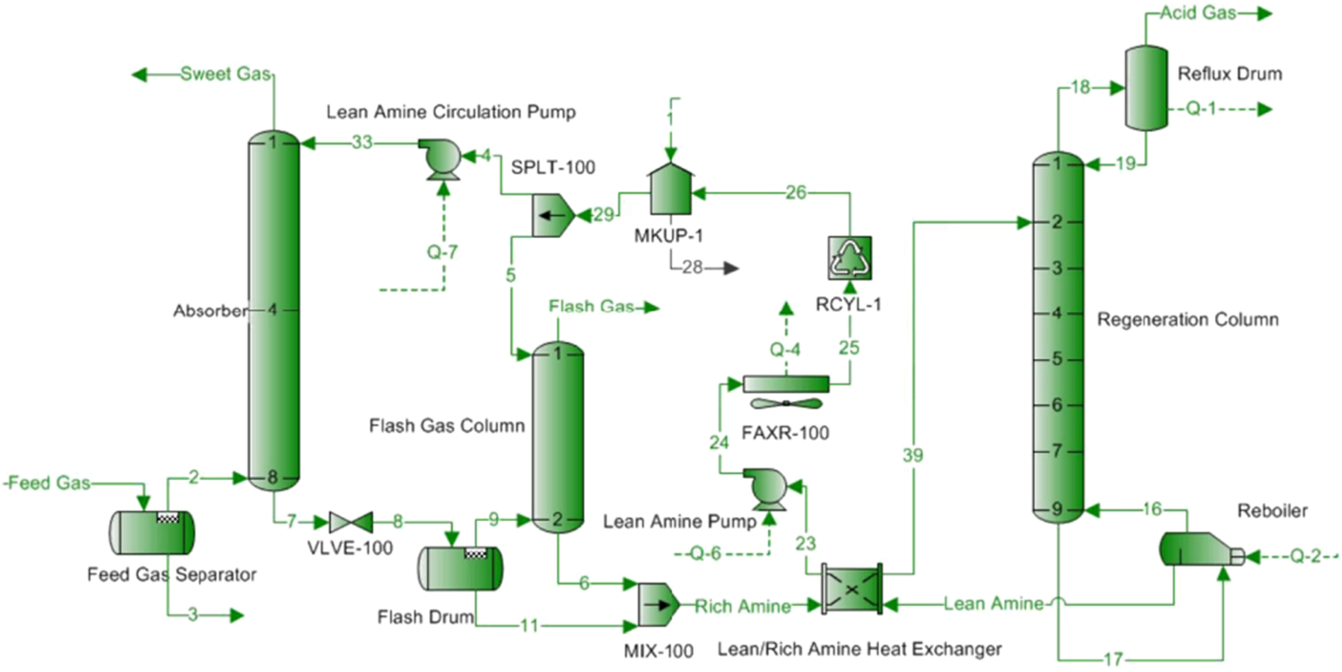

Figure 2. Simulation diagram of acid gas removal by traditional MDEA absorption.

3. SIMULATIONS AND CALCULATIONS OF THREE GAS SWEETENING METHODS

3.1. Traditional MDEA Absorption Method. A conventional 45% (wt) MDEA solvent was used as the chemical absorption solvent for assessing the performance of the traditional MDEA absorption process. The feed gas temperature and lean MDEA temperature to absorber were respectively 30 and 35 °C and were determined based on the common actual practices. The simulation model was established using professional software Promax 5.0, which is specially used in the natural gas desulfurization and decarbonization industry.[51] The fluid package selected for simulations by Promax was Amine Sweetening-PR, in which the Peng–Robinson state equation was used for the gas phase and the Electrolytic ELR model was used for the liquid phase. As the MDEA absorption technology is mature, only natural gas No. 2 was simulated. The process simulation diagram is given in Figure 2.

The simulation results of the traditional MDEA absorption process are summarized in Table 3.

