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Synthesis and application of a novel combined kinetic hydrate inhibitor

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In oil and gas exploration and transportation, low dosage hydrate inhibitors (LDHIs) are more favorably utilized to inhibit the formation of hydrates than thermodynamic inhibitors (THs) as a trend. However, there are no industrial products of LDHIs available domestically, and the corresponding application experience is in urgent need. In this paper, a combined hydrate inhibitor (HY-1) was synthesized after a series of reaction condition optimization, and its performance on THF hydrate inhibition was investigated using kinetic hydrate inhibitor evaluation apparatus with 6 cells bathing in air. The results show that when the reaction temperature is 60°C, the reaction time is 6 h, and the monomer: solvent ratio is 1:2, the product has the best kinetic hydrate inhibitor performance on THF hydrate. On these bases, the scale-up production of this combined hydrate inhibitor was carried out. Although the scale-up product (HY-10) performs less effectively on the THF hydrate inhibition than HY-1, it functions better than a commercial product (Inhibex501) during in-house tests. HY-10 was successfully applied to the gas production process. Field trials in northern Shaanxi PetroChina Changqing Oilfield Company (PCOC) show that 2 wt% of HY-10 is effective on natural gas hydrate inhibition. It is found through economic analysis that the use of HY-10 has obvious economical advantage over methanol and Inhibex501.

natural gas hydrate, combined hydrate inhibitor, kinetic hydrate inhibitors, natural gas production

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1 Introduction

The gas molecules and the water molecules can interact with each other to form ice-like crystalline solid hydrate at a certain temperature and pressure in oil and gas production, transport and processing [1]. The pipeline and gathering production equipment can be blocked by hydrate, which are detrimental to the natural gas and oil exploitation, gathering and processing, resulting in huge economic losses. For instance, the Jiannan natural gas field was plugged by hydrate 133 times from 1997 to 2007 [2]. How to prevent hydrate formation in the oil and gas production and transport process is a problem that the oil and gas industry needs to solve [3].

Four main methods have been investigated to combat hydrate blockage and ensure smooth flow: chemical method, thermal method, depressurization method and method of removing the water. The main purpose of these methods is to prevent hydrate formation conditions. The chemical method, which is the most widely used method, involves the injection of chemical additives in pipes that act differently on hydrate thermodynamic property, kinetic formation or agglomeration. The thermal method consists of delivery of

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heat flow to the plugged area in order to raise the system temperature above hydrate formation point, which may lead to pipe burst, even hydrate eruption, and it is unsuitable for subsea equipment. The depressurization method is impractical for normal operation since the operational pressure requirement is too high for transportation system. The method of depressurization and thermal method were utilized in hydrate exploitation recently [4, 5]. The method of removing the water, using the methods of separation and dehydration was expensive. It is difficult to prevent hydrate nuclei or free water absorbing on the rough pipe wall. Otherwise, the hydrate still can grow in the liquid hydrocarbon phase even the water molecules are rarely present. It is well acknowledged that the chemical method is the simplest, most economical, and most effective among the above-mentioned methods [6].

The chemical additives for hydrate inhibition mainly contain thermodynamic inhibitors (THs) and low dosage hydrate inhibitors (LDHIs). THs generally used are methanol or glycols, or aqueous electrolyte solutions, which are injected into the oil or natural gas pipeline to shift the equilibrium temperature for hydrate formation. However, this method is limited by the large amount (10 wt%−60 wt%) of the above-mentioned additives implemented in the field. Therefore, the cost of prevention of hydrate formation is high [1]. Besides, the toxicity of THs is large, and the hazard for the environment is severe. LDHIs primarily include kinetic hydrate inhibitors (KHIs) and anti-agglomerants (AAs). Among them, KHIs are water-soluble polymers, which function mainly as anti-nucleators, as well as hydrate crystal growth inhibitors. KHIs delay hydrate nucleation time and extend hydrate growth time, thus inhibiting hydrate formation. In addition, it does not affect the thermodynamic conditions of hydrate formation in process of hydrate inhibition [7]. The research and application of KHIs are the hot spots in LDHIs area.

