Chemical Engineering Science 168 (2017) 444–455

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Effect of monoethylene glycol and kinetic hydrate inhibitor on hydrate blockage formation during cold restart operation

Young Hoon Sohn, Yutaek Seo *

Department of Naval Architecture and Ocean Engineering, Research Institute of Marine Systems Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul, 08826, Republic of Korea

HIGHLIGHTS

- This work presents hydrate formation characteristics during cold restart operation.
- The hydrate blockage occured while varying mixing rate at 200, 400, and 600 rpm.
- Adding MEG 20.0 wt% to water phase suppressed the formation of hydrate blockage.
- KHI was effective to delay the hydrate onset, but eventually hydrate blockage was formed.

ARTICLE INFO

Article history:
Received 17 March 2017
Received in revised form 25 April 2017
Accepted 6 May 2017
Available online 12 May 2017

Keywords:
Flow assurance
Gas hydrate
Blockage formation
Under-inhibition
Flow regime
Cold restart

ABSTRACT

Hydrate blockage formation in offshore flowlines may induce production stoppage and operational hazards. Previous work suggested the risk of hydrate blockage became highest for water and decane mixture with 60% watercut, however the risk could be alleviated by adding a thermodynamic inhibitor along with the kinetic hydrate inhibitor. This work presents the effect of adding the hydrate inhibitors on hydrate blockage formation during cold restart operation, where the water and decane mixture stayed inside the hydrate formation region without mixing for 10 h then executed mixing at constant stirring rates of 200, 400, and 600 rpm. Depending on the mixing rate, liquid phase became stratified (200 rpm), partial dispersing (400 rpm), and full dispersing (600 rpm). Without hydrate inhibitors, hydrates formed instantly upon mixing of liquid phase with fast growth rate. The stirrer was eventually stopped due to the formation of hydrate blockage within 13.9, 18.8, and 42.2 min for stratified, partial dispersing, and full dispersing liquid phase, respectively. The resistance-to-flow could be estimated from the measurement of torque changes during the hydrate formation. Sever torque spikes were observed for the water and decane mixture without hydrate inhibitors. The hydrate growth rate decreases linearly as a function of hydrate fraction in liquid phase, then it drops upon torque spikes, possibly due to agglomeration and bedding of hydrate particles. Adding 20 wt% mono-ethylene glycol (MEG) to the water phase could suppress the torque spikes while hydrate formation proceeds to the final fraction, suggesting MEG may prevent the agglomeration and bedding of hydrate particles for all flow regimes. However its performance was limited at 10 wt% MEG concentration. The presence of kinetic hydrate inhibitor, Luvicap, was also found effective to suppress the hydrate formation for 155.0 min at mixing rate of 200 rpm, however soon lost its efficacy with increasing mixing rate to 400 and 600 rpm. These results suggested that the hydrate formation mechanism during cold restart would be highly dictated by the mixing rate and corresponding flow regime, thus appropriate hydrate inhibition strategy must be developed to manage its risk. For 10 wt % MEG and 0.1 wt% Luvicap solution, hydrate formation initiated in interface between water and decane, then proceeded to gas phase without affecting the resistance-to-flow. The performance of hydrate inhibitors must be evaluated based on relevant data measurement and visual observation to better describe the hydrate formation mechanism.

1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds, consisting of host water and guest hydrocarbon molecules such

* Corresponding author.
E-mail address: Yutaek.seo@snu.ac.kr (Y. Seo).

http://dx.doi.org/10.1016/j.ces.2017.05.010
0009-2509/

as methane, ethane, and propane (Sloan and Koh, 2008). They are formed through hydrogen bonding between water molecules enclathrating guest molecules at high pressure and low temperature. These conditions can be readily found in subsea flowlines transporting hydrocarbon fluids from subsea wells to offshore processing facilities. As recent offshore oil and gas development moves toward deep water region, the operation conditions of subsea flowlines are prone to the formation of gas hydrates, which are able to lead to a pipeline blockage. Industry practice has been relying on an injection of large amount of thermodynamic hydrate inhibitors (THIs) to thermodynamically shift the operation conditions of subsea flowlines outside of hydrate formation condition. However significant investment is required to accommodate the THIs handling systems such as large storage tanks, injection pumps, subsea distribution pipelines, and costly regeneration process, especially for monoethylene glycol (MEG) (Brustad et al., 2005; Sanford and Alapati, 2011).

Therefore there have been intensive efforts to develop the hydrate management strategy where the hydrate nucleation and growth would be controlled to avoid the formation of hydrate blockage. Alternative way to avoid large amount of THIs is kinetic hydrate inhibitors (KHIs). They are water soluble polymers that consist of a hydrophobic backbone with pendant groups which can hydrogen bond with the hydrate crystals. KHIs can delay hydrate formation by increasing the energy barrier to form hydrate nuclei, or by adsorbing to the surface of the hydrate crystals (Kelland, 2006). These include the homo- and co-polymers of N-vinyl carprolactam (VCap) and N-isopropyl acrylamide (NIPAM). However, performance of KHIs is affected by the subcooling temperature, indicating the temperature difference between the hydrate equilibrium temperature and the fluid temperature. In addition to KHIs, anti-agglomerants (AAs) are typically ionic surfactants that, upon hydrate formation, minimize the interaction between hydrate particles. Therefore, AA allows hydrate nucleation, but prevent the aggregation of hydrate particles by reducing the particle-particle interactions. The dispersed hydrate particles result transportable slurry with liquid phase and the hydrate blockage formation can be avoided. There are several examples of AAs that have been applied in the field. (Kelland, 2006; Aman et al., 2014) However, the AAs cannot be deployed when the water-cut is high (>50%) because the transportability decreases due to increased viscosity of liquid phase. Moreover, the environmental impact of quaternary ammonium based AAs remains a concern because they are biodegraded slowly and toxic, thus may induce bioaccumulation (Kelland, 2006). Understanding of hydrate formation characteristics including hydrate onset time and growth rate in the presence of hydrate inhibitors is central to address the effectiveness of the hydrate management strategies.

