



# Experimental investigation of gas consumption for simple gas hydrate formation in a recirculation flow mini-loop apparatus in the presence of modified starch as a kinetic inhibitor

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## Abstract

The main objective of the present work is to investigate experimentally of simple gas hydrate formation with or without the presence of kinetic inhibitors such as modified starch in a recirculation flow mini-loop apparatus. For this purpose, a laboratory recirculation flow mini-loop apparatus was set up to measure the induction time for hydrate formation and gas consumption rate when a hydrate forming substance (such as  $C_1$ ,  $C_3$ ,  $CO_2$  and  $i-C_4$ ) is contacted with water in the absence or presence of dissolved inhibitor under suitable temperature and pressure conditions. In each experiment, a water blend saturated with pure gas is circulated up to a required pressure. Pressure is maintained at a constant value during experimental runs by means of the required gas make-up. The effect of pressure on gas consumption during hydrate formation is investigated with or without the presence of poly vinylpyrrolidone (PVP) and modified starch as kinetic inhibitors at various concentrations. Our results were shown that the modified starch can be applied as inhibitors in prevention of simple gas hydrate formation in mini-loop apparatus.

**Keywords:** simple gas, kinetic inhibitor, modified starch, gas consumption, mini-loop

## Research Highlights

- Measuring the induction time and gas consumption for simple hydrate forming substance such as  $C_1$ ,  $C_3$ ,  $CO_2$  and  $i-C_4$
- Using modified starch as KHI (new KHI)
- Experimental investigation is in recirculating flow mini-loop apparatus



## 1. Introduction

Gas hydrates are ice-like crystalline inclusion compounds that are formed at high pressure and low temperature conditions by the hydrogen bonding of water molecules, with the assistance of gases such as methane, ethane, or propane [1]. Since Hammerschmidt [2] reported the formation of hydrates in gas pipelines in 1934, the problem of hydrate blockage of flow channels has been of major importance to the energy industry. The oil and gas industry is expanding into deepwater and frozen areas for exploration and production of oil and gas. Thus the problem of hydrate blockages is becoming more of a challenge.

Major efforts are being put forth to use traditional thermodynamic hydrate inhibitors such as methanol, glycol or electrolyte. The effectiveness of these inhibitors is well known, but large concentrations are needed, which sometimes impacts project economics. Some additives such as methanol are harmful to the environment. Low dosage hydrate inhibitors (LDHIs) have been proposed as a new means of preventing hydrate blockage in flow channels. LDHIs include anti-agglomerants (AAs) and kinetic hydrate inhibitors (KHIs). AAs can be effective at high degrees of subcooling, but need a liquid hydrocarbon phase in order to work. KHIs began to be developed in early 90's [3-4]. Over the past few years, many KHIs have been proposed and patented. In conferences of the Society of Petroleum Engineers, applications of KHIs for natural gas hydrate have been introduced [5-9].

In this work, a high pressure laboratory recirculation flow mini-loop apparatus was set up to measure the rate of hydrate formation for a pure gas component (such as methane, propane, isobutene and carbon dioxide) with or without the presence of kinetic hydrate inhibitors. The kinetic inhibitors are PVP ( $M_w=10000$  gr/mole) and modified starch ( $M_w=150000$  gr/mole). To our knowledge, no research paper is available on gas hydrate formation in a flow mini-loop apparatus for efficiency of modified starch as a kinetic inhibitor.