From the 1990s onwards, LDHIs have replaced a diverse range of THs abroad. Various kinds of KHIs have been developed, such as poly(vinylpyrrolidone) (PVP) [8, 9] and polyvinylcaprolactan (PVCap) [10, 11], which represent the inhibitors of low dosage, high efficiency and low cost. Moreover, antifreeze proteins [12, 13] and ionic liquids [14 16] etc. as hydrate inhibitors provide a guideline for the development of new green KHIs recently. There are varieties of KHIs utilized in the Gulf of Mexico, the Middle East for nearly a decade [17–20]. However, due to high cost for importing KHIs, there is few application in China, and the current technique to inhibit hydrate formation is still to inject alcohols such as methanol and ethylene glycol into pipelines. To satisfy the deep-sea oil and gas field development for hydrate blockage prevention, novel combined kinetic hydrate inhibitor HY series whose main component is PVP and the synergistic component is glycol ether was developed in this work. The inhibitory performance of HYs was investigated using hydrate inhibitor evaluation apparatus. The laboratory evaluation results show that the combined kinetic hydrate inhibitor has good inhibitory performance. To verify the results of laboratory evaluation, complete on-site filling process, and monitor the effect of measures of stopping pipeline plugging, the second gas production well of northern Shaanxi PetroChina Changqing Oilfield Company (PCOC) was selected for on-site application, and good results were achieved.

2 Experimental

2.1 Experimental materials

Tetrahydrofuran (THF, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China); distilled water (produced in our laboratory); glycol ether (industrial product, Tianjin Kermel Chemical Reagent Co., Ltd, Tianjin, China); N-vinyl-2-pyrrolidone, (NVP, industrial product, Henan Boai corporation, Henan, China); isobutyronitrile (industrial product, Tianjin Kebo Chemical Reagent Co., Ltd. Tianjin, China); Inhibex501 (ISP, International Specialty Products Inc., USA).

2.2 Experimental apparatus

The inhibitory performance of KHIs on THF hydrate was evaluated in kinetic hydrate inhibitor evaluation apparatus of 6 cells [21] shown in Figure 1. The apparatus consisted of 6 identical magnetic-stirred steel cells and the refrigeration vessel (Xutemp Temptech Co., Ltd. Hangzhou, China). The volume of the steel cell was 100 mL. The temperature in the cells was measured by the thermocouples (type J) with an accuracy of ±0.1°C. High-pressure nitrogen and vacuum pump were used to convey solutions. The experimental data were recorded by the data acquisition instrument.

2.3 Experimental process

2.3.1 Synthetic experiments

HYs were synthesized in glycol ether using NVP in a slightly positive pressure; the reaction was under nitrogen atmosphere without oxygen and water. The reagents were mixed evenly at 60°C during the reaction time (about 6 h); then stop heating, let the solution cool, and inhibitor samples were then synthesized.

2.3.2 Performance experiments

19 wt%THF solution (phase equilibrium point is 4.4°C at 1 atm) and THF solutions with additives were prepared first. The temperature of vessel was risen to 30°C and kept for 120 min later. Finally, vessel was cooled to the desired temperature continuously or with a stepping method. The temperatures of the solutions were collected by the data acquisition instrument during cooling.