According to Table 3, the traditional MDEA chemical absorption process can remove almost all of the H_2S and most of the CO_2 in the feed gas. However, after the process has been carried out, the H_2S composition in the sweet gas remains at 7.68 mg/m^3, which only meets Class II in the sales gas specification (Table 1) but not Class I. Meanwhile, the MDEA method has a large circulation rate (1200 m^3/h), which means large energy consumption and high regeneration duty (about 104 120 kW). Therefore, it can be stated that the MDEA process would lead to high costs for natural gas treatment plants.

Table 3. Simulation Results of the Traditional MDEA Chemical Absorption Process

parameters	units	MDEA chemical absorption process (feed gas No. 2)
feed gas flow rate	kmol/h	14 118
product gas flow rate	kmol/h	11 416
H_2S composition in feed gas	vol %	15
CO_2 composition in feed gas	vol %	6
H_2S composition in product gas	mg/m^3	7.68
CO_2 composition in product gas	vol %	2.18
MDEA circulation rate	m^3/h	1200
acid gas load in rich amine[a]	mol/mol	0.58
H_2S composition in acid gas	vol %	73.54
CO_2 composition in acid gas	vol %	20.85
acid gas flow rate	kmol/h	2873
regeneration duty	kW	104 120

[a] Acid gas loadings are intended as moles of acid gas per mole of MDEA.

3.2. Hydrate-Based Gas Separation Method. It can be seen from Table 2 that the H_2S and CO_2 contents in the feed gas are high, and it is known that H_2S and CO_2 are more likely to form hydrates than CH_4. Thus, the hydrate-based gas separation method was adopted for acid gas removal. To evaluate the performance of the hydrate-based gas separation method, we conducted hydrating experiments under constant pressure (P = 2.0 MPa). The initial temperature of the reactor was 4 °C, which is equal to the temperature of the water bath around the reactor.

3.2.1. Calculation of CO_2 and H_2S Recovery Factor. CO_2/H_2S recovery or split fraction (R) indicates the recovery efficiency of CO_2/H_2S from the total CO_2/H_2S feed supplied to the reactor and is calculated by the following equation (eq 1).[52]

$$R_{CO_2/H_2S} = \left(1 - \frac{n^{V}_{CO_2/H_2S}}{n^{F}_{CO_2/H_2S}}\right) \times 100\% \quad (1)$$

where $n^{F}_{CO_2/H_2S}$ represents the moles of CO_2 or H_2S in the feed gas and $n^{V}_{CO_2/H_2S}$ represents the moles of CO_2 or H_2S in the gas phase at the end of the experiments.

3.2.2. Results and Discussion. Tables 4 and 5 show the results for H_2S and CO_2 removal from the $H_2S/CO_2/CH_4$ gas mixture using hydrate formation, respectively. The experimental temperature was fixed at 277 K, and the pressure was fixed at 2.0 MPa.

Table 4. H_2S Composition Variation and Recovery Rate

feed gas sample	No. 1	No. 2	No. 3	No. 4	No. 5
H_2S composition (vol %) (t = 0)	10	15	20	25	30
H_2S composition (vol %) (t = 550 min)	1.63	2.18	8.04	13.67	19.56
H_2S composition decrease rate (%)	−8.37	−12.82	−11.96	−11.33	−10.45
recovery fraction (R) (%)	83.71	85.53	59.18	45.32	34.8

Table 5. CO_2 Composition Variation and Recovery Rate

feed gas sample	No. 1	No. 2	No. 3	No. 4	No. 5
CO_2 composition (vol %) (t = 0)	5	6	7	8	10
CO_2 composition (vol %) (t = 550 min)	5.23	5.24	5.19	5.99	7.2
CO_2 composition decrease rate (%)	+0.23	−0.76	−1.81	−2.11	−2.80
recovery fraction (R) (%)		12.66	25.86	25.13	28.00

From Table 4, when the H_2S composition in the feed gas is in the range of 10−15%, the H_2S removal performance improves with a higher recovery fraction, which is more than 80%. When the H_2S composition in the feed gas is higher at 20−30%, the recovery fraction decreases significantly. As can be seen in Table 5, when the CO_2 composition in the feed gas is 5%, the CO_2 composition increases after the reaction. Moreover, the CO_2 split performance improves when the CO_2 composition in the feed gas increases to 7% or higher. Therefore, it can be concluded that the hydrate separation process could be used to remove the high-sour natural gas for initial separation, which could remove most of the H_2S and part of the CO_2 in the $H_2S/CO_2/CH_4$ gas mixture. Also, to obtain higher H_2S/CO_2 removal efficiency, the preferable feed gas conditions for the hydrate-based gas separation method are that the H_2S content is higher than 15% and the CO_2 content is higher than 6%.

