



# A Thermal Chemical Reaction System for Natural Gas Hydrates Exploitation

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The methodology of using CO<sub>2</sub> to replace CH<sub>4</sub> to recover the natural gas hydrates (NGHs) is supposed to avoid geological disasters. However, the reaction path of the CH<sub>4</sub>-CO<sub>2</sub> replacement method is too complex to give satisfactory replacement efficiency. Therefore, this study proposed a thermochemical reaction system that used the heat and the nitrogen released by the thermochemical reactions to recover NGHs. The performance of the thermochemical reaction system (NaNO<sub>2</sub> and NH<sub>4</sub>Cl) regarding heat generation and gas production under low temperature (4°C) conditions was evaluated, and the feasibility of exploiting NGHs with an optimized formula of the thermochemical reaction system was also evaluated in this study. First, the effects of three catalysts (HCl, H<sub>3</sub>PO<sub>4</sub>, and NH<sub>2</sub>SO<sub>3</sub>H) were investigated at the same reactant concentration and catalyst concentration. It was confirmed that HCl as a catalyst can obtain better heat generation and gas production. Second, the effect of HCl concentration on the reaction was investigated under the same reactant concentration. The results showed that the higher the HCl concentration, the faster is the reaction rate. When the concentration of HCl was greater than 14 wt%, side reactions would occur to produce toxic gas; hence, 14 wt% was the optimal catalyst concentration for the reaction of NaNO<sub>2</sub> and NH<sub>4</sub>Cl at low temperatures. Third, the heat generation and gas production of the thermochemical reaction systems were evaluated at different reactant concentrations (1, 2, 3, 4, 5, and 6 mol/L) at 14 wt% HCl concentration. It was found that the best reactant concentration was 5 mol/L. Finally, the feasibility of exploiting NGHs with the optimal system was analyzed from the perspectives of thermal decomposition and nitrogen replacement. The thermochemical reaction system provided by this study is possible to be applied to explore NGHs' offshore.

**Keywords:** NGHs, thermochemical reaction, heat generation, gas production, replacement efficiency

## 1 INTRODUCTION

As a new type of clean energy, NGHs have huge reserves. It is estimated that the carbon content of NGHs is twice more than that of the known fossil fuels in the world (Chen et al., 2020). Owing to the enormous amount of natural gas stored in the global NGH reserves, NGHs are considered promising energy resources in the future (Chong et al., 2016). At present, there are four main production methods in recovering NGHs, namely, depressurization, thermal stimulation, inhibitor injection, and CH<sub>4</sub>-CO<sub>2</sub> replacement method (Li et al., 2014; Song et al., 2015; Choi et al., 2020; Choi et al., 2021; Liu et al., 2021). In general, depressurization, thermal stimulation, and inhibitor injection methods are based on the disruption of the NGH equilibrium (Yuan et al., 2011; Song et al., 2019) to destroy the structure of NGHs, which might result in geological disasters

due to the collapse of NGH formation. CH<sub>4</sub>-CO<sub>2</sub> replacement, on the other hand, has been proposed as a nondestructive method to recover CH<sub>4</sub> (Zhang et al., 2017a; Sun et al., 2019) and sequester CO<sub>2</sub> (Teng and Zhang 2018; Sun et al., 2021a). However, each method has its limitations. The thermal stimulation method has low gas production efficiency and high cost, and it is difficult to build and maintain the heating equipment; The use of the CH<sub>4</sub>-CO<sub>2</sub> replacement method must be with a sufficient CO<sub>2</sub> gas source and transportation pipe, and the replacement efficiency of this method is low (Zhang et al., 2019). To improve the replacement efficiency, Koh et al. proposed to replace CO<sub>2</sub> with flue gas (CO<sub>2</sub>/N<sub>2</sub>). Their research results showed that the replacement efficiency increased from approximately 64–85% (Kph et al., 2012). In practice, the above methods are combined to obtain better results, e.g., electric heating-assisted depressurization, CH<sub>4</sub>-CO<sub>2</sub> replacement-assisted depressurization, and co-injection of the inhibitor and CO<sub>2</sub> (Li et al., 2010; Gupta and Aggarwal 2014; Minagawa 2015; Khlebnikov et al., 2017). Accordingly, we propose a thermochemical reaction to utilize both the heat generated by a thermochemical reaction to provide heat for NGH decomposition and the gas generated by the thermochemical reaction to replace the methane in NGHs.

