

# EFFECT OF WAX ON HYDRATE FORMATION IN OIL-DOMINATED SYSTEM

Wei Wang<sup>1</sup>, Qiyu Huang<sup>1\*</sup>, Dongxu Zhang<sup>1</sup>

<sup>1</sup> China University of Petroleum – Beijing, Beijing 102249, People's Republic of China

Corresponding author: Qiyu Huang (ppd@cup.edu.cn)

## ABSTRACT

Hydrate formation and wax precipitation can occur simultaneously due to the high pressure and low temperature conditions in subsea pipelines, leading to complicated flow assurance issues. In this study, we provided direct measurements of hydrate induction time with different wax contents by using a high pressure autoclave equipped with an online viscometer. It was found that the presence of wax can significantly increase the hydrate induction time for the diesel oil systems. The petroleum samples from an operational well and real wax deposits from the pigging process were also mixed and used to represent in the field and real hydrate formation conditions. The hydrate induction time of field fluids showed that the presence of wax deposition could weaken the inhibiting effect of wax on hydrate nucleation by causing a reduction in the amount of wax adsorbed at the water/oil interface.

**Keywords:** hydrate nucleation, interfacial adsorption, wax deposition, mass transfer resistance

## 1. INTRODUCTION

With the rapid development of petroleum exploitation technologies, oil and gas transportation is moving to the offshore condition that seen previously. Gas hydrates can form in the pipelines after the equilibrium conditions are reached [1]. Formed hydrate particles may agglomerate together or settle on the pipeline wall [2]. In the multiphase flow of an oil and gas pipeline, due to the shearing action of turbulent flow, water is dispersed into the oil phase. The hydrates will grow along the water-oil interface forming a hydrate shell [3]. The hydrate induction time represents the ability of a supersaturated system to remain in a

metastable state after the hydrate equilibrium conditions have been reached [4, 5]. Long induction times would avoid hydrate formation during the transportation of petroleum fluid [6].

The wax deposition is also a common flow assurance issue in the pipelines. When the wall temperature of the pipeline is lower than the wax appearance temperature during the transportation of waxy crude oil, the wax molecules could precipitate and form a deposition layer on the pipe wall [7, 8].

The low temperature and high pressure conditions of subsea pipelines may cause simultaneous hydrate formation and wax precipitation [9]. Gao et al. [10] found that the presence of hydrates can facilitate the wax deposition through the experimental observation. Raman et al. [11] determined that the wax could affect the amount of formed hydrate as well.

The presence of wax extremely complicates hydrate formation, causing changes in the mass transfer, heat transfer, and interfacial behavior of hydrates. Since the influence of wax on hydrate formation has not been deeply studied, this work provides the direct measurements of hydrate induction time with different wax contents in different systems to better understand hydrate/wax interactions.

## 2. MATERIALS AND METHODS

### 2.1 Experimental Apparatus

The high pressure autoclave (shown in Figure 1) used in this work consisted of a pressure and temperature control system, a magnetic stirring device, and a high pressure online viscometer (VISCOpro 2000). The online viscometer has a magnetic piston which is driven by two coils to move back and forth in the measurement chamber. The round trip travel time of the piston is

recorded in order to determine the apparent viscosity. The maximum working pressure of this experimental apparatus is 12 MPa.