### 1.1. Modified starch

Starch is a polysaccharide, a chain of many glucose molecules. It is the main carbohydrate store in roots and seeds. There are two types of glucose chains in starch. One is a simple chain called amylose, and the other is a complex branched form called amylopectin. Starches can be modified in several ways to change their function as additives in products. They can be cross-linked, where the chains get stuck together into a mesh. Starches can have hydrogen replaced by something else, such as a carboxymethyl group, making carboxymethyl starch. Starches can be esterified by modifications with an acid. An ester is the result of reacting an alcohol with an acid. The starch loses a hydroxyl group, and the acid loses hydrogen. These combine to form water as the other product of the reaction. Using acetic acid, starch acetates are formed, which are used as film-forming polymers for pharmaceutical products, and as the polymer in biodegradable packing foam "peanuts". Starch acetates have a lower tendency to create gels than unmodified starch. Acids can also break the long chains into shorter molecules; much like heat does, to form polydextrins, malto-dextrin, or dextrin. Enzymes are also used to do the same thing. Cross-linking occurs when a hydroxyl group (OH) on one chain bonds with a hydroxyl group on an adjacent chain. This toughens the starch, and helps it resist heat and acids. Cross-linking can be done by heating, or by reacting with compounds such as phosphates, or glycerol. Starches are also sometimes "pregelatinized" to make them easier to dissolve during product manufacture. Starches, especially modified starches, are also used as glues in cardboard manufacturing. Starches such as Gum Arabic and Gum Tragacanth are used as the glue for stamps and postal envelopes. Oxidized starch, usually oxidized with

sodium hypochlorite, is whiter than unmodified starch, has increased clarity, and a lower viscosity [10].

## 2. Experimental Apparatus

A laboratory flow mini-loop apparatus was set up to allow the study of simple gas hydrate formation with or without the presence of the kinetic inhibitors [11-12]. The flow line is made of 316 stainless steel schedule 80 pipe with an inner diameter of 10.6 mm and a pressure rating 10 MPa. The mini-loop layout, shown in Fig. 1 is 2 m wide by 4 m long (four 90-degree elbows) for a total length of 12 m. Water is injected to the loop by means of a piston pump (Pump 2) and flow is implemented with a Kracht screw pump (Pump 1) with variable rates up to 0.85 m<sup>3</sup>/hr. Temperature control of the flow loop is implemented using pump fed water (Pump 3) circulation through insulated 15 and 32 mm diameter PVC pipes those encompasses the loop. Cooling is achieved by circulating of ethylene glycol as a coolant prepared in a cooling system operated as a refrigerator. The current temperature range is 2 to 8 °C with a maximum continuous cooling rate about 100 °C/ hr. The loop is monitored by three temperature sensors (platinum resistance thermometers or PT-100, T1-T3), two pressure sensors (P1 and P2), one Endress-Hauser magnetic flowmeter (F) and one Rosemount pressure drop transmitter (DP1) arrayed around the flow mini-loop apparatus. Gas injection rate is monitored by the means of a Rosemount pressure drop transmitter and an orifice plate (DP2). The pressure of flow mini-loop maintained at a constant value during experimental runs by means of a regulator and gas make-up. All parameters and data are controlled and recorded every 60 s. The accuracy of the pressure and temperature measurements is estimated to be +/- 0.05 bar and +/- 0.1 K, respectively.

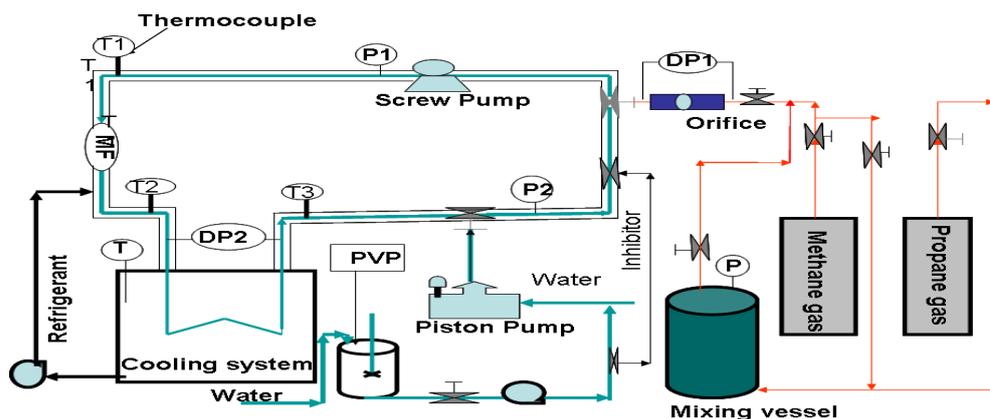


Figure (1) - Process flow diagram of a laboratory scale for recirculation flow mini-loop apparatus