Comparing the H_2S removal, the CO_2 removal shows weak performance that the concentration decreases 2.8% in sample No. 5 only, which is the highest decrease rate in all cases. In terms of hydrate formation in the $H_2S/CO_2/CH_4$ gas mixture, the CO_2 hydrate formation is considered to be hindered by H_2S hydrate formation, which means that the H_2S hydrate formation has priority over that of CO_2. This is probably attributed to that H_2S is easier to form hydrates, the coefficient of fugacity of CO_2 is higher than that of H_2S, and the H_2S hydrate structure is more stable than the CO_2 hydrate structure.

To fully investigate the hydrate formation process, the liquid temperature in the reactor and the gas consumption amount at different reaction times were recorded. Figures 3 and 4 present the relationship between liquid temperature, gas consumption, and reaction time under constant pressure. It can be seen that for feed gas Nos. 1−5, the liquid temperature and gas consumption variation trends with reaction time are almost consistent. Thus, feed gas No. 1 was taken as an example to illustrate the hydrate reaction process. As time passed, from 0 to 180 min, the liquid temperature declined sharply from 293.15 K to about 275 K, which is almost equivalent to the temperature of the water bath. Following this, the liquid temperature increased slightly and then fluctuated, which was mainly attributed to the hydrate reaction generating some heat and releasing it into the system. Correspondingly, it can be seen in Figure 4 that the gas consumption was low and nearly stayed constant (about 17 cm^3/min) when passing from 0 to 120 min, which is due to it being in a liquid temperature decrease stage under the effect of the water bath, and there only being a small part of natural gas dissolving in the liquid. At this stage, almost no hydrate reaction occurred. After that, the gas consumption amount increased quickly till 420 min and the peak value reached to 432 cm^3/min. This was due to the fact that natural gas was consumed due to the acid components' hydrate formation and thus more feed gas was needed to be supplemented to maintain the system pressure.

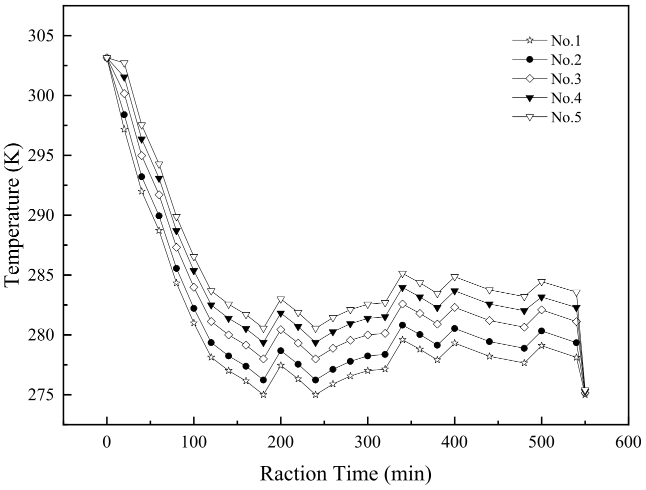

Figure 3. Liquid temperature variation trend with reaction time in a constant-pressure system.

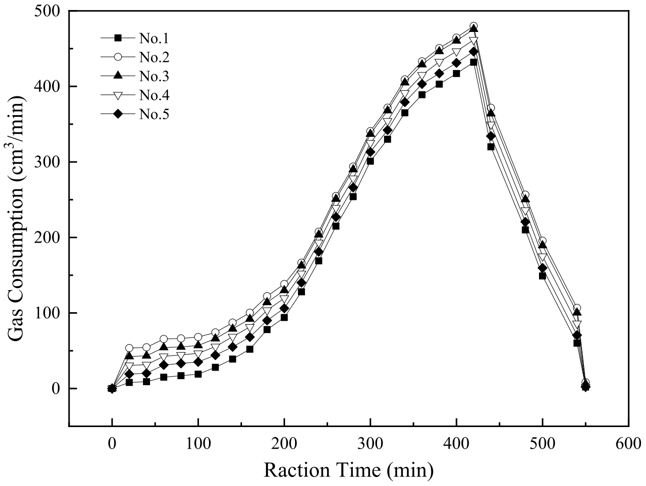

Figure 4. Gas consumption variation trend with reaction time in a constant-pressure system.