Thermochemical reactions are widely used in heavy oil development, reservoir fracturing, and plugging removal (Mahmoud et al., 2019). However, the research studies of applying the thermochemical reactions to develop NGHs are rare. Xu et al. proposed a novel method for NGH production, namely, depressurization and *in situ* supplemental heat (calcium oxide, CaO powder) to provide a large amount of heat for the decomposition of NGHs. At the same time, the Ca(OH)<sub>2</sub> produced by the reaction will fill the void volume left by NGH decomposition and hence, improve the permeability of the reservoir (Xu et al., 2021). This method, however, is not verified by experiments. The commonly used thermochemical reaction systems in oil fields include the NH<sub>4</sub>Cl and NaNO<sub>2</sub> system, the urea and NaNO<sub>2</sub> system, and the H<sub>2</sub>O<sub>2</sub> system. Considering the factors of heat production, gas production, safety, corrosivity, and cost, the NH<sub>4</sub>Cl and NaNO<sub>2</sub> system is obviously advantageous in NGH production.

Nguyen et al. mentioned that the reaction rate of NH<sub>4</sub>Cl and NaNO<sub>2</sub> is related to the initial temperature, hydrogen ion concentration, and reactant concentration (Nguyen et al., 2003). This reaction of NH<sub>4</sub>Cl and NaNO<sub>2</sub> cannot happen at room temperature unless an acid catalyst is added to the system (Sun et al., 2021b). Normally, the rate of thermochemical reaction increases with the increase of acid catalyst concentration until a threshold concentration is reached which can produce harmful NO<sub>2</sub> (Qian et al., 2019). Some researchers have studied the influences of acid catalysts on the reaction and suggested that the pH value of the reaction system shall be controlled within a reasonable range. The experimental results may not exactly be the same, depending on the experimental conditions. Wang et al. mentioned that a red-brown gas was produced when the hydrogen ion concentration

reached 0.0356 mol/L (the pH value was ~1.5) at 30°C (Wang et al., 2020). Wu et al. pointed out that the pH value should be around three for the reaction system of NaNO<sub>2</sub> and NH<sub>4</sub>Cl so that the reaction can occur smoothly at room temperature without producing lots of poisonous red-brown gas (Wu et al., 2007). It is noteworthy that these experiments were carried out above room temperatures. If the NH<sub>4</sub>Cl and NaNO<sub>2</sub> system was applied to exploit the NGHs, it is necessary to study the effect of acid catalyst on the reaction of NaNO<sub>2</sub> and NH<sub>4</sub>Cl under low temperatures of a real NGH reservoir.

This study, thus, aims to use the thermochemical reaction system of NH<sub>4</sub>Cl and NaNO<sub>2</sub> with an acid catalyst to recover the NGH reservoir in the South Sea, China. The heat generation and gas production performance of the thermochemical reaction system of NH<sub>4</sub>Cl and NaNO<sub>2</sub> under the reservoir temperature (4°C) were evaluated, and the influences of catalyst and reactant concentrations were studied by the experiments to obtain an optimal formula for the thermochemical reaction system. In the end, the feasibility of using the optimal thermochemical reaction system to recover NGHs was determined to guide the application of our system in exploiting the NGH reservoir.

## 2 MATERIALS AND METHODS

### 2.1 Materials

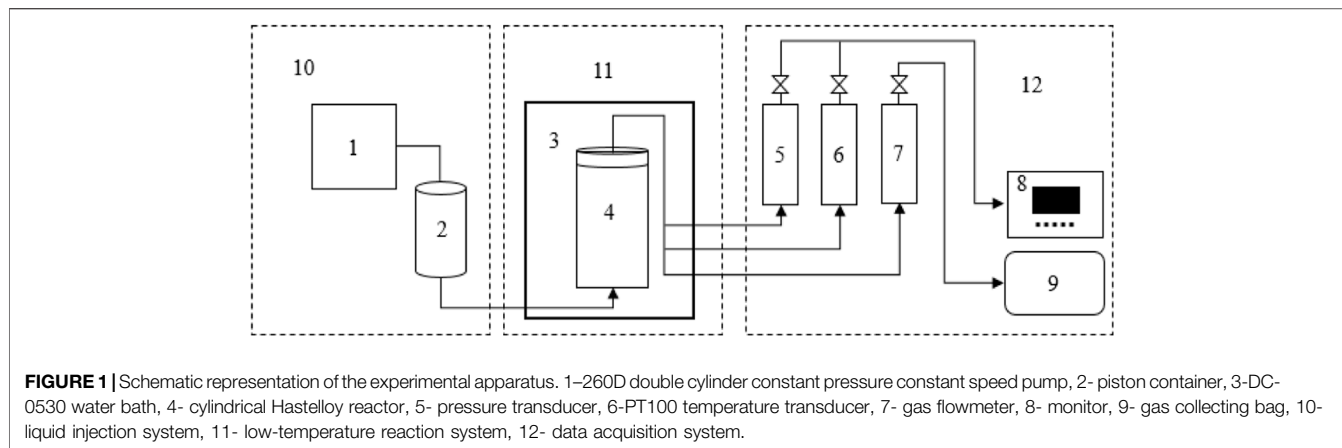
The chemical reagents used in the experiments include NH<sub>4</sub>Cl (analytical purity), NaNO<sub>2</sub> (analytical purity), HCl (37.5%), NH<sub>2</sub>SO<sub>3</sub>H (analytical purity), H<sub>3</sub>PO<sub>4</sub> (analytical purity), and ethylene glycol (EG, 98%). NH<sub>4</sub>Cl and NaNO<sub>2</sub> were used as reactants. HCl or NH<sub>2</sub>SO<sub>3</sub>H or H<sub>3</sub>PO<sub>4</sub> was used as a catalyst. EG was used to mix with distilled water as an anti-freezer for maintaining low temperature in a water bath. The experimental temperature in the reactor was maintained at 4°C to simulate the real reservoir temperature (Li et al., 2013; Yu et al., 2014; Natural Gas Hydrates in Flow Assurance 2010). The chemicals used in this study were purchased from Quanrui Reagent Co., Ltd. (Liaoning, China).