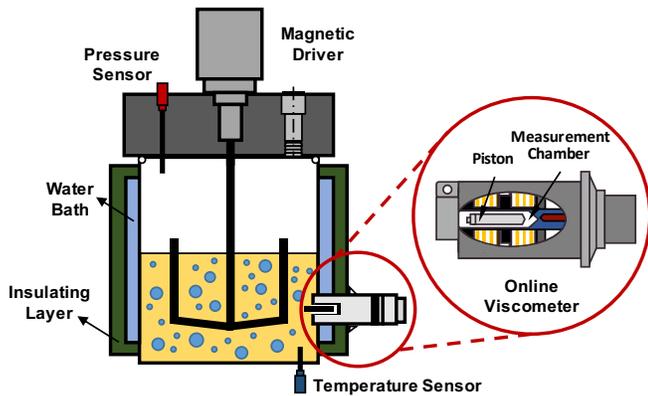


Fig 1 Schematic diagram of the experimental apparatus

## 2.2 Experimental Materials

Diesel oil was mixed with a paraffin wax mixture (carbon number distribution can be seen in Figure 2) and emulsified with deionized water to form water-in-oil emulsions (stirred at 800 rpm for 30 min). The petroleum samples from an operational well and real wax deposits from the pigging process were mixed and used to provide realistic hydrate formation condition (this was done because it better represents field production scenarios). The hydrate former used in the experiments was CO<sub>2</sub> which can form sl hydrate. The water cut used in all experiments was 20%.

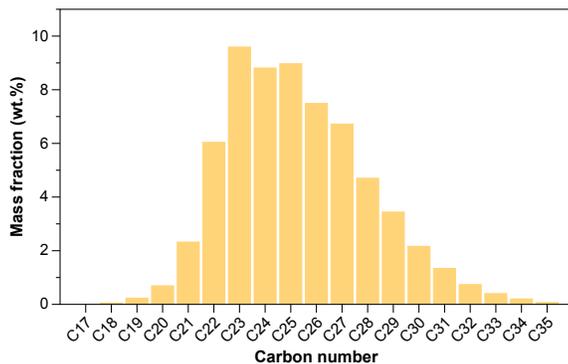


Fig 2 Carbon number distribution of paraffin wax mixture

## 2.3 Experimental Procedure

The as-prepared emulsions were placed into the autoclave and pressurized by CO<sub>2</sub> until the target pressure was reached. The emulsions were then cooled to the target temperature at a constant cooling rate (0.1 °C/min) until hydrate formation. The cooling process was kept at constant pressure and the hydrate formation was kept at constant volume. The stirring rate of the

autoclave was maintained at 300 rpm for the entire duration of the experiment.

## 2.4 Determination of Hydrate Induction Time

The typical temperature, pressure and apparent viscosity profiles of a 20% water cut, 6 wt.% wax, 2000 ppm Span 80, diesel oil emulsion at 2.9 MPa are shown in Figure 3. Once the hydrate growth started, the temperature increased significantly because hydrate formation is a highly exothermic process. In the meantime, the apparent viscosity of the system also increased, which was caused by the transition from a liquid-liquid system to solid-liquid system. The formed hydrate particles also aggregated together through a water capillary bridge and blocked the piston of the online viscometer, leading to the observation of zero apparent viscosity values after 200 min. Additionally, the pressure decreased during the hydrate formation because of the gas consumption of the hydrates. Based on the results of the temperature, apparent viscosity, and pressure profiles, the hydrate induction time was defined. It starts when the temperature reaches the equilibrium temperature under the target pressure, and ends when the temperature and apparent viscosity show significant increases.

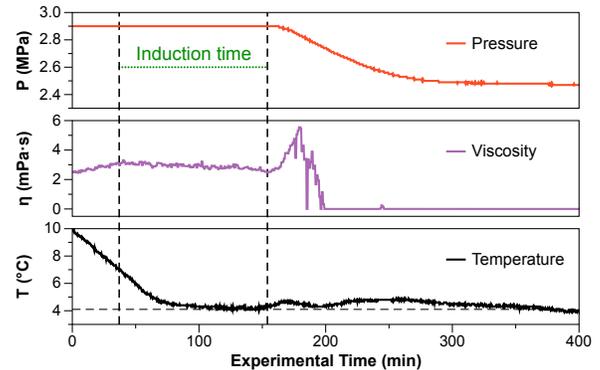


Fig 3 Temperature, pressure, and apparent viscosity versus time during hydrate formation of a waxy diesel oil emulsion

## 2.5 Results

### 2.5.1 Influence of wax on induction time with diesel oil

The influence of wax on hydrate induction time in water-in-diesel oil emulsions with/without Span 80 are shown in Figure 4.