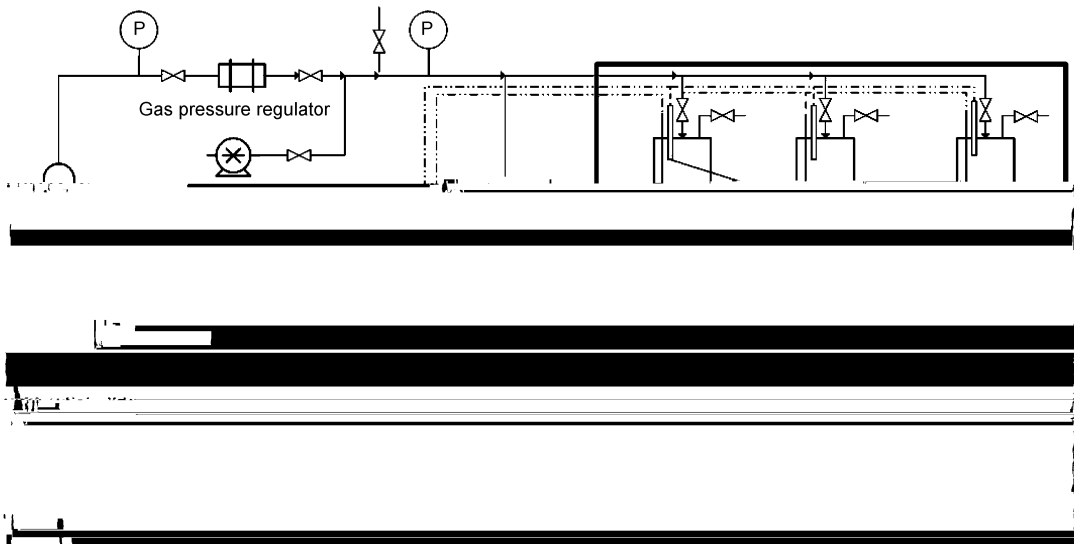

Figure 1 Kinetic hydrate inhibitor evaluation apparatus of 6 cells.

3 Results and discussion

3.1 Synthesis optimization and KHI performance testing

3.1.1 Synthesis and KHI performance testing of small-scale sample

In the laboratory synthesis of HYs, the main reaction factors investigated were polymerization temperature, ratio of monomer to solvent, reaction time, and the amount of initiator.

Polymerization temperature would affect the reaction rate and the molecular weight of PVP. In the beginning of the reaction, certain temperature had to be maintained in order to initiate the reaction. During the polymerization process, the polymerization temperature was required to keep constant (60°C). When the polymerization reaction took place, it generated a great deal of heat. If the heat was not properly abstracted, it could easily lead to flash polymerization, which was destructive for scale-up synthesis.

In the small-scale solution polymerization, the higher the content of NVP monomer, the more conducive to the growth of chain reaction and the greater the molecular weight of PVP. However, if NVP concentration was high, the generated PVP concentration in the reaction system would be high too, which would result in high viscosity in the reaction system and it was not easy to transfer the heat

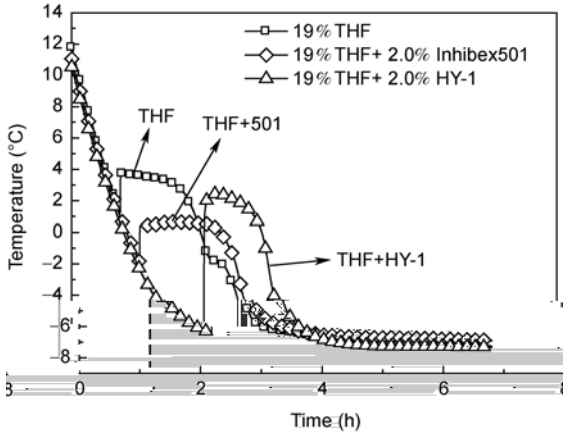

Figure 2 Performance of 2.0% HY-1 and Inhibex501 on THF hydrate.

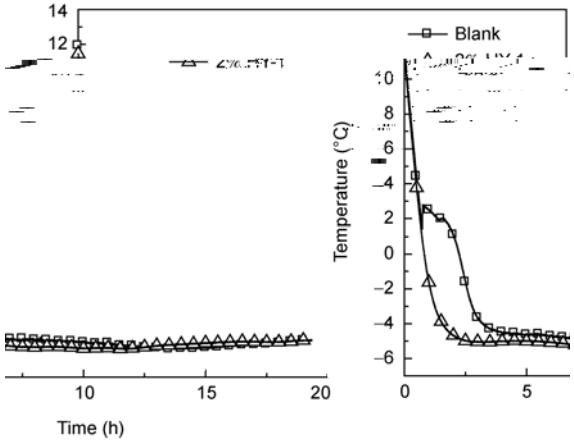

Figure 3 Performance of 2.0% HY-1 on THF hydrate at −5°C.

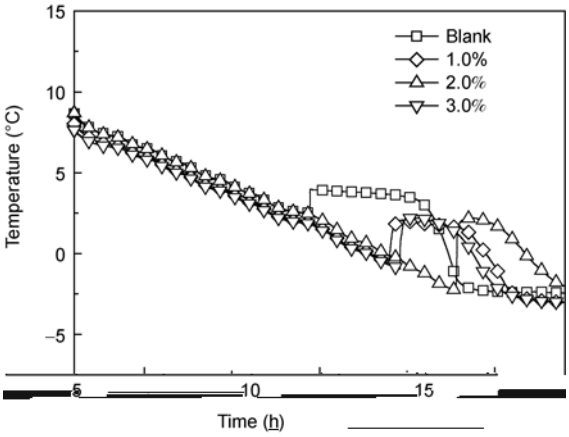

Figure 4 Performance of HY-10 on THF hydrate with different concentrations.