The materials used for the experiments are fresh water as an aqueous phase, carbon dioxide, methane gas with 99.95% purity, propane gas with 99.9% purity, iso-butane gas with 99.99% purity as the hydrate former. In the experiments with presence of kinetic inhibitors, the inhibitor is typically (such as PVP or modified starch) injected into the loop as an aqueous solution to produce the desired weight percent concentration of inhibitor in the aqueous solution. In this setup, aqueous phase is saturated by the pure gas component (such as C1, C3, i-C4 and CO<sub>2</sub>) and is circulated through the flow loop. Saturation of the aqueous phase by the pure gas component is performed in a mixing tank. The fluid is circulated at a constant

velocity. The stream temperature is adjusted by a cooling system operated as a refrigerator and stream pressure is adjusted by the injection of the gas from storage tank. The loop and its pump lay in a controlled temperature water bath for controlling the temperature of the fluid circulating in the loop. The ethylene glycol from a bath is circulated through the external jacket of the pipe to ensure having uniform temperature. As the loop pressure changes or as hydrates form, the gas volume in the loop will change accordingly. Gas pressure drop is monitored while operating the system and abrupt change of the pressure drop in the loop is a measure for the pipe plugging by the hydrate crystals.

Investigation of hydrate formation in the flow loop was performed by considering the following conditions.

1. Operating temperature for methane, propane, carbon dioxide experiments is 4 °C and for iso-butane experiments is 2 °C.
2. Operating pressures for CO<sub>2</sub>, methane, propane and iso-butane are in the range of 7 – 10 MPa, 7-10 MPa, 1-4 MPa and 1-4 MPa, respectively.
3. Two types of the kinetic inhibitors such as PVP with 100 and 200 ppm and modified starch with 100, 200 and 2500 ppm concentrations are tested.

### 3.Results and Discussion

In this work, a high pressure laboratory flow mini-loop apparatus was set up. Then, the experiments were carried out for simple gas hydrate formation for components such as carbon dioxide, methane, propane and isobutene with or without presence of the kinetic inhibitors at various pressures (1 to 10 MPa) and specified temperature (275 - 277 K). In these experiments, the effect of the pressure on the hydrate formation condition with or without presence of the kinetic inhibitors was determined. A typical plot of pressure and temperature data in the loop for a test carried out by only distilled water during the CO<sub>2</sub> gas hydrate formation process is shown in Figure 2. The pressure keeps dropping in the figure during the reaction process until the pressure is below 5.0MPa but without an abrupt drop. The initial temperature drop in the figure represents the cooling of gas in the loop toward 4C, within 30mins, temperature begins to rise to 10.2 °C, and then drop again.

At about 140mins it keeps around 4C for a long time. Hydrates begin to form at the first temperature rising for reaction heat. Temperature curve is serrate in this condition, which maybe means gas hydrate forms step by step, so the formation time is only a few minutes at experimental condition. This hydrate formation in pure water provides a standard to the inhibitors test. The gas consumption for CO<sub>2</sub> during the gas hydrate formation at the nominal temperature of 277.15 K and operating pressure range of 7 to 10 MPa is shown in Fig. 3. According to this figure, by increasing the pressure of the system, the experimental rate of hydrate formation increase. Also, for example, the induction time for CO<sub>2</sub> during the hydrate

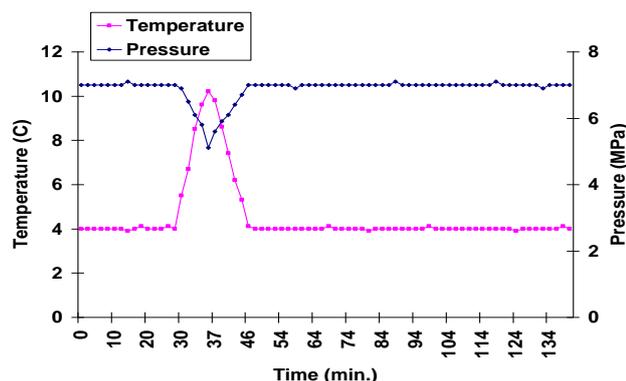


Fig. 2: Flow loop pressure and temperature for CO<sub>2</sub> during gas hydrate formation in a flow mini-loop apparatus