### 2.2 Methods

**Figure 1** is a schematic graph of the experimental apparatus for the reaction and data collection. The apparatus includes a liquid injection system, low-temperature reaction system, and data acquisition system. The liquid injection system consists of a pump and a steel piston container (200ml, ≤ 32 MPa). The low-temperature reaction system consists of a cylindrical Hastelloy reactor (500ml, ≤ 70 MPa) and a water bath (10 L). The data acquisition system consists of a gas flowmeter, gas collecting bag, temperature, and pressure transducers with an accuracy of ±0.1°C and ±0.01 MPa, respectively.

#### 2.2.1 Experimental Operation Process

The first step was to prepare the solution. First, the aqueous solution of NaNO<sub>2</sub> (75 ml) was prepared, and then, it was put into the piston container. Second, the aqueous solution of NH<sub>4</sub>Cl

**TABLE 1** | Experimental scenarios in the study.

Scenario No	Case No	Catalyst Kind	Catalyst Concentration (wt%)	Reactant concentration (mol/L)
scenario 1	1	HCl	14	5
	2	H <sub>3</sub> PO <sub>4</sub>	14	5
	3	NH <sub>2</sub> SO <sub>3</sub> H	14	5
scenario 2	4	HCl	6	5
	5	HCl	10	5
	6	HCl	14	5
scenario 3	7	HCl	14	1
	8	HCl	14	2
	9	HCl	14	3
	10	HCl	14	4
	11	HCl	14	5
	12	HCl	14	6

(75 ml) was prepared, and then, it was put into the reactor. Third, the acid catalyst solution (5 ml) was prepared, and then, it was slowly dropped into the reactor. After the mixed solution was electronically stirred at 500 rpm for 10 min, the reactor was sealed.

The second step was to inject the solution. 75 ml NaNO<sub>2</sub> solution was injected into the reactor by a double cylinder pump at a rate of 40 ml/min. The pump was quickly closed after the injection of NaNO<sub>2</sub> solution, and the reactor was shaken for 30 s to mix the solution thoroughly.

The third step was to observe the experimental phenomenon and record the data. The temperature change in the reactor was recorded by the data acquisition system, and meanwhile, the gas production rate of the reaction was measured by the gas flowmeter, and the cumulative gas production was collected by the gas collection bag. The overall reaction lasted 1 h.

### 2.2.2 Optimization of the System Formula

It has been reported that when the molar concentration ratio of NaNO<sub>2</sub> with NH<sub>4</sub>Cl was 1:1, the reaction system can produce more gas at a better gas production rate (Wang et al., 2020). Therefore, the experiments of this study were carried out at a molar concentration proportion of 1:1 of NaNO<sub>2</sub> with NH<sub>4</sub>Cl. Three scenarios and twelve experiments were carried out in this study to investigate the effects of the catalyst type, catalyst concentration, and reactant concentration, respectively (see

**Table 1**). Temperature, gas production rate, and (the total of something over time) cumulative gas production were selected as key parameters to evaluate the performance of the thermochemical reaction systems to select the best formula.

In scenario 1, the heat generation and gas production performance of the thermochemical reaction system was investigated by using three kinds of acid catalysts at a reactant concentration of 5 mol/L and catalyst concentration of 14 wt%. In scenario 2, the best catalyst from scenario 1 was utilized to evaluate the influence of catalyst concentration at 6, 10, and 14 wt% on the heat generation and gas production of the thermochemical reaction system. While in scenario 3, the concentration of the reactants was changed from 1 to 6 mol/L to explore the impact of reactant concentrations on the heat generation and gas production performance of the thermochemical reaction system; the optimum catalyst kind from scenario 1 and the optimal catalyst concentration from scenario 2 were used in scenario 3.

