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# Natural gas hydrate formation and inhibition in gas/crude oil/aqueous systems

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ABSTRACT

Gas hydrate formation in multi phase mixtures containing an aqueous phase (with dissolved salts), reservoir fluid (crude oil) and natural gas phase was investigated by using a standard rocking cell (RC-5) apparatus. The hydrate formation temperature was reduced in the presence of crude oils in comparison with that in pure water. This observed hydrate inhibition potential shows significant variation depending on the type of crude oil. The influence of crude oil composition (saturates, aromatics, resins and asphaltenes) on this behavior was probably due to the existence of a combination of different inhibition mechanisms and potentially a competition among inhibition–promotion mechanisms. Moreover, the hydrate formation time has been determined at different water cuts in each crude oil and it was found that the inhibition capability increases with an increase in the oil content. The effect of the biodegradable commercial kinetic inhibitor (Luvicap-Bio) on natural gas hydrate formation with and without crude oil (30%) was investigated. The strength of kinetic inhibitor was not affected by salts, but decreased significantly in the presence of crude oil. Data for hydrate formation at practical conditions can contribute to the safe operation of sub sea pipelines in the oil and gas industry.



## 1. Introduction

Gas hydrates are ice-like crystalline formations which entrap gas molecules in water molecule skeletons under appropriate pressure/temperature conditions [1–3]. Gas hydrate formation in oil and gas transport pipelines is one of the most challenging issues in the modern oil industry [4,5]. Hydrate formation will significantly reduce production and increase the risk of accident with potentially tremendous environmental impact [6–8]. Hydrate management traditionally consists of costly pipeline insulation, pressure reduction, steam injection or use of chemicals such as the thermodynamic inhibitors methanol and glycols, which work by shifting the pressure/temperature equilibrium of the system to lower temperatures [2,5]. Several new techniques are under development in order to replace or improve conventional methods (methanol injection, temperature increase) for hydrates – plugging prevention. Several chemical and biologic kinetic inhibitors have been developed and investigated as alternative solutions to these traditional thermodynamic inhibitors [9–24]. Some compounds naturally found in sea water and reservoir fluids also act as inhibitors [25,26]. Such compounds may influence the required amounts of added inhibitor and their effect should thus be considered when optimizing hydrate management [27]. The behavior of natural gas–aqueous–crude oil systems are complex and is not completely understood due to the fact that it is affected by many factors such as gas–crude oil compositions (heavy hydrate formers, asphaltenes–resins, phenols, wax, naphthenic acids), physicochemical properties of the hydrocarbon phase (viscosity, solubility of the individual oil fractions), properties of the aqueous phase (pH, salinity) and other parameters which are not fully identified. In literature, there are conflicting conclusions concerning the influence of crude oil on hydrate formation. This is likely due to the unique nature of certain components in each crude oil and the presence of many parameters (identified or not) which are able to modify subcomponents solubility and affect hydrate promotion or inhibition [21,25,28–30]. Water cuts from older oil and gas wells tend to be higher, and since the amount of hydrate inhibitor is proportional to the volume of water, inhibitor costs increase. Moreover, there is evidence that high water cut systems behave differently compared to low water cut systems [31,32]. Despite the complexity of these systems, it is crucial to identify the factors which affect them and govern hydrates formation and inhibition.

The aim of the current study is to simulate practical conditions inside oil and gas pipelines in a rocking cell apparatus (RC-5 by PSL Systemtechnik) and investigate hydrate formation with various

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crude oils and natural gas. The main advantage of rocking cell devices is that they are able to simulate flow conditions in pipelines. Similar RC setups are increasingly being used in different hydrate research labs, a standardization which enables better comparison of data from different research groups. Three crude oils from different oil fields were tested at 80%, 70% and 60% water cuts. The effect of commercial biodegradable kinetic inhibitor Luvicap-Bio on natural gas hydrate formation in the presence of dissolved salts and crude oil was investigated. The results obtained here show the complexity of natural gas–aqueous–crude oil systems while highlighting certain interesting features which require further scientific investigation and open new horizons for hydrate inhibition research

## 2. Experimental section

### 2.1. Materials

The natural gas mixture (Table 1) used in the present work was supplied by Air Liquide. Deionized water was used to perform the experiments. A model sea water was prepared with 5 wt% NaCl (>99.5% purity) supplied from Merck. Hydrate inhibitor tested in this work is Luvicap Bio from BASF. Luvicap Bio is a commercial formulation based on the polymer PVCap which has a higher degree of biodegradability than the pure polymer. Three different crude oils, crude-G (0.8771 g/cc) from Germany, crude-D (0.8469 g/cc) from Denmark and crude-M (0.8515 g/cc) from the Middle East were used as reservoir fluids.