As shown in Figure 4, the hydrate induction time significantly increased with increasing wax content for both cases with and without the presence of Span 80. The precipitated wax particles in the bulk phase can be independently adsorbed or synergistically adsorbed [12] with surfactant at the water/oil interface. This forms a

barrier to the gas diffusion, which may block or warp the diffusion path of gas molecules and decrease the diffusion rate. For water-in-oil emulsion systems, the hydrates will nucleate along the water-oil interface forming molecular clusters once the temperature reached hydrate equilibrium temperature. However, before the critical size of hydrate clusters is reached, the clusters may either grow or shrink [13]. Hence, the barrier effecting by wax particles could reduce the formation rates of hydrate clusters. The increased wax content enhanced this barrier effectiveness, leading to the increased hydrate induction time.

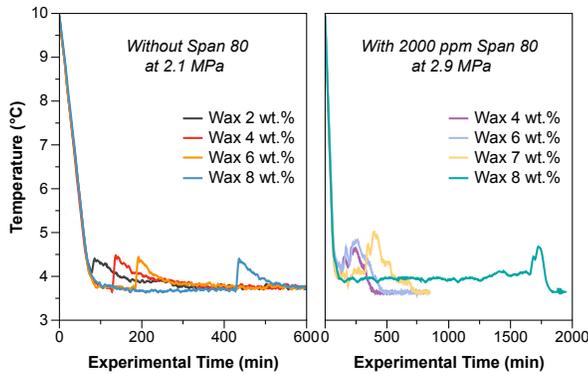


Fig 4 Comparison of temperature with different wax contents in experiments with/without Span 80

### 2.5.2 Influence of wax on induction time with petroleum

The same experimental procedure was also used with petroleum fluids mixed with real wax. The experimental pressure is 3.1 MPa. The comparison of the temperature profiles with different wax contents can be seen in Figure 5.

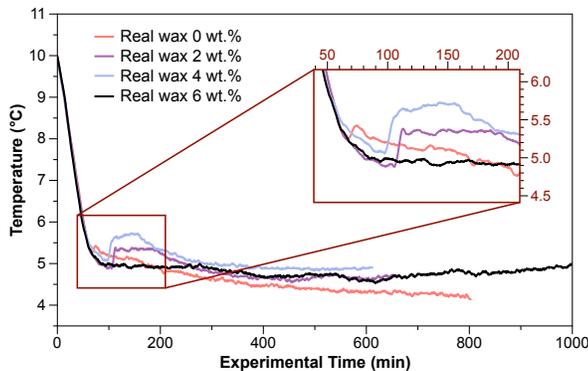


Fig 5 Temperature profiles with different wax contents in petroleum fluid system

As shown in Figure 5, the induction times for the systems with 2 wt.% and 4 wt.% real wax are longer than the control system (0 wt.% real wax). Additionally, no hydrate formation was observed in the experimental with 6 wt.% real wax within 1000 min, suggesting that

the induction time of this case will be >1000 min. However, the induction time with 2 wt.% real wax was found slightly longer than the case with 4 wt.% real wax. This phenomenon can be explained by Figures 6-9.

As shown in Figure 6 (0 wt.% real wax), during the cooling process, the temperature had a slight influence on apparent viscosity. Figure 7 (2 wt.% real wax) shows that the online viscometer was blocked at 15.3 °C leading to the zero apparent viscosity. However, there was no hydrate formation within this temperature range based on the temperature being outside the hydrate equilibrium conditions. Therefore, zero apparent viscosity could be caused by the wax deposition occurred on the inner wall of the autoclave, which can also block the piston of the online viscometer.