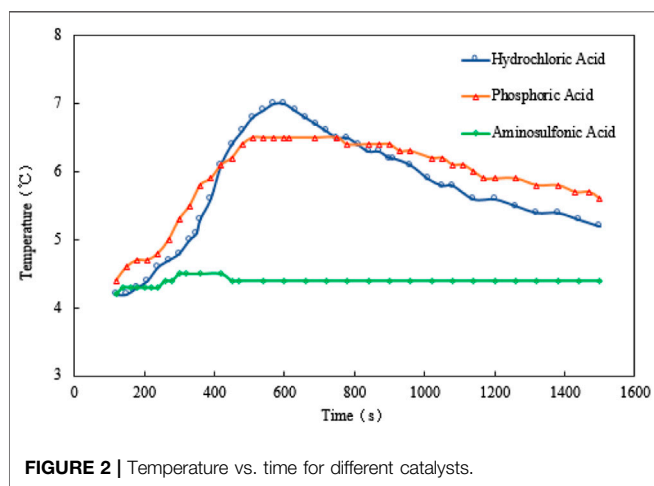
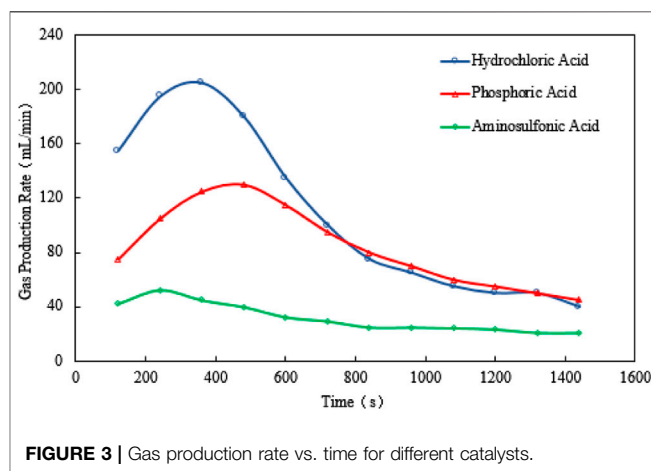
## 3 RESULTS AND DISCUSSION

### 3.1 Effect of the Catalyst Type

In scenario 1, the reaction was performed at NaNO<sub>2</sub> or NH<sub>4</sub>Cl concentration of 5 mol/L and acid catalysts' concentration of

**TABLE 2** | Experimental results of scenario 1

Catalyst type	Peak temperature (°C)	Cumulative gas production (ml)	Time of reaching the peak temperature (s)	Maximum gas production rate (ml/min)	Time of reaching the maximum gas production rate (s)
HCl	7.0	3,540	570	205	320
H <sub>3</sub> PO <sub>4</sub>	6.5	3,335	510	130	480
NH <sub>2</sub> SO <sub>3</sub> H	4.5	1,282	300	52.5	240

**FIGURE 2** | Temperature vs. time for different catalysts.**FIGURE 3** | Gas production rate vs. time for different catalysts.

14 wt% by using three kinds of catalysts, that is, HCl, H<sub>3</sub>PO<sub>4</sub>, and NH<sub>2</sub>SO<sub>3</sub>H. The temperature, gas production rate, and cumulative gas production profiles were compared at the equal volume of these three catalyst solutions. The experimental results are shown in **Table 2**.

For scenario 1, the temperature, gas production rate, and cumulative gas production are plotted against the time (see **Figure 2–4**). It is implied from the figures that NaNO<sub>2</sub> and NH<sub>4</sub>Cl can react at 4°C with the three kinds of catalyst, whereas the effects of each kind of catalyst are different. **Figure 2** gives the reaction temperature of different kinds of catalysts within 1-h reaction. The peak reaction temperature of using HCl, H<sub>3</sub>PO<sub>4</sub>, and NH<sub>2</sub>SO<sub>3</sub>H as the catalyst is 7°C, 6.5°C, and 4.5°C, respectively. In addition, as shown in **Figure 3** and **Figure 4**, the peak gas production rate is 205 ml/min at 320 s, and the cumulative gas production is 3,540 ml by using HCl as the catalyst. The peak gas production rate is 130 ml/min at 480 s, and the cumulative gas production is 3,335 ml using H<sub>3</sub>PO<sub>4</sub> as the catalyst. The peak gas production rate is 52.5 ml/min obtained at 240 s, and the cumulative gas production is 1,282 ml using NH<sub>2</sub>SO<sub>3</sub>H as the catalyst. By comparing the results of these three catalysts, it is found that the peak heat value reaches at the shortest time for NH<sub>2</sub>SO<sub>3</sub>H, while the gas production rate and the cumulative gas production are the lowest. It is supposed that when the solid acid dissolves in the water, H<sup>+</sup> slowly ionizes, resulting in mild reaction and hence long reaction time; however, such a long reaction time is not favorable as it will cause excessive heat loss. In

the end, HCl is selected as the optimal catalyst due to its better performance in heat and gas production within a reasonable reaction time at low temperatures.