After 450 min, the gas consumption declined sharply and finally, at 550 min, to 0 when the hydrate reaction finished.

Figures 5 and 6 outline the hydrating experimental results for feed gas Nos. 1−5. It can be seen that the variation trends of H_2S and CO_2 compositions in five different types of feed gases are consistent. Specifically, the H_2S content declined linearly with the reaction time from 0 to 400 min. The CO_2 content decreased with the reaction time in feed gas No. 1, No. 2, and No. 3, while in feed gas No. 4 and No. 5, the CO_2 content tended to stabilize when it was below 6%. This indicated that when the CO_2 content was less than 6% in natural gas, and it could hardly form hydrates. The content of H_2S and CO_2 remained nearly unchanged when the reaction time was more than 400 min, implying that the reaction approached the equilibrium state. After reacting for 550 min, the H_2S content in feed gas No. 2 decreased from 15 to 2.18% and the CO_2 content declined from 6 to 5.24%. These results demonstrated that the acid components removal efficiency of the hydrate-based gas separation method was limited and fine removal of H_2S and CO_2 through this method could not be achieved. Although the final content of H_2S and CO_2 was much higher than that obtained by the traditional MDEA absorption method, the hydrate-based gas separation method was still proven to be able to effectively remove acid components. Most of the H_2S and a part of CO_2 were seen to form hydrates and finally separate from the feed natural gas. The mass transfer of gas molecules to the liquid phase for hydrate growth is hindered by the accumulation of gas hydrates at the gas/liquid interface, resulting in a significant decrease in the rate of hydrate growth.

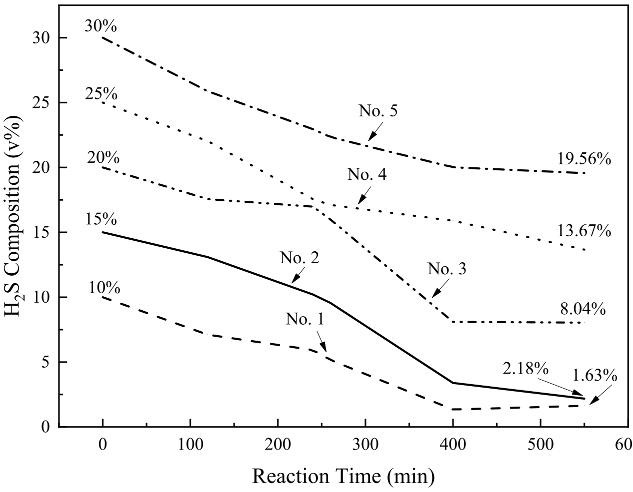

Figure 5. H_2S composition variation trend in the gas phase with reaction time.

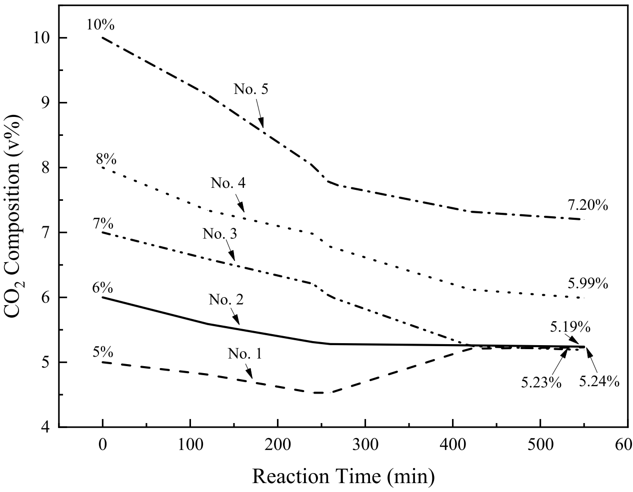

Figure 6. CO_2 composition variation trend in the gas phase with reaction time.