Although there have been numerous application of KHIs and AAs in offshore oil and gas fields, MEG is still a reliable solution to avoid hydrate blockage formation in offshore flowlines. The required concentration of MEG in aqueous phase to avoid hydrate blockage may be more than 50 wt% in deep water or arctic oil and gas fields, therefore a reduction in the MEG concentration can result in significant investment saving. Our previous works suggested that the growth rate of hydrates can be controlled in the MEG concentration lower that the value required to fully avoid the hydrate formation, so called under-inhibition with MEG (Kim et al., 2014; Sohn et al., 2015; Kim et al., 2017). Hydrate fraction in liquid phase maintained less than 28 vol.% with negligible resistance-to-flow in MEG 20 wt% solution, although the required MEG concentration was 42 wt% to thermodynamically avoid the hydrate formation. Similar observation was made by Hemmingsen et al. (2008), Li et al. (2011), and Akhfash et al. (2013). However it has not yet been studied whether the under-inhibition is effective for the subcooled hydrocarbon fluids in extended shut-in and cold restart operation. During the extended shut-in period of subsea flowlines, the temperature and pressure of hydrocarbon fluids may be shifted into the hydrate formation region as fluid temperature would decrease down to seabed temperature. Coexisting three phases, natural gas, oil or condensate, and water, would be separated into layers due to lack of mixing exerted by fluids flow. Flowloop experiments suggested that gas hydrates formed as a thin layer in interface between oil/condensate and water during the shut-in period, however subsequent cold restart of the fluids resulted the fast growth of the hydrate particles in liquid phase and the formation of hydrate blockage eventually (Joshi et al., 2013). Aman et al. (2015) represented that hydrate growth rate was faster up to order of magnitude in cold restart experiment than the continuous cooling with mixing experiment. They suggested that kinetically limited initial growth rate increased with Reynolds number and higher rates of initial shear exerted on the hydrate film broke it into smaller pieces that would catalyze fast growth of hydrate particles. Industry reports also suggested that the risk of hydrate blockage formation would be much higher in cold restart operation as its formation rate was almost instant and there would be limited time to avoid. Mehta et al. (2002) reported continuous pressure increase for almost five days in the subsea flowline since the onset of hydrate formation was detected during normal production operation. The temporary injection of additional methanol into the flowline removed the hydrates obstruction and restored normal gas production. Kashou et al. (2004) reported that 10 in. gas pipeline was plugged within an hour due to hydrate blockage upon cold restart operation. They spent three days to remediate the hydrate blockage and to resume the gas production. Other reports also indicated that hydrate formation upon cold restart operation induced instant production stoppage. The remediation procedure must be pre-established and initiated quickly to remove the hydrate blockages (Kane et al., 2008; Zabaras and Mehta, 2004; Bilyeu and Chen, 2005). Therefore the prime objective of this work is to investigate the hydrate formation characteristics including hydrate onset time, growth rate, hydrate fraction, and resistance-to-flow to verify the effectiveness of under-inhibition with MEG during cold restart operation.

Sohn et al. (2015) showed significant increase in the motor torque required to mix the hydrocarbon fluids along with the hydrate particles at constant rotational speed, thus qualitatively suggesting the increase of resistance-to-flow in the presence of agglomerating or bedding of hydrate particles. The resistance-to-flow showed severe fluctuation in case of hydrate formation in liquid mixture having water volume fraction of 60%. Aman et al. (2011) demonstrated that the cohesion force becomes higher when water is present between hydrate particles in a cyclopentane phase. This enhances sintering of the hydrate particles by formation of a hydrate-bridge between particles. Recently Akhfash et al. (2016, 2017) suggested a new conceptual mechanism for hydrate blockage formation based on disruption of phase interface in partially dispersed systems. Moreover the FBRM measurements suggested that the onset of a moving hydrate bed may occur at much lower hydrate concentrations than those inferred from macroscopic measurement techniques. The changes of slurry density and the particle chord length distribution suggested the agglomeration was highest in the slug flow, while the deposition was highest in the annular flow. (Ding et al., 2017) A high pressure rocking cell study suggested that the relative motion of hydrates to the cell wall and the final morphology of the hydrate chunks are found to be two critical parameters for evaluating hydrate deposition characteristics in the flow system. (Zhao et al., 2017) Therefore the other objective of this work is to address the mechanism of hydrate blockage formation in segregated, partial dispersing, and full dispersing systems. A high pressure autoclave was used to simulate