### 3.2 Effect of Catalyst Concentrations

In scenario 2, the reactions were performed at a concentration of 5 mol/L of NaNO<sub>2</sub> or NH<sub>4</sub>Cl with the HCl catalyst at the concentrations of 6, 10, and 14 wt%. To compare the resultant temperature, gas production rate, and cumulative gas production profiles, an equal volume of the catalyst solutions was injected in the three cases. The experimental results are shown in **Table 3**.

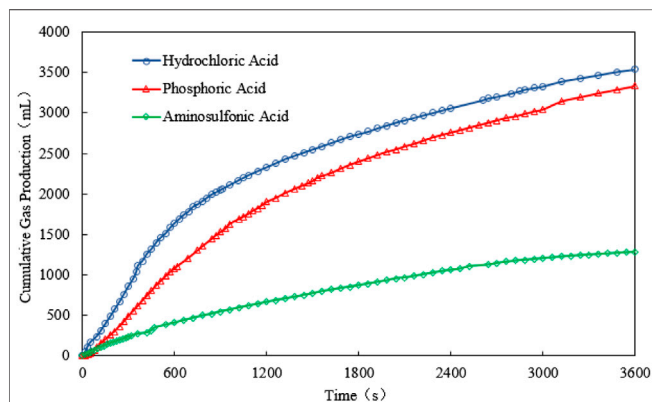
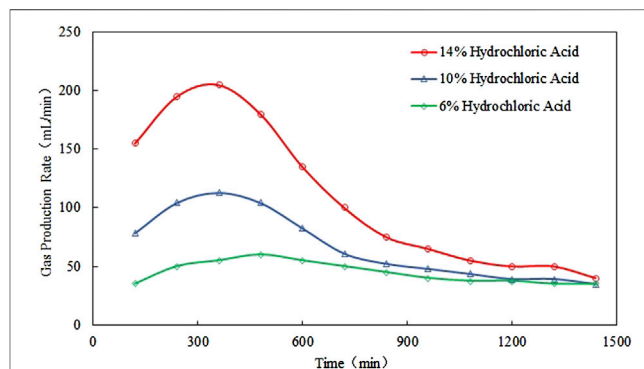
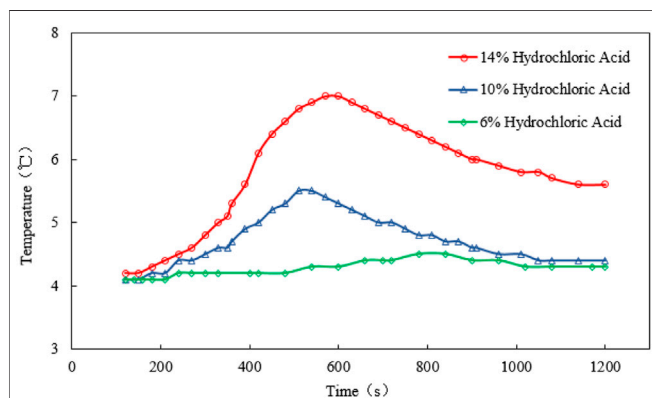
For scenario 2, the temperature, gas production rate, and cumulative gas production are plotted against the time (see **Figures 5, 6, and 7**). It is observed that the peak temperature, gas production rate, and the cumulative gas production increase with the increase in the catalyst concentration. It should be noted that the concentration of H<sup>+</sup> in the solution cannot be too high because H<sup>+</sup> will react with NO<sub>2</sub><sup>-</sup> to form unstable nitrite, which is easy to decompose into toxic NO and NO<sub>2</sub> gases. During the experiment, it was found that when the catalyst concentration exceeds 14% or the H<sup>+</sup> concentration of the reaction system is larger than 0.132 mol/L (pH value is less than 1), a reddish-brown irritant gas will be produced. Therefore, 14% is the optimum HCl concentration when being used as the catalyst.

### 3.3 Effect of Reactant Concentrations

In scenario 3, the reactions were performed at NaNO<sub>2</sub> and NH<sub>4</sub>Cl concentrations of 1–6 mol/L at an HCl concentration of 14 wt%.

**TABLE 3** | Experimental data for scenario 2.

HCl concentrations (wt%)	Peak temperature (°C)	Peak gas production rate (ml/min)	Cumulative gas production (ml)
6	4.5	60	1830
10	5.5	113	2,670
14	7	205	3,540

**FIGURE 4** | Cumulative gas production vs. time for different catalysts.**FIGURE 6** | Gas production rate vs. time at different HCl concentrations.**FIGURE 5** | Temperature vs. time at different HCl concentrations.

