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Abstract. This study proposes a simulator of the growth kinetics of gas hydrates occurring in the porous-scale, its agglomeration in the interparticle- and particle-scales, coupled to gas-(water-in-oil) slug flow hydrodynamics and heat transfer in the macro-scale. Closure is obtained from slurry apparent viscosity models, droplet size models, and specific slug flow correlations for translational velocity, slug aeration and slug frequency. The results capture four types of systems, namely active surface-, dissolution-, heat transfer- and pressure drop-limited systems. This paper discusses when and why each type of system occurs.

Keywords: gas hydrates, slug flow, water-in-oil dispersion, flow assurance

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1 Introduction

Gas hydrate formation, agglomeration and plugging are nowadays regarded as the top worrisome flow assurance problems in most oil companies (Cardoso et al., 2015). Crystallization of a single component, such as ice, is limited by heat transfer only. But for gas hydrates, formed by gas and water molecules, the mass transfer of those up to the crystal growing surface can limit the crystallization as well (Bassani et al., 2020b). The complexity of the problem substantially increases when dealing with hydrate formation in oil flowlines, where the mass transfer process is inherent to the multiphase flow.

In the case of oil-dominants systems, and for the range of velocities and liquid loadings that are representative of oil production, slug flow is the most likely flow pattern (Barnea, 1987), as presented in Fig 1. The liquid phase, by its turn, is composed of water-in-oil dispersions, often with fine (mm-sized) droplets because of the naturally existing surfactants in crude oils. Because of the hydrophilic nature of those crystals, the water gets instantly entrapped inside the porous hydrate particles during the onset of formation (Bassani et al., 2019). The problem is therefore to define the mass transfer of the gas molecules from the gaseous free phase up to each particle inside the oil continuous flow. The

gas molecules then solubilize into the water entrapped in the porous crystals, and crystallization takes place in the capillary walls, decreasing the particle porosity (Bassani et al., 2020b).

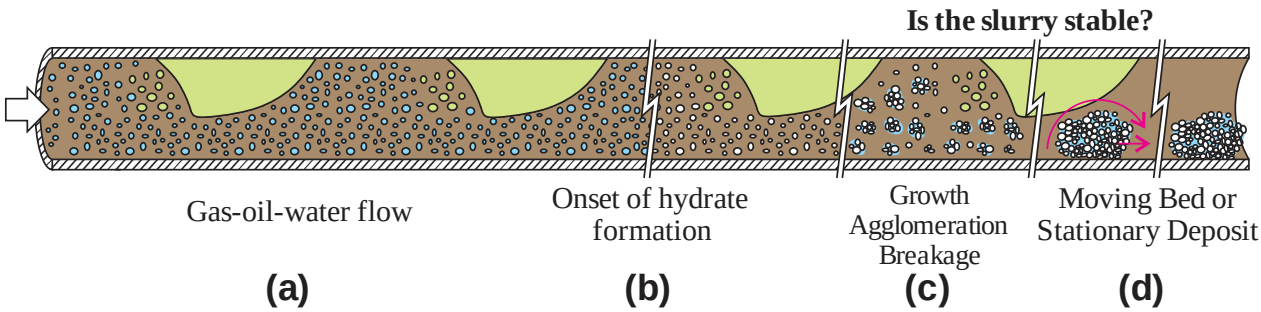

Fig. 1 Problem depiction of gas hydrate crystals forming, growing, agglomerating and breaking in a gas-(water-in-oil) slug flow. The engineering question to be answered is whether the slurry is stable or not.

The water inside the porous particles continuously permeates and spreads over the outer surface of the particles (Bassani et al., 2019; Shi et al., 2011), forming a water layer that promotes liquid bridges upon collision between particles that leads to agglomeration (Bassani et al., 2020a). As the particle porosity decreases, the water gets sealed inside the porous crystal, thus preventing liquid bridge formation and ceasing the agglomeration process. That is, the crystallization occurring in the capillary-sized scale (100s-of-nm) and coming from the mass transfer process of the gas-liquid slug flow in the macroscale, directly affects the time window where agglomeration happens. Indeed, for higher subcoolings, the particles get quickly sealed and no macroscopic agglomeration was experimentally observed (Kakitani, 2019).