3.2.3. Hydrate-Based Gas Separation Process Design and Evaluation Results. Based on the experimental results, the conceptual process flow for hydrate-based gas separation was designed and proposed (Figure 7). The sour gas is first sent to a feed gas separator, where the liquid hydrocarbon and impurities are removed. The gas is then cooled by a feed gas cooler to a temperature 2−3 °C higher than the hydrate forming point. After that, the gas enters the hydrating reactor from the bottom, contacting the water from the top of the reactor in a countercurrent manner. To enhance the gas−liquid mass-transfer efficiency, a floating valve-type column could be installed. Most of the H_2S and a part of the CO_2 are converted to hydrates, which then flow to the downstream hydrate heater. After being heated to 5 °C above the hydrate decomposition temperature, the water and hydrates mixture enters the hydrate decomposer and decomposes into acid gas (H_2S and CO_2) and water. The acid gas is then delivered to the sulfur recovery facilities, while water is pumped to the hydrate reactor for recycling after being cooled down.

The experimental results of the hydrate-based gas separation process for feed gas No. 2 are summarized in Table 6.

According to Table 6, most of the H_2S and a part of the CO_2 can be removed by hydrate-based gas separation. In doing this, the water circulation rate reaches 1675 m^3/h, and the energy consumption becomes extremely low (only 5416 kW). However, despite these advantages, neither the H_2S content nor the CO_2 content in the sweet gas meets the sales gas specification in Table 1 when using this process. Thus, it can be concluded that using the hydrate-based gas separation process alone is not suitable for sour natural gas sweetening. Nevertheless, the hydrate-based gas separation process has two outstanding advantages, namely, having an extremely low energy consumption and requiring relatively simple steps.

3.3. New Method Integrated Hydrate-Based Gas Separation and MDEA Absorption. Based on the above analysis, the traditional MDEA absorption method and the hydrate-based gas separation method have their own advantages and limitations. By adopting the positive points from these two methods and bypassing their shortcomings, a new combined method for acid gas removal can be proposed, as demonstrated in this work.

3.3.1. Process Description. The process block diagram for the integrated method is presented in Figure 8. It includes two steps: the hydrate-based gas separation process for sour gas pretreatment and the traditional MDEA absorption for the fine removal of acid components.

Sour gas from the upstream gas gathering pipeline is delivered to the hydrate-based gas separation block for initial separation. During this phase, a part of the acid components (H_2S and CO_2) will form hydrates and be removed from the feed gas. The pretreated natural gas is then sent to the MDEA absorption block. In this block, the remaining sour components will react with MDEA and be absorbed. In this way, the sweet gas is able to meet the requirement of the sales