To compare the temperature, gas production rate, and cumulative gas production profiles, an equal volume of catalyst solutions was injected in the six cases. The experimental results are shown in **Table 4**.

For scenario 3, the temperature, gas production rate, and cumulative gas production are plotted against the time (see **Figures 8–10**). It is implied from the figure that  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  can react at  $4^\circ\text{C}$  with the presence of HCl catalyst. **Figure 8** shows the reaction temperature changes at different concentrations of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  within 1 h. The temperature is observed to increase with the increase of reactant concentrations. The peak temperature reaches after 600 s, and additionally, the higher the concentration of the reactants, the faster the peak temperature reaches. Moreover, although the temperature profile is the highest

when the reaction concentration is 6 mol/L, the temperature profile at the reactant concentration of 5 mol/L is close to it.

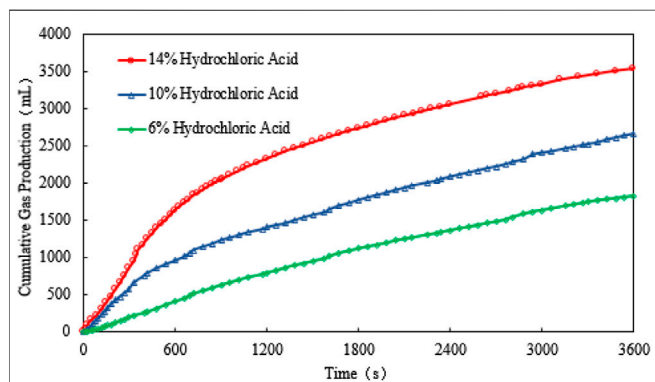
In **Figures 9, 10** it is implied that the gas production rate or the cumulative gas production increases when the reactant concentration increases from 1 mol/L to 6 mol/L; however, when the concentration of the reactants reaches 5 mol/L, the growth rate slows down. Again, the gas production rate and the cumulative gas production profiles of 5 mol/L reactants are close to those profiles of 6 mol/L reactants. On the other hand, when the concentration of the reactants is larger than 3 mol/L, the gas production rate peak is watched before 600 s, whereas the temperature peak is observed after 600 s. The difference in these two peak times is probably due to the time delay caused by the heat exchange between the cold fluid and hot fluid in the reactor.

Peak temperature and peak time are plotted against the concentration of the reactants (see **Figure 11**). It is obvious that with the increase of the reactant concentration, the peak temperature increases gradually. When the concentration of the reactants reaches 5 mol/L, the peak temperature can reach more than  $7^\circ\text{C}$ . When the concentration of the reactants reaches 6 mol/L, although the peak temperature still increases, the upward trend slows down. With the increase of the reactant concentration, the time to reach the peak temperature gradually decreases. When the concentration of the reactants reaches 5 mol/L, the downward trend of the peak time slows down, indicating that once the concentration of the reactants is greater than 5 mol/L, the heat generation rate becomes similar.

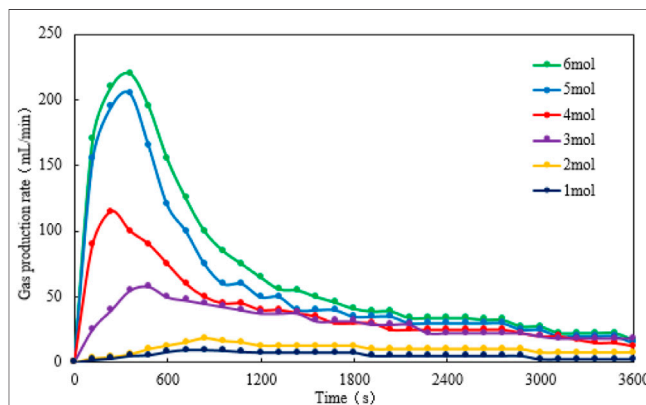
Gas production of per mole reactant and gas production efficiency are plotted against the concentration of the reactants