formation is displayed in Fig. (4). This figure shows that increasing the pressure of the system, the induction time of CO<sub>2</sub> during the hydrate formation decrease. Similarly, the results for methane hydrate formation at a nominal temperature of 277.15 K and operating pressure range of 7 to 10 MPa are shown in Fig. (5). The results show the experimental rate of hydrate formation increase, by increasing the pressure of the system. The time dependence of the experimental rate of propane hydrate formation at a nominal temperature of 277.15 K and operating pressures of 1, 2, 3 and 4 MPa is displayed in Fig (6). The comparison results between measured rates of propane hydrate formation at different pressures indicate that increasing the pressure of the system, the measured rate of propane hydrate formation increase. Fig. (7) shows the experimental rate for iso-butane during the hydrate formation at a nominal temperature of 275.15 K and operating pressures of 1, 2, 3 and 4 MPa. As can be seen in this figure, the experimental rate of gas hydrate formation increase, by increasing the pressure of the system.

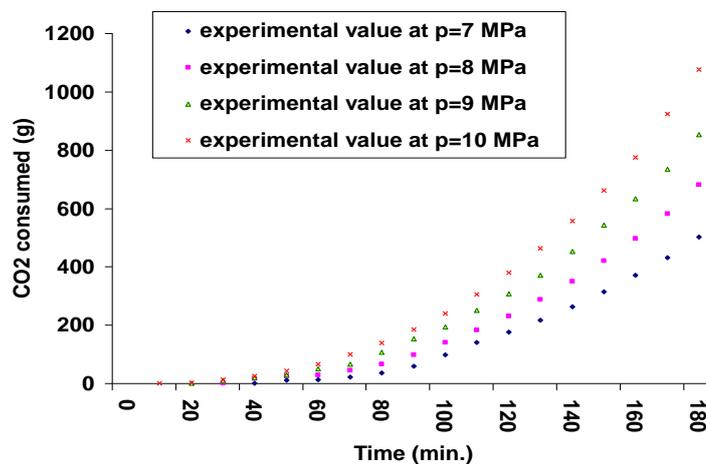


Fig. 3: Experimental curves for CO<sub>2</sub> consumed during gas hydrate formation at a temperature of 277.15 K in a circulation mini-loop apparatus

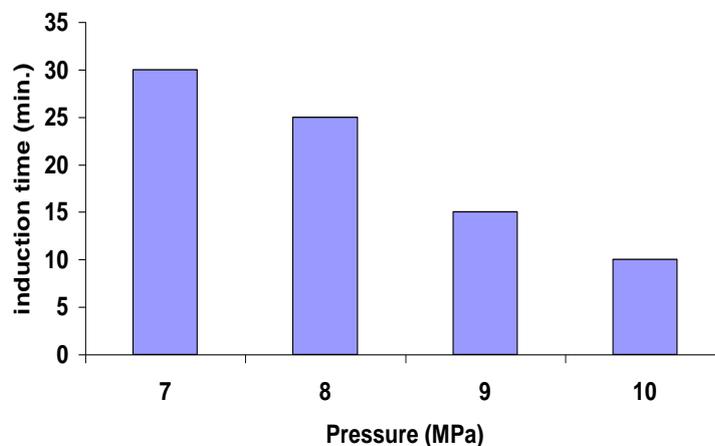


Fig.4 :Pressure dependence on the induction time during CO<sub>2</sub> gas hydrate formation at a temperature of 277.15 K in a flow mini-loop apparatus

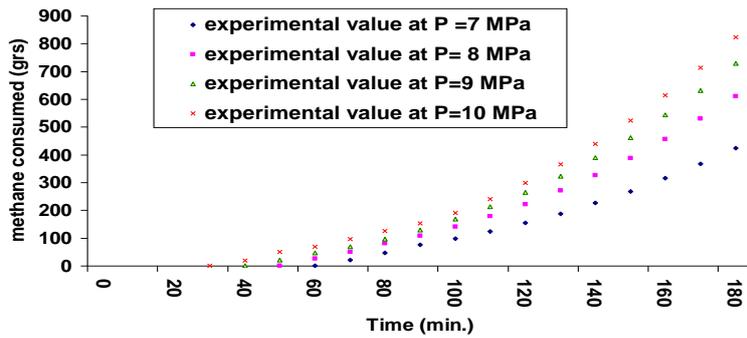


Fig. 5: Experimental curves for methane consumed during gas hydrate formation at a temperature of 277.15 K in a circulation mini-loop apparatus