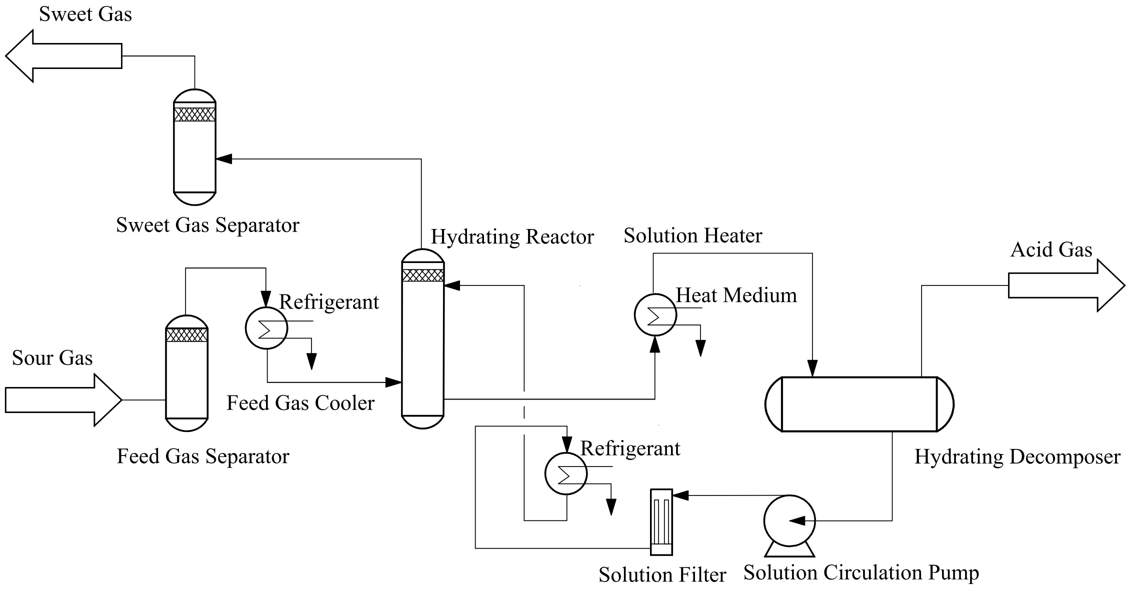

Figure 7. Process flow diagram of acid gas removal by hydrate-based gas separation.

Table 6. Experimental Data of the Hydrate-Based Gas Separation Process

parameters	units	hydrate-based gas separation process (feed gas No. 2)
feed gas flow rate	kmol/h	14 118
product gas flow rate[a]	kmol/h	12 123
H_2S composition in feed gas	vol %	15
CO_2 composition in feed gas	vol %	6
H_2S composition in product gas	vol %	2.18
CO_2 composition in product gas	vol %	5.24
water circulation rate[a]	m^3/h	1675
H_2S content in acid gas	vol %	92.90
CO_2 content in acid gas	vol %	10.61
acid gas flow rate[a]	kmol/h	1995
cooling and heating duty[a]	kW	5416

[a] The data is calculated according to the experimental results.

gas specifications. The acid gas produced by the two blocks will be collected and sent to the downstream acid gas treatment unit. The detailed hydrate-based gas separation flow and MDEA absorption flow are shown in Figures 7 and 2, respectively.

3.3.2. Performance Evaluation. As mentioned above, the integrated process includes both hydrate-based gas separation and MDEA absorption. The sour gas condition from the hydrate-based gas separation part to the MDEA absorption part is described in Table 6. During the MDEA absorption phase, MDEA was used as the solvent and the widely used Promax was employed for simulations and calculations. Since the integrated method showed basically the same sweetening effect on natural gas Nos. 1−5 (Table 2), we only analyzed the results from natural gas No. 2 (Table 7).

As indicated in Table 7, the new integrated process can efficiently remove almost all of the H_2S and most of the CO_2. After the process, the H_2S content and CO_2 contents in the product gas are 4.23 mg/m^3 and 1.94%, respectively, which meet the Class I sales gas specifications outlined in Table 1.

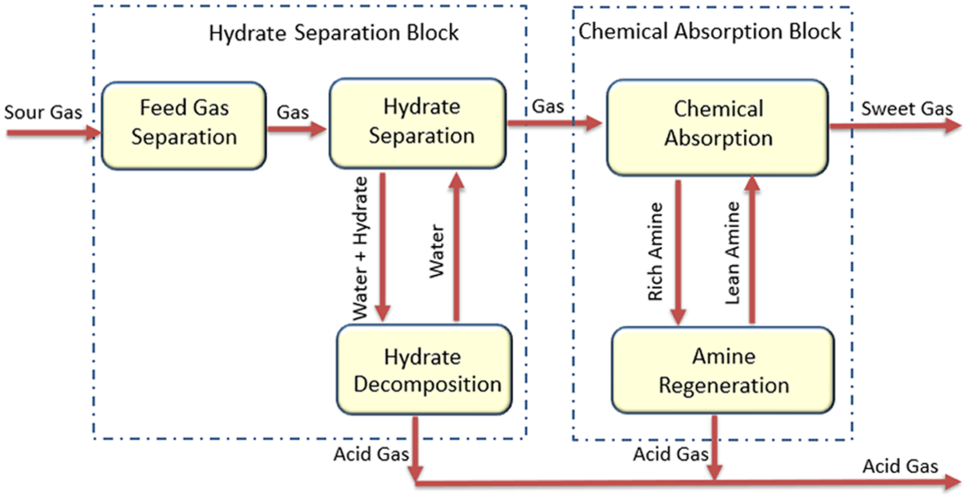

Figure 8. Block diagram of the hydrate-based gas separation coupling chemical absorption process.