Depending on the agglomerate size achieved, there is a minimum mixture velocity assuring that turbulent lift forces overcome the buoyancy ones, thus keeping the system dispersed (Oroskar and Turian, 1980). This is the ideal production scenario, where the pump shall be designed in order to overcome any increased friction because of the apparent slurry viscosity (Krieger and Dougherty, 1959), but partial restrictions will never occur because the particles are assured to be fully suspended. Since the whole process occurs in long flowlines subjected to high P&T variations, a further complexity arises from the fact that phase changes (evaporation or condensation, solubilization or gas release, or hydrate formation itself) cause the mixture velocity to substantially change along the flowline, thus affecting the lift forces.

This study proposes a simulator of gas hydrate formation and agglomeration inside gas-(water-in-oil) slug flow coupling multidisciplinary models covering the aforementioned phenomena.

2 Overview of the Growth and Agglomeration Model of Gas Hydrates coupled to Slug Flow

The simulations shown in this paper consist of coupling three models published by our group (Bassani et al., 2020b, 2020a, 2018). The exact shape of the equations can be found in the original papers, whereas the focus herein is on what they represent physically. The gas consumption rate occurring in the capillary walls of the porous particles is estimated from eqs (11), (23) and (33) of Bassani et al (2020b) and depends: (i) on the subcooling of crystallization, (ii) on the gas concentration in the oil bulk, which evolves in time because of the competition between gas absorption in the gas-liquid interface versus gas depletion because of hydrate formation, following the eq (4) of Bassani et al (2020b) and (iii) on the porosity of the particle, which decreases exponentially in time because of crystallization in the capillary walls, following eq (32) of Bassani et al (2020b).

The average particle size evolves in time because of particle growth and agglomeration, whereas breakage is neglected. It comes from the system of ordinary differential equations, eqs (6) and (26) of Bassani et al (2020a), and depends on the subcooling, on the porosity, on the oil-water interfacial properties that play a role on permeation, and on the mixture superficial velocity that promotes collision between particles and disruption of aggregates hold by liquid bridges. When the time-decreasing porosity reaches a value where all water arriving at the outer surface of the particle is instantly crystallized, water stops accumulating over the particle and the liquid bridge ceases to form. That marks the transition from a wet to a dry particle, and the system achieves a maximum, stable agglomerate size. Mathematically, this happens when the Damköhler number is above unity, as defined by eq (42) of Bassani et al (2020b). The particle size during the onset of hydrate formation is considered equal to the water droplet size, a hypothesis valid for dilute flows. The droplet size comes from Brauner's (2001) model, which depends on the oil properties, on the water cut and on the mixture velocity.

As hydrates grow and agglomerate, they are carried by the multiphase gas-oil-hydrate flow. Considering that the gas-liquid is in the slug flow pattern at steady-state, and neglecting slip between particle and oil and thus the hydrate-in-oil slurry having homogeneous properties, then velocity, pressure and temperature are updated along the flowline as per eqs (6-8), (23-24) and (35-38) of Bassani et al (2018). Those depend on the slug flow geometry, estimated from Taitel and Barnea's (1990) model coupled to slug flow specific closure correlations for the unit cell translational velocity (Bendiksen, 1984), the slug flow frequency (Hernandez-Perez et al., 2010) and the slug aeration (Barnea and Brauner, 1985). Hydrates influence the velocities because of gas and water consumption to form a solid, the pressure distribution because of the slurry apparent viscosity coming from Krieger and Dougherty's (1959) model, and the temperature distribution because of the exothermic nature of this phase change.

Separated validations of each one of the presented models for growth kinetics, agglomeration and multiphase flow were already presented in the original studies. The gas-liquid slug flow model stays within the ±30% deviation rate when compared to databases covering velocities of 1 to 3 m/s for air-water flow in a 1 to 2" ID pipeline, at ambient conditions. The growth kinetic and agglomeration models were fitted for methane hydrates in oil continuous systems, at 70-80 bar, with subcooling from 7 to 18 K, for light oils of up to 10 cP in up to 30% water cut systems.

3 Using the Simulations to Understand the Behavior of Hydrate Forming Systems

Experimental literature of gas hydrates reports results mainly for temperature and water conversion into hydrates. Water conversion can be either linear or asymptotic in time. Temperature can rebound after the onset of hydrate formation, reaching a temperature plateau close to the equilibrium, or can gradually move away from the equilibrium temperature. Literature is however still unclear about when and why exactly each one of these trends occur, and these answers are addressed in this section.