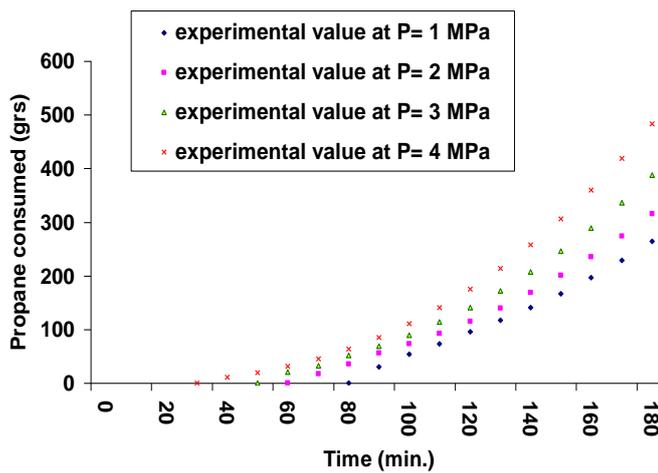


Fig. 6: Experimental curves for propane consumed during gas hydrate formation at a temperature of 277.15 K in a circulation mini-loop apparatus

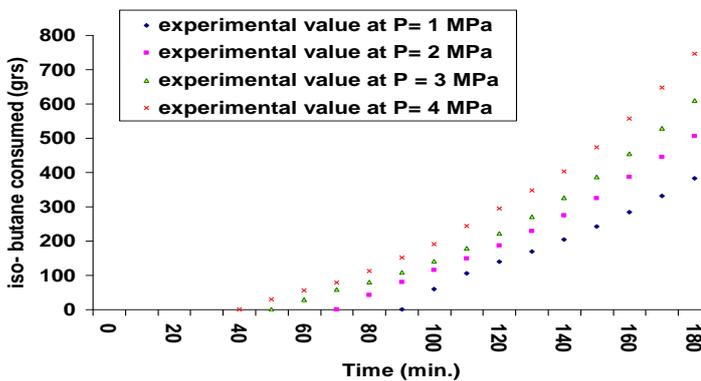


Fig. 7: Experimental curves for iso-butane consumed during gas hydrate formation at a temperature of 275.15 K in a circulation mini-loop apparatus

Finally, for measuring of the gas consumption rate during of gas hydrate formation in presence of the kinetic inhibitors in a flow mini-loop apparatus, the efficiency of two types of the kinetic additives such as PVP and modified starch is developed to avoid either nucleation or crystal growth of simple gas hydrates is tested based on the proposed experimental procedure. The time dependence of the experimental gas consumption during the gas hydrate formation in presence of PVP and modified starch at various temperatures, pressures and inhibitor



concentrations are shown in Figs. (8) to (15). The CO<sub>2</sub> hydrate formation experiments are run for pressures of 7, 8, 9 and 10 MPa. Typically, the comparison results between the experimental carbon dioxide consumed during the gas hydrate formation in presence of 100, 200 ppm PVP and 100, 200 and 2500 ppm modified starch at a temperature of 277.15 K and operating pressures of 7 and 9 MPa are shown in Figs. 8 and 9, respectively. The methane hydrate formation experiments are run for pressures of 7, 8, 9 and 10 MPa. Typically, the experimental values for methane consumed during the hydrate formation in presence of 100, 200 ppm PVP and 100, 200 and 2500 ppm modified starch at a temperature of 277.15 K and operating pressures of 8 and 10 MPa are shown in semi-log Figs. 10 and 11, respectively. The both propane and iso-butane hydrate formation experiments are run for pressures of 1, 2, 3 and 4 MPa. Typically, the measured propane consumed during the hydrate formation at a temperature of 277.15 K and operating pressures 1 and 2 MPa are shown in Figs. 12 and 13, respectively. Also, the gas uptake curves for the experimental iso-butane hydrate formation in aqueous PVP or modified starch solutions at a temperature of 275.15 K and operating pressures 3 and 4 MPa are shown in Figs. 14 and 15, respectively. The concentrations of the inhibitors in the propane, iso-butane and methane experiments are the same. In these figures (8 to 15), the natures of the experimental curves are similar for all isotherms. As can be seen, increasing the pressure of the system, leads to decrease the induction time of gas hydrate formation.