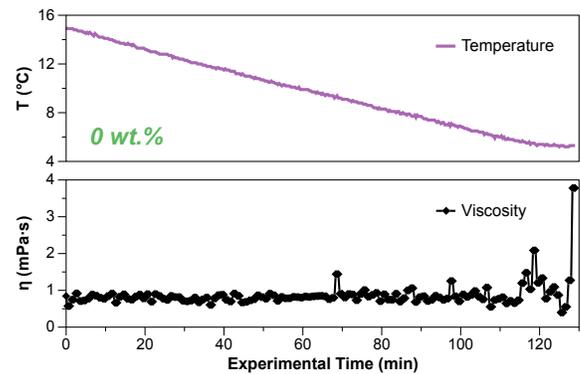


Fig 6 Apparent viscosity and temperature of petroleum fluid with 0 wt.% real wax during cooling process

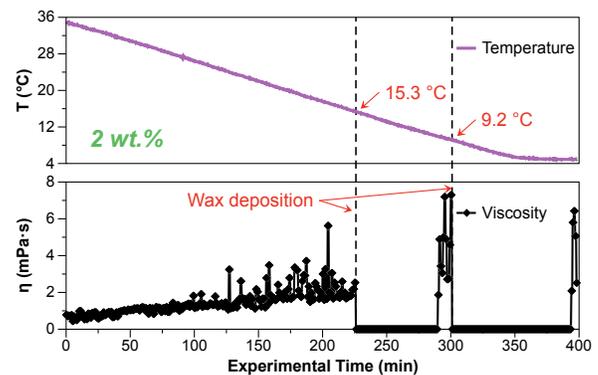


Fig 7 Apparent viscosity and temperature of petroleum fluid with 2 wt.% real wax during cooling process

As seen in Figure 8, the zero apparent viscosity caused by wax deposition occurred at 29.7 °C with 4 wt.% real wax, which is higher than the temperature that wax deposition occurred in the system with 2 wt.% real wax. This phenomenon suggests the mass of wax deposits increased with increasing wax content from 2 to 4 wt.%. According to the results of the experiments with diesel oil, the wax content on the water/oil interface could significantly affect the hydrate nucleation. However, for

the experiments with petroleum samples and real wax, the decreased composition of wax in the liquid phase (caused by wax deposition) could lead to the decreasing amounts of wax remained on the water/oil interface. This will cause less inhibiting effect of wax on hydrate nucleation. Therefore, the wax remained on the water/oil interface for the case with 4 wt.% real wax might be less than it with 2 wt.% real wax, leading to the inhibiting effect of the wax on hydrate nucleation to be weakened.

For the case with 6 wt.% real wax (Figure 9), the temperature of the wax deposition occurrence was slightly higher than the case with 4 wt.%. However, the system had enough wax remained on the water/oil interface for preventing the hydrate from nucleating during the experimental time (1000 min).

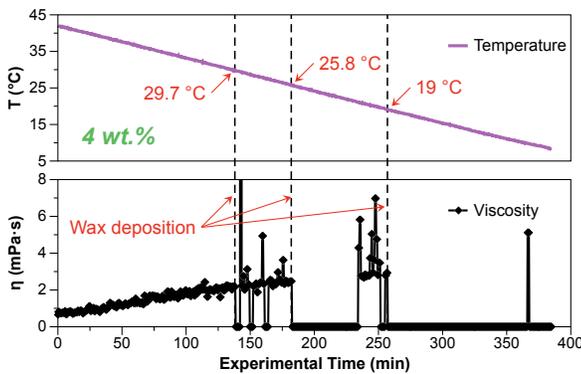


Fig 8 Apparent viscosity and temperature of petroleum fluid with 4 wt.% real wax during cooling process

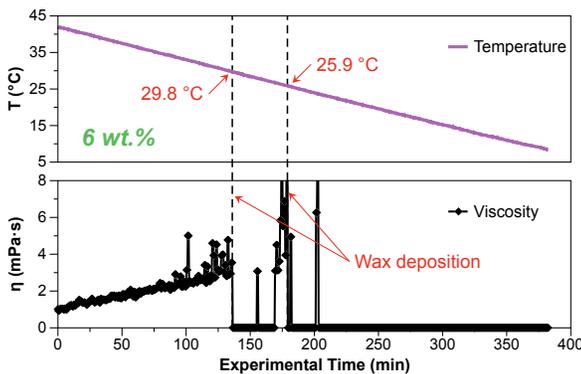


Fig 9 Apparent viscosity and temperature of petroleum fluid with 6 wt.% real wax during cooling process

The wax deposition only occurred in the experiment with the petroleum fluid and real wax rather than the diesel oil system. This phenomenon could be due to the fact that the petroleum had heavier component and less wax solubility than the diesel oil, leading to a higher WAT and a denser wax deposition layer.