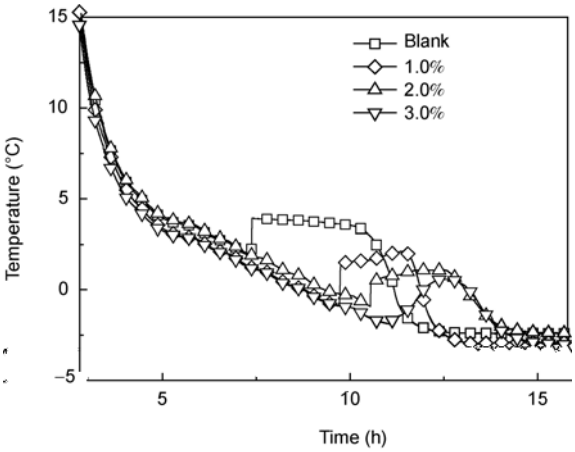

Figure 5 Performance of Inhibex501 on THF hydrate with different concentrations.

speed, similar experiments reaction conditions in accord with small-scale sample (HY-1) were eventually obtained.

Figures 4 and 5 show the evaluation results of HY-10 (prepared in scale-up synthesis) and inhibex501. With a 2°C h^{-1} gradual cooling method, different concentrations of HY-10 and inhibex501 were compared with their attainable subcooling and inhibition time. When the concentration of Inhibex501 was 3 wt%, and the concentration of HY-10 was 2 wt%, they had the best inhibitory effect. Both of them can inhibit THF hydrate formation for 7 h. However, compared with the HY-1, HY-10 inhibitory effect was weakened to some extent. This may be attributed to the amplification of polymerization reaction. As the polymer molecular weight and molecular weight distribution are different between laboratory small-scale sample and the scale-up product, HY-10' KHI performance was evidently affected [23, 24].

3.2 Application of KHIs in gas production field

3.2.1 Introduction of gas production site

The field test pipeline was located in northern Shaanxi PCOC gas field. The gas field consists of large contiguous composite gas area, which is characterized by deep burying, low permeability, low abundance, and low yielding. Moreover, the site environment is severe, especially in winter. The test pipeline has been put into operation since October 2003, and the gas production process is as follows: high-pressure natural gas is exploited and heated through the wellhead, and then is transported to gas gathering station through pipeline; after those procedures, the gas is dehydrated and then purified before transportation to gas plant. The field produces natural gas of 2×10^4 m^3 d^{-1}, as well as 0.5–1 m^3 d^{-1} water. The initial temperature of the gas is about 10°C and the initial pressure of the gas is about 10 MPa. The parameters of the ground gas pipeline are Ø76 mm × 7 mm × 3.6 km specifically, and the wellhead pipeline specifications are Ø27 mm × 5 mm × 3.6 km. These pipelines are not insulated because of the undulating terrain. The composition analysis results of the natural gas are shown in Table 1. The main components are methane and ethane, which are easy to form the structure II of gas hydrates. The natural gas contains 1.73% CO_2, resulting in

Table 1 Components of pipeline natural gas

Component	CO_2	N_2	C1	C2	C3	iC4
Mole percentage (%)	1.73421	0.31257	93.84406	3.22203	0.45726	0.07859
Component	nC4	iC5	nC5	C6	C7	C8
Mole percentage(%)	0.08019	0.05704	0.02976	0.07997	0.0504	0.02894
Component	C9	C10	C11	C12	C13	C14
Mole percentage(%)	0.0142	0.00565	0.0017	0.001	0.0005	0.0003
Component	C15	C16	C17			
Mole percentage(%)	0.00011	0.00004	0.00003			

hydrate phase equilibrium curves moving to low pressure and high temperature region [25].

The equilibrium temperature for hydrate formation is 15°C at 10 MPa. This enables easy formation of hydrates in this well. Especially in winter, it is prone to have hydrate plug. Each time after hydrate blockage, anti-plugging measures such as venting have to be taken. In order to prevent the plugging and ensure safe production, multi-well high-pressure alcohol injection technology is applied to control the formation of hydrate in pipeline currently. The amount of methanol injected into pipeline is 400 L d^{-1} during the trial period.