Several simulations using this simulator were presented by Bassani (2020). Some selected cases are shown here to evidence the capabilities of the simulator to capture four different types of systems, and to discuss the phenomena that lead to each behavior. The classification is done regarding the mechanism that limits hydrate formation. The simulations are for methane-oil-water slug flow, where oil has a 10 cP viscosity, in a 75-mm ID and 30-km long flowline. The pressure and temperature at the flowline inlet are fixed at 130 bar and 18°C. The external medium is at 4°C and the flowline has an insulation of 0.3 W/(mK) with a thickness of 37.5 mm. The gas and liquid superficial velocities are 0.5 m/s each, and the water cut is 30%.

3.1 Active Surface-Limited Systems

In general terms, the water conversion into hydrates is proportional to $A_i \Delta\mu$, where A_i is the active surface of crystallization and $\Delta\mu_{(C,P,T)}$ is the driving force of crystallization expressed in terms of the chemical potential, which depends on the gas concentration in water close to the active surface, and on the system pressure and temperature. An active surface-limited system occurs when A_i decreases in time up to limiting the water conversion into hydrate. That implies in an asymptotic water conversion, as presented in Fig 2(a,b).

As a rule-of-thumb, active surface-limited systems are the general case of hydrocarbon gases in oil-continuous systems. The primary effect is the porosity decrease in time, Fig 2(b). When agglomeration is enabled, Fig 2(a), then the decreased particle-bulk interfacial surface acts as a secondary effect on limiting the active surface of crystallization. Experimental evidences of such systems are found in Kakitani (2019).

3.2 Dissolution-Limited Systems

Whenever the gas absorption by the continuous phase and/or the gas distribution up to each particle is slow, the system starts getting limited by dissolution. In this case, the driving force $\Delta\mu$ decreases until a stable value is reached. That occurs when the gas mass transfer rate by dissolution equals the hydrate formation rate. Because the driving force converges to a lower value, then the porosity has a much slower decrease and the active surface of crystallization remains nearly constant. This causes the water conversion into hydrates to become linear, as presented in Fig 2(c).

Dissolution-limited systems happen when the gas has low affinity with the liquid continuous phase. In the case of oil-continuous systems, CO_2 could be one type of gas that is limited by dissolution, but no experimental evidences were found in literature for the behavior of such system. Although the simulator is not prepared to handle water-continuous systems, the mathematics of absorption and depletion of the bulk still hold in these scenarios, pointing out that any hydrocarbon gas in water-continuous systems is limited by dissolution. That goes alongside the classic experiments of Englezos et al (1987).

3.3 Heat Transfer-Limited Systems

Gas hydrate formation is an exothermic phase change. When the system cannot exchange heat at the same rate it is generated, the mixture reheats toward the equilibrium temperature of hydrate formation, as presented in Fig 2(d). This causes the driving force $\Delta\mu$ to decrease in a similar fashion to dissolution-limited systems, but because of temperature variations instead of concentration ones. The system attains a linear water conversion into hydrates, similarly to dissolution-limited systems. Heat transfer-limited systems occur in insulated flowlines and are independent on water or oil being the continuous phase. The temperature plateau is experimentally observed by Joshi (2012).

3.4 Pressure Drop-Limited Systems

The driving force can as well be limited by pressure drop. A common representation is the equilibrium temperature associated to the system pressure, dashed lines of Fig 2. Pressure drop-limited systems are commonly reported in pressure cell experiments when no gas reinjection is done after the onset of hydrate formation, see Straume (2017). In these cases, the pressure drops considerably as gas is consumed until equilibrium conditions are reached and the hydrate formation stops, which causes an asymptotic water conversion. This is however not the case occurring in flowlines, where the pressure drop is considerably much smaller than in the mentioned isochoric pressure cells. Fig 2(e) presents the comparison of a simulation with and without pressure drop along the flowline, and it can be observed that pressure drop is a secondary effect on hydrate formation in flowlines.