Table 7. Experimental and Simulating Data from the Hydrate-Based Gas Separation Coupling Chemical Absorption (Feed Gas No. 2)

parameters	units	hydrate-based gas separation	MDEA absorption
feed gas flow rate	kmol/h	14 118	12 123
product gas flow rate	kmol/h	12 123	11 515
H_2S composition in feed gas	vol %	15	2.18
CO_2 composition in feed Gas	vol %	6	5.24
H_2S composition in product gas	mg/m^3		4.23
CO_2 composition in product gas	vol %		1.94
water circulation flow rate	m^3/h	1675	
MDEA circulation flow rate	m^3/h		320
acid gas load in rich amine			0.51
H_2S composition in acid gas	vol %	92.90	37.60
CO_2 composition in acid gas	vol %	10.61	56.72
acid gas flow rate	kmol/h	1995	670.21
hydrating cooling and heating duty	kW	5416	
MDEA regeneration duty	kW		43 420

Moreover, its MDEA regeneration duty is notably lower than that of the traditional chemical absorption process.

4. TECHNICAL COMPARISON, ENERGY CONSUMPTION, AND ECONOMIC EVALUATION OF THE THREE METHODS

To fully evaluate and compare the performance of the three kinds of acid gas removal processes, the key parameters (e.g., the product gas condition, the acid gas condition, the water and solvent circulation flow rate) are compared in Table 8. As shown, the new integrated method has a much lower amine circulation rate than the conventional MDEA method. Furthermore, the H_2S content in the product gas of the integrated method is 4.23 mg/m^3, which is lower than that of the traditional MDEA absorption method (7.68 mg/m^3) and the new hydrate-based gas separation method (2.18%).

The economic cost is the key to the industrial application of a new process. Therefore, for a thorough economic analysis, both the CapEx (Capital Expenditures) and OpEx (Operating Expense) are estimated and calculated using questor software, which includes a comprehensive database specific to the worldwide oil and natural gas. As the quotations vary among different countries, we only displayed the results from the Middle East, an area typically considered rich in natural gas. The CapEx and OpEx values for the three methods are presented in Table 9. Their energy consumption amount and the differences between their CapEx and OpEx values are compared in Figure 9. As suggested in Figure 9, the traditional MDEA process has the highest energy consumption and cost for gas sweetening. The hydrate-based gas separation process

Table 9. Cost Comparison for the Three Acid Gas Removal Processes (Feed Gas No. 2)[a,b]

parameters	feed gas flow rate (kmol/h)	CapEx (kUSD)	OpEx (kUSD/a)
traditional MDEA process	14 118	35 060	16 450
hydrate-based gas separation process	14 118	15 800	825
hydrate-based gas separation coupling MDEA process	14 118	23 500	7750

[a] OpEx includes raw material costs, utility costs, maintenance costs, and labor charges. [b] kUSD refers to thousand dollars.

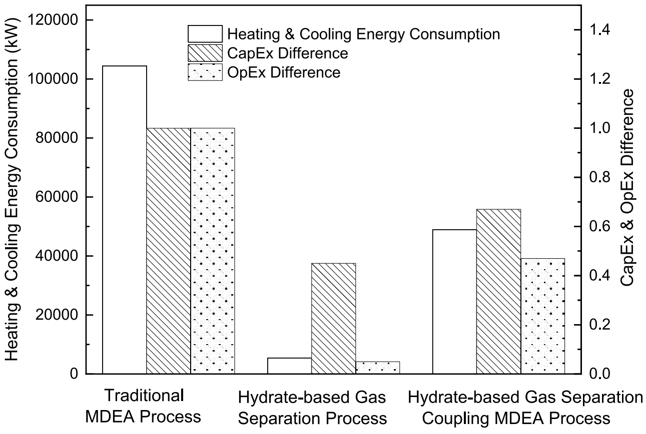

Figure 9. Comparison of energy consumption and cost for the three processes (Feed gas No. 2).