### 2.2. Apparatus and procedure

A rocking cell (RC-5; has 5 test cells, PSL Systemtechnik, Germany) was used to test the natural gas hydrate formation at different practical conditions. Each test cell has a volume of 40.13 $cm^3$ and is capable of operating up to 200 bar working pressure. A stainless steel ball (Dia: 17 mm) is placed inside and rolls back and forth along the length of the cell to induce the mixing inside the cell. The mixing in the cells was controlled by rocking the cells back and forth between an angle of −45° and + 45°. The most important advantage of this experimental system is that it is programmable through WinRC software in order to perform complicated experimental procedures, such as automatic isothermal or ramping tests with modifications of temperature, rocking rate,-angle, and frequency. Pressure is the only parameter which is regulated manually. The fact that the RC-5 is able to execute serially saved commands gives the ability to repeat experimental procedures with high accuracy. Moreover, since the RC-5 has five cells, required run time is significantly reduced, since five different experiments can be performed simultaneously. Once all the cells are loaded with the experimental solution, they are placed in a cooling bath controlled by an external refrigerator, which can be operated between −20 °C and +60 °C. The pressure and temperature of the cells are monitored by the data acquisition system throughout the experiment. Generally two main types of experimental tests were carried out in this investigation: (a) Ramping tests: Temperature is decreased from 25 to 1 °C or increased from 1 to 25 °C at the rate of 0.1 °C/min. (b) Isothermal tests: temperature is decreased from 25 °C to the temperature of interest and maintained at this temperature for about 10 h. The details of the experimental setup and procedures have been described elsewhere [33].

**Table 1**
Natural gas composition.

| Natural gas compounds | Molar composition (%) |
|---|---|
| Oxygen | 0.24 |
| Nitrogen | 3.68 |
| Methane | 87.81 |
| Ethane | 6.6 |
| Propane | 1.22 |
| n-Butane | 0.17 |
| i-Butane | 0.22 |
| n-Pentane | 0.02 |
| i-Pentane | 0.03 |
| n-hexane | 0.01 |

## 3. Results and discussion

A rocking cell apparatus was used to evaluate the effect of reservoir fluids on natural gas hydrate formation, tests which can provide important information about hydrate formation temperatures. The formation temperatures are identified as a sudden pressure drop owing to the gas consumption due to hydrate formation (Fig. 1). The idea behind these tests is that once the pressure reaches experimental pressure (100 bar) inside the cells, the temperature is decreased and increased in a cycle (from 25 °C to 1 °C) in order to identify the hydrate formation temperature on the cooling cycle and the dissociation temperature on the heating cycle. Hydrate formation is identified as a deviation from the normal pressure trend line (gas thermal contraction).

A heptane-containing system was examined in order to investigate the influence of light paraffins on hydrate formation. A mixture of heptane (50% v/v) and toluene (50% v/v) was tested to compare the influence of the aromatic rings (polar) and paraffins (non-polar) on hydrate formation. It was found that these components cannot always be used as model components to provide a rule of thumb indication for the influence of crude oils paraffin and aromatic fractions, since actual crude oils are too complex and variable [26]. Three different crude oils were used in order to simulate practical conditions in oil and gas pipelines. The effect of heptane (light paraffin), heptane/toluene (paraffin-aromatic components) and three different reservoir fluids (crude D, crude G and crude M) on natural gas hydrate formation was investigated and the results are summarized in Fig. 1. The hydrate formation temperature in the presence of distilled water (control) was observed at 15.7 °C. This result is in good agreement with our previous studies [27].The presence of a hydrocarbon layer reduces the hydrate formation temperature (Fig. 2). For example the formation

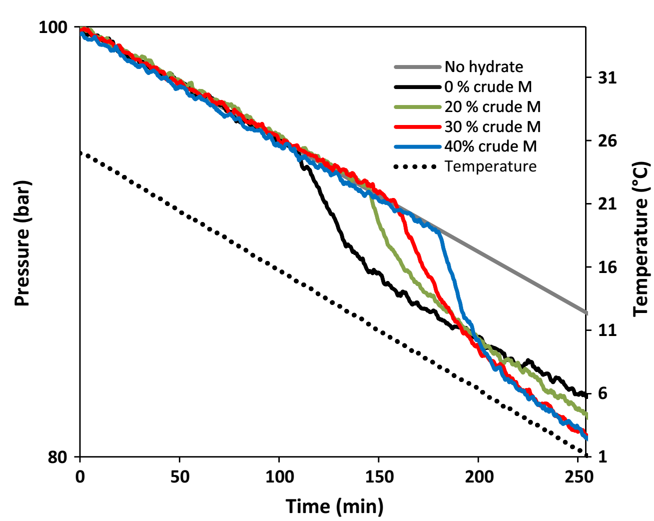


**Fig. 1.** Typical pressure and temperature change inside the rocking cell during temperature ramping test with different water cuts.