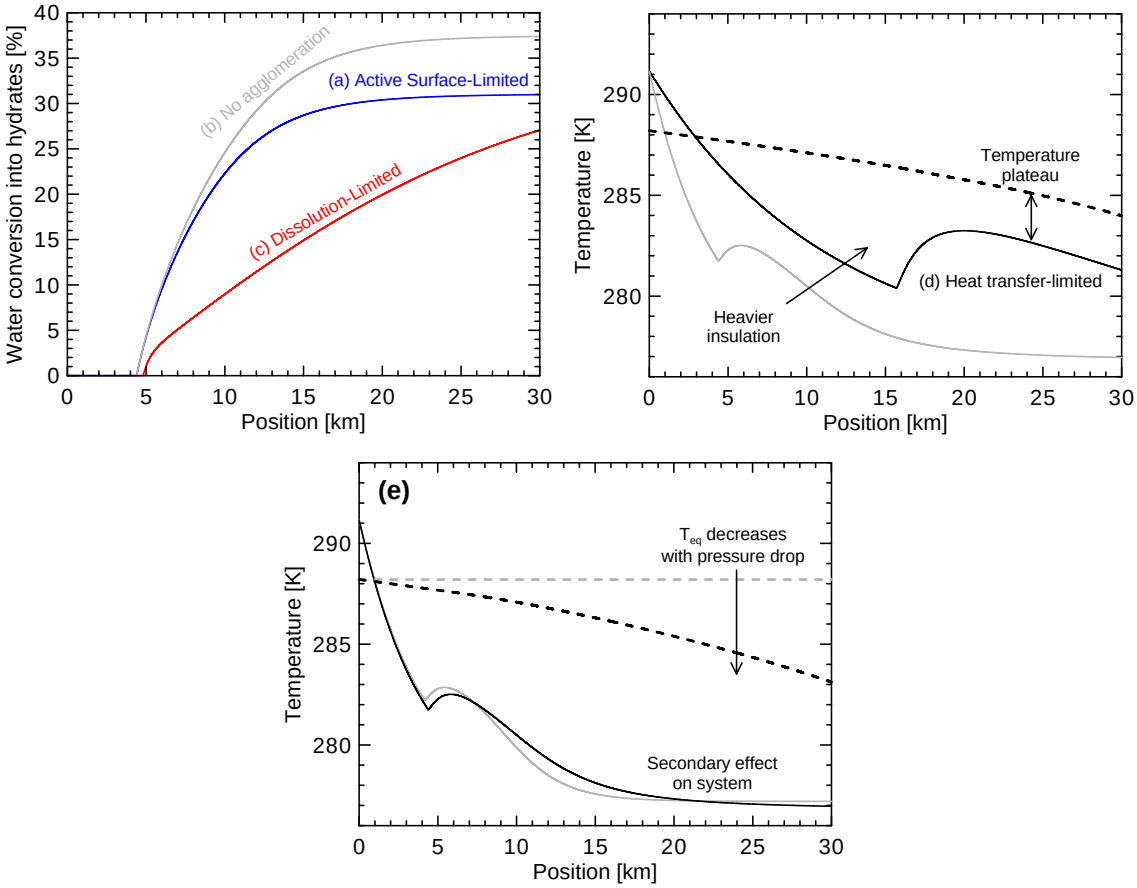

Fig. 2 System behaviors captured by the simulations of gas hydrate formation and agglomeration occurring in gas-(water-in-oil) slug flow. (a) Active surface-limited systems, characterized by an asymptotic water conversion into hydrates. (b) Same simulation, but disabling agglomeration. This evidences that the particle sealing-up process is the major effect on limiting hydrate formation, whereas agglomeration is secondary. (c) Dissolution-limited systems, characterized by a linear water conversion. Simulation considering that gas has chemical affinity with water of one order magnitude smaller (representative of CO_2 in oil or of methane in water). (d) Heat transfer-limited systems, characterized by a temperature plateau. Simulation considering a heavier flowline insulation, with 0.1 W/(mK) thermal conductivity. (e) Comparison with a simulation where pressure is kept constant along the flowline. This highlights that pres-

sure drop has secondary effect on limiting hydrate formation in flowlines.

4 Conclusions

This is the first study in literature that couples the porous-, the particle- and the macro multiphase flow-scales in order to simulate gas hydrate formation, agglomeration and transportability with application to flow assurance. The simulator captures four types of systems:

- Active surface-limited systems, characterized by an asymptotic water conversion into hydrates and occurring for hydrocarbon gases in oil-continuous systems.
- Dissolution-limited systems, characterized by a linear water conversion into hydrates and occurring for gases with low affinity with the continuous phase.
- Heat transfer-limited systems, characterized by a temperature plateau and occurring in heavily insulated flowlines.
- Pressure drop-limited systems, occurring mainly in pressure cell experiments following isochoric procedures, and representing only a secondary limitation of hydrate formation in flowlines.

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