3.2.2 Field application conditions and results

Table 3 Injection conditions and results

Test time	Injection ratio (%)			Flow (L h^{-1})	Pipeline situation
	HY-10	Methanol	Water		
21:30 of March 15–14:50 of March 16	6	18	76	30	normal
14:50 of March 16–18:00 of March 16	stop injection	stop injection	stop injection	0	normal
18:00 of March 16–02:00 of March 17	5	15	80	20	normal
02:00 of March 17–11:00 of March 17	3	6	91	20	normal
11:00 of March 17–12:30 of March 18		100		30	normal
12:30 of March 18–22:30 of March 18	2		98	9.2	normal
22:30 of March 18–02:40 of March 19	2		98	16	normal
02:40 of March 19–10:30 of March 20		100		20	normal
10:30 of March 20–20:00 of March 20	3	6	91	9.6	normal
20:00 of March 20–01:00 of March 21	3	6	91	20	normal
01:00 of March 21–18:30 of March 21		100		20	normal
18:30 of March 21–13:00 of March 22	3		97	9.6	normal

generally injected in the day time, and in night time the low volume was 16 L h^{-1}. No hydrate plugs occurred during this period. The repeated test for the next 5 days verified the inhibitory effect of HY-10 by inhibitor application experiment. It was found that 2% HY-10 of the water content could inhibit gas hydrate formation. Compared with the injection amount of methanol, injection amount of HY-10 has been largely reduced. The reason for this is that methanol functions as hydrate inhibitor because of the attractive nature of methanol oxygen atoms for neighboring water molecules. Under high water cut condition, the amount of methanol added to the pipeline to inhibit hydrate formation is large [1]. While KHIs work due to polymer molecules' interaction with the hydrate cages to inhibit hydrate nucleation and growth. Even if the polymer concentration is low, it can play a very good inhibition function [7].

According to the field experiments, when KHIs such as HY-10 are injected into the pipeline, the following should be noted:

(1) The amount of KHIs should be 1 wt% –5 wt% based on the amount of water, preferably with a small amount of ethylene glycol or triethylene glycol instead of water during the injection;

(2) If THs are used before KHIs, THs cannot be directly replaced by KHIs in the beginning. KHIs should be used in conjunction with alcohol. The alcohol amount will be slowly decreased to the desired concentration;

(3) Ensure that KHIs can be evenly distributed in the pipeline;

(4) When the subcooling exceeds 10°C or mutation of temperature or pressure occurs, certain amount of THs has to be used.

3.3 Economic analysis of KHIs

Both the effectiveness and the cost should be considered in the development of the inhibitors. HY-10 inhibitory effect has passed laboratory evaluation and field experiments described above. As for its economic analysis, the results are shown in Table 4.

As can be seen from Table 4, HY-10 and Inhibex501 compared with methanol can save the cost more than 22.5% under the same conditions and HY-10 is even less than Inhibex501. Compared to the cost of methanol including its transport and storage, using the kinetic hydrate inhibitor HY-10 has more cost advantage than using methanol. Moreover, if the sewage collection and treatment with methanol's utilization are taken into account, using KHIs has obvious economical advantage.

4 Conclusion

The reaction conditions of a novel combined kinetic hydrate inhibitor were determined through a series of lab experiments and sample KHI performance tests. The synthetic sample HY-1, which was obtained at 60°C for 6 h, with monomer : solvent at 1∶2 and initiator dosage of 1%, could inhibit hydrate formation longer than 18 h at –5°C. On the basis of lab experiments, the scale-up product HY-10 was

Table 4 Economic analysis for different inhibitors

Inhibitor	Unit price (RMB/kg)	Inhibitor amount (%)	Cost (RMB/ton water)	Other costs
Methanol	3	15–20	450–600	sewage collection and treatment
Inhibex501	160	0.5	800	none
HY-10	30	1–2	300–600	none

Note: The above prices are calculated according to industrial standard of China

obtained. HY-10 could inhibit the formation of THF hydrate for 7 h at −2°C. Its performance is similar to Inhibex501.

From the laboratory evaluation, the natural gas production field trials confirmed the performance of HY-10, which has a good inhibitory effect for low condensate natural gas. HY-10 can effectively prevent pipelines plugs or blockages in PCOC gas field. The test conditions of the gas field are as follows: gas pressure about 15 MPa, air temperature −6–5°C, gas temperature around 10°C, along with the production of 1 m^3 d^{-1}