**TABLE 4** | Experimental data for scenario 3

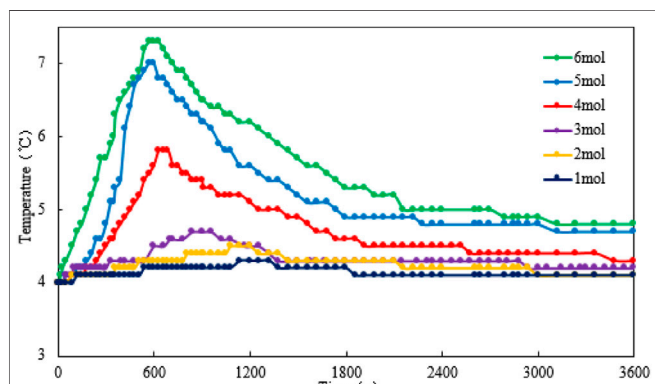
Reactant concentrations (mol/L)	Peak temperature (°C)	Cumulative gas production (ml)	Time of reaching the peak temperature (s)	Peak gas production rate (ml/min)	Time of reaching the peak gas production rate (s)
1	4.3	104	1,160	9.5	720
2	4.5	495	1,100	18	840
3	4.7	1,008	950	58	480
4	5.3	2055	600	115	280
5	7	3,540	500	205	400
6	7.3	3,760	490	220	360



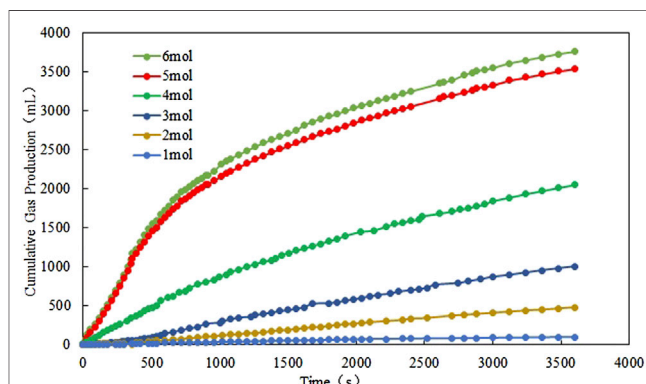
**FIGURE 7** | Cumulative gas production vs. time at different HCl concentrations.



**FIGURE 9** | Gas production rate vs. time at different reactant concentrations.



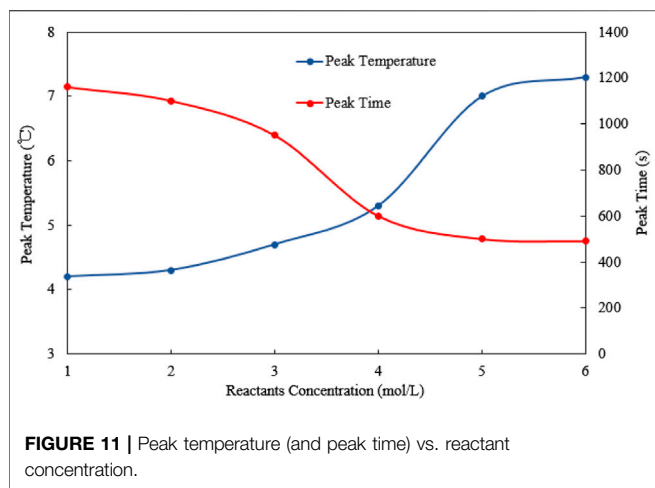
**FIGURE 8** | Temperature vs. time at different reactant concentrations.



**FIGURE 10** | Cumulative gas production vs. time at different reactant concentrations.

in **Figure 12**. Here, the gas production efficiency is defined as the ratio of the actual gas production volume to the theoretical gas production volume wherein the theoretical gas production volume is the gas volume obtained when all reactants are converted into products based on the principle of material conservation (Wang et al., 2020). It was implied that the gas production efficiency increases when the reactant concentration increases from 1 mol/L to 5 mol/L, whereas when the concentration of the reactants

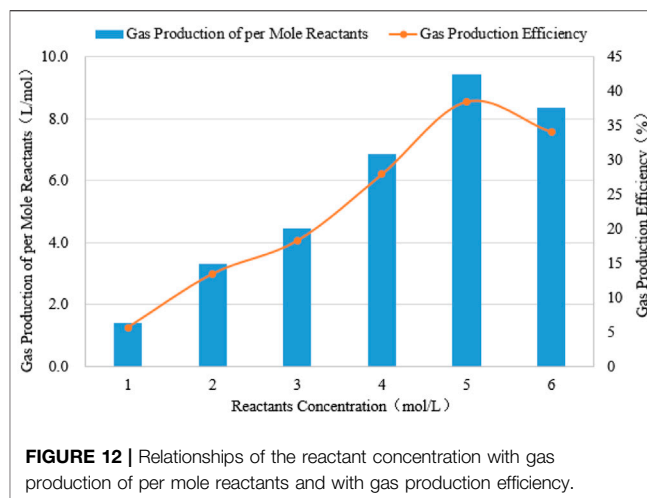
further increases, it exerts a negative effect on the gas production efficiency, as shown in **Figure 12**. The highest incremental gas production efficiency can be obtained when 5 mol/L reactants are used. Whereas further increasing the concentration of the reactants, will reduce the incremental gas production efficiency, and the gas production of reactants per mole also decreases, which could be due to the occurrence of side



reactions under high concentration conditions. In conclusion, 5 mol/L is the concentration of the optimum reactants.