Also, the comparison results between the measured gas hydrate formation in presence of the kinetic inhibitor indicate that increasing the pressure of the system, cause to increase the experimental gas consumption. In addition, the curves indicate that the gas consumed is either slightly smaller (using the PVP as an inhibitor) or in the case of modified starch clearly smaller than for blank water. Moreover, the extent of hydrate formation at a given time is clearly less in the presence of the inhibitors. Also, when comparing the gas consumption during the hydrate formation for the mentioned gases in presence of PVP and modified starch inhibitors, it is seen that the gas consumption in the presence of modified starch is lower than of PVP for all experiments. Also, in all experiments, when comparing the induction time during the hydrate formation for mentioned gases in the presence of PVP and modified starch inhibitors, it is seen that the induction times in the presence of modified starch are higher than that of PVP. Although, the PVP as a kinetic inhibitor, increased the induction time and decreased the gas consumption rate, but this inhibitor also exhibited a weak inhibiting effect on simple gas hydrate formation. Whereas, the modified starch exhibited a strong inhibiting effect on the pure gases during the gas hydrate formation.

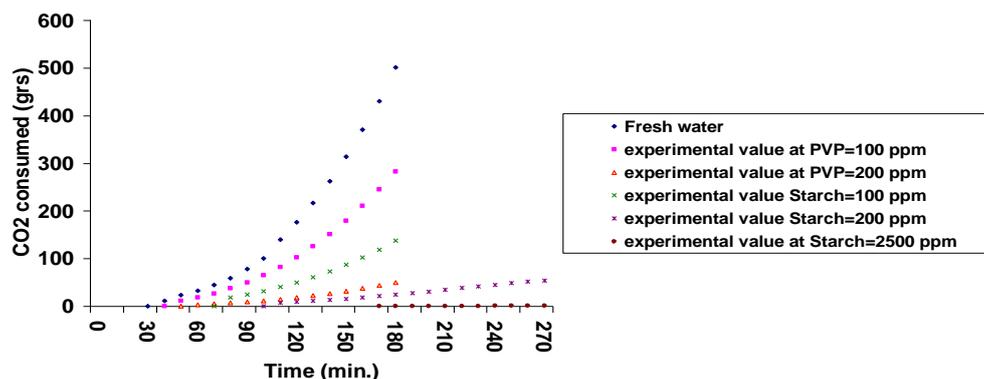


Fig. 8: Experimental curves for CO<sub>2</sub> consumed during gas hydrate formation in presence of PVP & Starch at pressure of 7 MPa and temperature of 277.15 K in miniloop apparatus

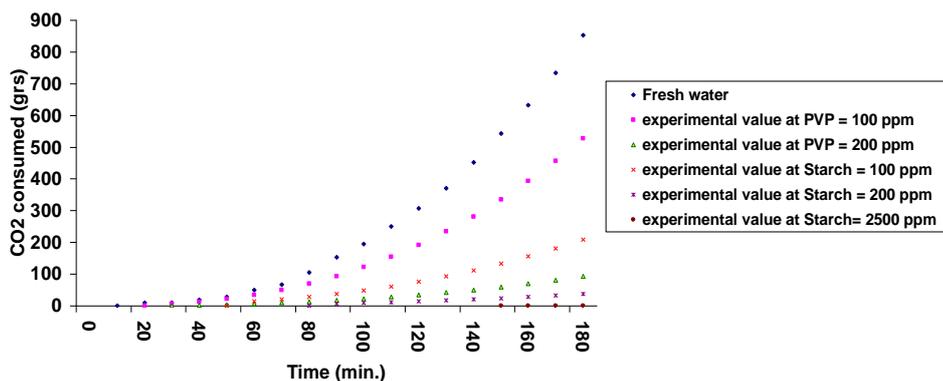


Fig. 9: Experimental curves for CO2 consumed during gas hydrate formation in presence of PVP & Starch at pressure of 9 MPa and temperature of 277.15 K in miniloop apparatus