Table 8. Performance Comparison between the Three Acid Gas Removal Processes (Feed Gas No. 2)

parameters	units	traditional MDEA process	hydrate-based gas separation process	hydrate-based gas separation coupling MDEA process
feed gas flow rate	kmol/h	14 118	14 118	14 118
product gas flow rate	kmol/h	11 416	12 123	11 515
H_2S composition in feed gas	vol %	15	15	15
CO_2 composition in feed gas	vol %	6	6	6
H_2S composition in product gas	mg/m^3	7.68	2.18 (vol %)[a]	4.23
CO_2 composition in product Gas	vol %	2.18	5.24	1.94
water circulation flow rate	m^3/h		1675	1675
MDEA circulation flow rate	m^3/h	1200		320
acid gas load in rich amine		0.58		0.51
H_2S composition in acid gas	vol %	73.54	92.90	78.99
CO_2 composition in acid gas	vol %	20.85	10.61	22.21
acid gas flow rate	kmol/h	2873	1995	2665

[a] This value refers to the volume percentage of H_2S in the product gas. 2.18 (vol %) equals 33 100 mg/m^3.

meanwhile, although having the lowest energy consumption and cost, is unable to meet the sales gas specification with regard to its H_2S and CO_2 contents in the product gas. In contrast, the amine regeneration duty of the new integrated method for sweetening feed gas No. 2 is 43 420 kW, which is only 42% that of the traditional MDEA absorption process. What is more, the CapEx and OpEx values of the integrated method are respectively 68 and 48% those of the conventional method, which are remarkably lower than those of the traditional MDEA absorption process. To sum up then, the new integrated method integrates the advantages of the traditional MDEA process and hydrate-based gas separation process. By adopting this integrated technique, the product gas can not only meet the sales gas specification but also lower the energy consumption and cost.

5. CONCLUSIONS

In this work, three processes for H_2S and CO_2 removal from $CH_4/H_2S/CO_2$ mixture gas (79 mol % CH_4, 15 mol % H_2S, and 6 mol % CO_2) were present and evaluated based on the feed gas flow rate of 280 MMscfd.

The MDEA process simulated by Promax shows that it could remove almost all H_2S (7.68 mg/m^3 H_2S remaining) and part of CO_2 (2.18 mol % CO_2 remaining) from the mixture gas with the highest cost (35 060 kUSD CapEx and 16 450 kUSD OpEx).

The hydrate-based gas separation process performance is based on the experiment. The experiment of hydrate formation for H_2S and CO_2 removal from a $H_2S/CO_2/CH_4$ mixture gas (five sample Nos. 1−5 with CH_4 mol concentration from 85 to 60%, H_2S mol concentration from 10 to 30%, CO_2 mol concentration from 5 to 10%) was evaluated in a liquid water system. The impact of acid component concentration was studied that the final gas uptake, the maximum H_2S recovery factor is at No. 2 (79 mol % CH_4, 15 mol % H_2S, and 6 mol % CO_2), and the maximum CO_2 recovery factor is at No. 5 (60 mol % CH_4, 30 mol % H_2S, and 10 mol % CO_2), indicating that the competition between H_2S and CO_2 molecules for the occupancy of hydrate cavities became stronger at high concentrations as well as they are interacting. Based on sample No. 2 (79 mol % CH_4, 15 mol % H_2S, and 6 mol % CO_2), the hydrate-based gas separation process could remove most of the H_2S (2.18 mol % H_2S remaining) and a small part of CO_2 (5.24 mol % CO_2 remaining) from $H_2S/CO_2/CH_4$ mixture gas with the lowest cost (15 800 kUSD CapEx and 825 kUSD OpEx). It could not meet the specification of the H_2S and CO_2 concentration in sales gas.

The new process integrating the MDEA process and the hydrate-based gas separation process is for complying with the specifications and energy saving. It presents the good performance for removal of H_2S (4.23 mg/m^3 H_2S remaining) and CO_2 (1.94 mol % CO_2 remaining) from mixture gas, as well as the lower cost (23 500 kUSD CapEx and 7750 kUSD OpEx).

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Notes

The authors declare no competing financial interest.

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