## 2.6 Conclusions

The hydrate induction time was found to increase with increasing wax content, showing a significant inhibiting effect of wax on hydrate nucleation. The wax can be adsorbed at the water/oil interface forming a barrier to the gas diffusion, leading to a mass transfer resistance for hydrate nucleation and a reduction in nucleation rates in the oil-dominated system. The wax deposition was also found to play a role in the hydrate nucleation. The wax consumed by wax deposition will cause a reduction in the amount of the wax remained on the water/oil interface, leading to the inhibiting effect of wax on hydrate nucleation being weakened.

## ACKNOWLEDGEMENT

Thanks for the support from the project of the National Natural Science Foundation of China No.51534007 for this research.

## REFERENCE

- [1] Sloan ED, Koh CA. Clathrate Hydrates of Natural Gases; New York: CRC Press; 2008.
- [2] Hu SJ, Koh CA. Interfacial Properties and Mechanisms Dominating Gas Hydrate Cohesion and Adhesion in Liquid and Vapor Hydrocarbon Phases. *Langmuir* 2017;33:11299-11309.
- [3] Taylor CJ, Miller KT, Koh CA, Sloan ED. Macroscopic Investigation of Hydrate Film Growth at the Hydrocarbon/Water Interface. *Chem Eng Sci* 2007;62:6524-6533.
- [4] Servio P, Englezos P, Bishnoi PR. Kinetics of Ethane Hydrate Growth on Latex Spheres Measured by a Light Scattering Technique. *Annals of the New York Academy of Sciences* 2000;912:576-582.
- [5] Palermo T, Goodwin SP. Pilot Loop Tests of a Threshold Hydrate Inhibitor. *Annals of the New York Academy of Sciences* 2000;912:339-349.
- [6] Kashchiev D, Firoozabadi A. Induction Time in Crystallization of Gas Hydrates. *J Cryst Growth* 2003;250:499-515.
- [7] Wang W, Huang QY, Zheng HM, Li S, Long Z, Wang QC. Investigation of Wax Deposition and Effective Diffusion Coefficient in Water-in-Oil Emulsion System. *J Therm Anal Calorim* 2018;134:1031-1043.
- [8] Li WD, Huang QY, Wang WD, Dong X, Gao XD, Hou L. Estimating the Wax Breaking Force and Wax Removal Efficiency of Cup Pig Using Orthogonal Cutting and Slip-Line Field Theory. *Fuel* 2019;236:1529-1539.
- [9] Zheng HM, Huang QY, Wang W, Long Z, Kusalik PG. Induction Time of Hydrate Formation in Water-in-Oil Emulsions. *Ind Eng Chem Res* 2017;56:8330-8339.

- [10] Gao SQ. Investigation of Interactions between Gas Hydrates and Several Other Flow Assurance Elements. *Energy Fuel* 2008;22:3150-3153.
- [11] Raman AKY, Aichele CP. Effect of Particle Hydrophobicity on Hydrate Formation in Water-in-Oil Emulsions in the Presence of Wax. *Energy Fuel* 2017;31:4817-4825.
- [12] Ma Q, Wang W, Liu Y, Yang J, Shi B. Wax Adsorption at Paraffin Oil–Water Interface Stabilized by Span80. *Colloids & Surfaces A Physicochemical & Engineering Aspects* 2017;518:73-79.
- [13] Sloan ED, Fleyfel F. A Molecular Mechanism for Gas Hydrate Nucleation from Ice. *Aiche J* 1991;37:1281-1292.