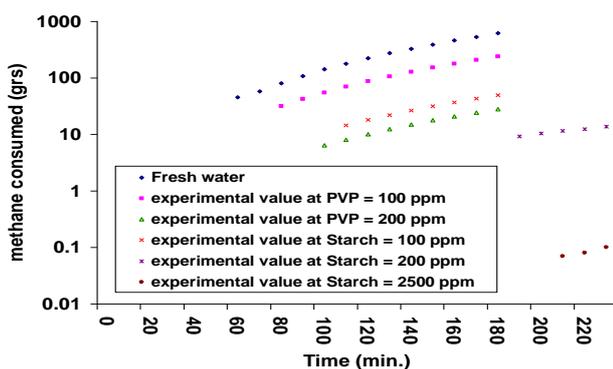


Fig. 10: Experimental curves for methane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 8 MPa and temperature of 277.15 K in miniloop apparatus

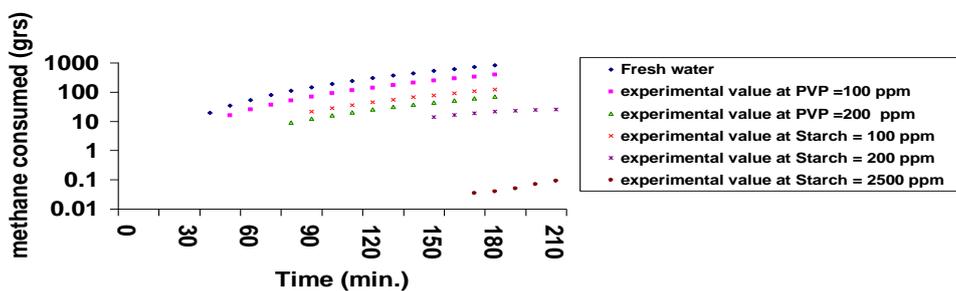


Fig. 11: Experimental curves for methane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 10 MPa and temperature of 277.15 K in miniloop apparatus

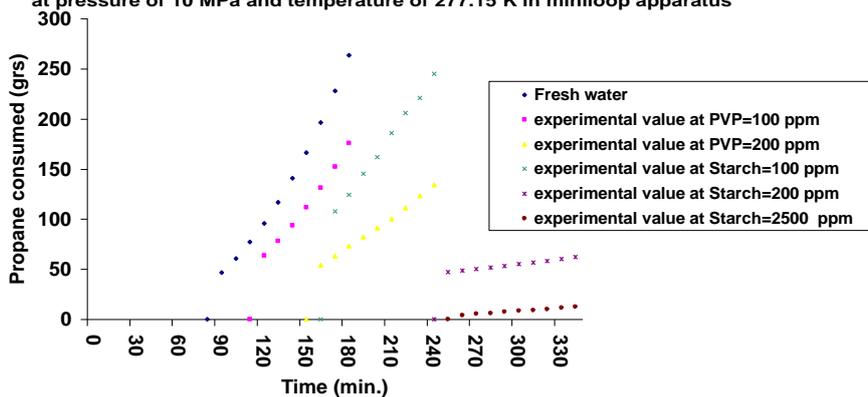


Fig. 12: Experimental curves for propane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 1 MPa and temperature of 277.15 K in miniloop apparatus