## 4 DISCUSSION

Hydrate-based technologies are all built on the simple rationale that hydrate formation and dissociation can induce a reversible phase change in water through pressure and temperature manipulations (Dong et al., 2021). The thermochemical reaction system of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  has good heat generation and gas production performance. Theoretically, the reaction of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  can release 333 kJ heat per mole (Wang et al., 2020). In this study, when the volume of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  solution is 75 ml, respectively, and the concentration of these two reactants is 5 mol/L, hence the amount of  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  is 0.375 mol, respectively. Assuming that the reactants can react completely, they will release 125 kJ heat and produce 8,400 ml  $\text{N}_2$ . The experimental results show that 0.375 mol  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  produce 3,540 ml  $\text{N}_2$  within 1 h at 4°C and 14 wt% catalyst concentrations. This calculation suggests that the reaction degree of the thermochemical reaction system with the optimal formula is 42%, and the actual heat released by the reaction is 52.56 kJ. The decomposition latent heat of NGHs is 52.0–54.5 kJ/mol (Rydzynski et al., 2007). Therefore, the heat released by 0.375 mol  $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$  can decompose 0.96–1.01 mol NGHs at the low temperature of 4°C. From the perspective of thermal decomposition, the thermochemical reaction system in this study is feasible in exploiting the of NGH reservoir. Moreover, a novel concept of injecting air or gaseous  $\text{N}_2$  into NGHs has been proposed recently (Panter et al., 2011; Wang et al., 2015; Zhang et al., 2017b; Okwananke et al., 2018). As  $\text{N}_2$  is injected at the gaseous state, it can readily be dispersed in plugged pipelines or NGH-saturated layers with high permeability. Haneda et al. observed that the NGHs dissociated in the sediment were closely examined for the gas production from the NGHs by continuously injecting the  $\text{N}_2$  gas (Haneda et al., 2009). Panter et al. also investigated the NGH dissociation behavior inside a blocked pipeline during  $\text{N}_2$  gas injection and they found that the continuous injection of gaseous  $\text{N}_2$  as a thermodynamic inhibitor into structure I/structure II hydrates resulted in NGH crush through



channel formation, unlike the radial dissociation observed in the depressurization method (Panter et al., 2011). The experimental results indicated the synthesis effects of  $\text{N}_2$  as both an inhibitor to dissociate the NGHs and an external medium to replace the  $\text{CH}_4$  molecules in the NGH cages (Mok et al., 2021). The above discussion, thus, shows that the thermochemical reaction system in this study is also feasible in the exploitation of the NGHs from the perspective of nitrogen inhibition and replacement. Further studies are therefore needed to determine the NGHs' recovery efficiency of the optimal formulation system by experiments based on the mass-transfer theory of hydrate formation and decomposition (Liang et al., 2022).

## 5 CONCLUSION

This study investigated the heat generation and gas production performance of the thermochemical reaction system ( $\text{NaNO}_2$  and  $\text{NH}_4\text{Cl}$ ) under a low temperature condition (4°C) of real marine NGH reservoirs. It was found that the thermochemical reaction system can react at low temperature with the presence of acid as the catalyst, and it can release heat and produce nitrogen. By comparing the reaction rates of three acid catalysts, the results indicated that HCl was the best acid catalyst for the thermochemical reaction system in this study. In addition, with the increase of HCl concentration, the produced heat and gas by the thermochemical reaction system increased. However, when the catalyst concentration exceeded 14 wt%, a reddish-brown irritant gas was produced during the experiment at the experimental temperature of 4°C; hence 14 wt% HCl was the optimal concentration for the thermochemical reaction at 4°C in this study in considering the application security. The impacts of reactant concentrations were also analyzed by this study. An increase in the reactant concentration could assist the gas production efficiency from 6 to 42%, after which it had a negative effect on the gas production efficiency. In conclusion, an optimal formula of the thermochemical reaction system was 5 mol/L  $\text{NaNO}_2$  or  $\text{NH}_4\text{Cl}$  as reactants and 14 wt% HCl as the catalyst.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/supplementary material; further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

YW and ZS conceived the study; YW, ZS, QL, XL, and YG contributed to methodology; ZS, QL, XL, and YG carried out the investigation; YW, ZS, QL, XL, and YG were responsible for validation; YW, ZS, QL, XL, and YG wrote the original draft; YW,

ZS, QL, XL, and YG reviewed and edited the draft; YW, ZS, QL, XL, and YG were responsible for visualization; QL contributed to project administration; QL, XL, and YG helped with the funding acquisition. All authors have read and agreed to the published version of the manuscript.

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