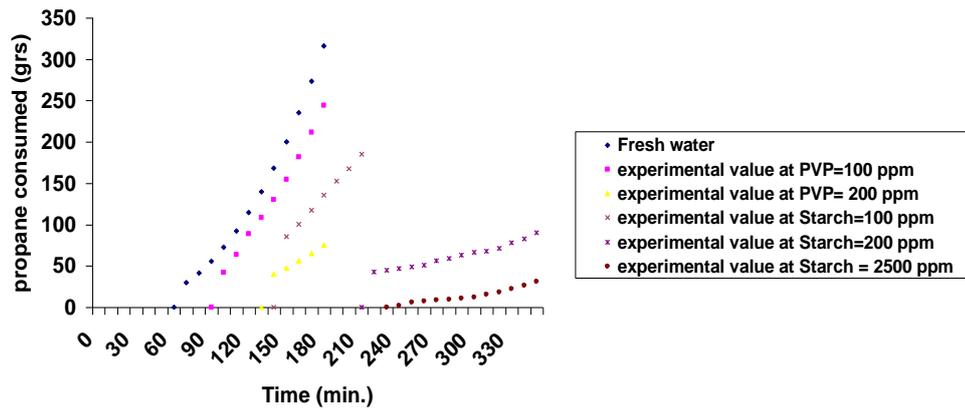


Fig. 13: Experimental curves for propane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 2 MPa and temperature of 277.15 K in miniloop apparatus

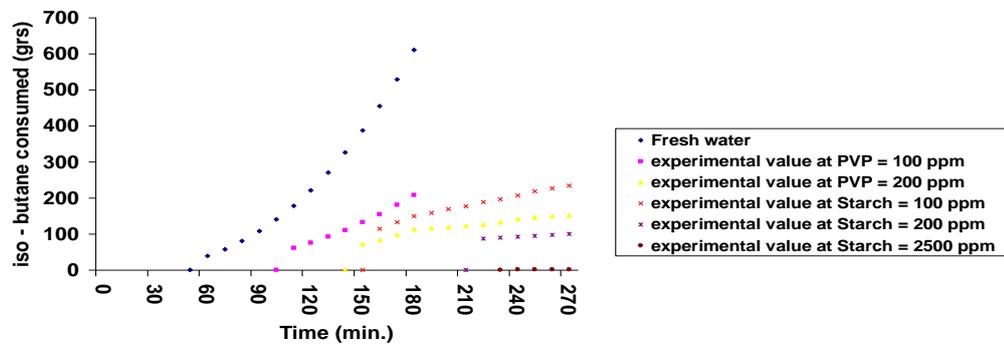


Fig. 14: Experimental curves for iso-butane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 3 MPa and temperature of 275.15 K in miniloop

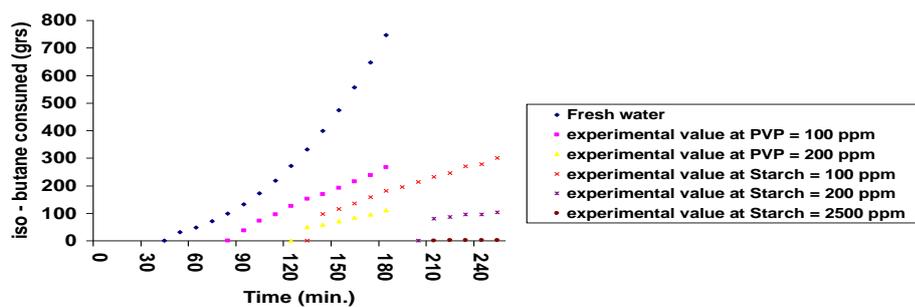


Fig. 15: Experimental curves for iso-butane consumed during gas hydrate formation in presence of PVP & Starch at pressure of 4 MPa and temperature of 275.15 K in miniloop



#### 4. Conclusions

The experimental data on the kinetics of gas hydrate formation from four types of pure gas (C1, C3, i-C4 and CO<sub>2</sub>) with or without presence of the kinetic inhibitors (PVP and modified starch) are presented. The nature of the experimental curves is similar for all isotherms. Observing the data at any particular isotherm, it is seen that there is a strong dependence of the rate of formation on the driving force which indicates that greater driving force causing higher consumption rates. As can be seen from the figures, at higher driving forces the rate of gas hydrate formation is larger. In addition, although this is not indicated in the plots, it was observed that the induction period becomes shorter when the driving force used is larger. The gas hydrate formation rate or gas consumed during the gas hydrate formation is always smaller when PVP or modified starch is present in the liquid phase. The results show, that the efficiency of modified starch is higher than the PVP, because, the induction time for simple gas hydrate formation in presence of modified starch is greater than by using the PVP.

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