Chemical Engineering Science 64 (2009) 5066 – 5072

Contents lists available at ScienceDirect

Chemical Engineering Science

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

Direct conversion of water droplets to methane hydrate in crude oil

D.J. Turner, K.T. Miller, E.D. Sloan*

Colorado School of Mines, Center for Hydrate Research, Golden, CO 80401, USA

ARTICLE INFO

Article history:
Received 11 July 2009
Accepted 9 August 2009
Available online 18 August 2009

Keywords:
Methane hydrate
Emulsion
Multiphase flow
Particle formation
Petroleum
Size distribution

ABSTRACT

Water droplets suspended in a crude oil were converted to methane hydrate by pressurization in an autoclave cell. Droplet size distributions were monitored using a focused beam reflectance method (FBRM) particle size analyzer as the water converted to hydrate. The droplet size distribution did not change significantly during conversion of nearly all the water to hydrate. The preservation of the distribution during conversion indicates that water droplets act as individual reactors and supports a hydrate shell formation model. Water droplet size distributions were measured with the FBRM probe at multiple shear rates in four crude oils (Albacora Leste, Conroe, Petronius, and a West African oil) with various surface tensions and viscosities. The water droplet size distributions, and thus hydrate particle distributions, were found to be lognormal with breadth increasing with mean. A correlation model has been developed to predict the entire size distribution of water droplets in these oils as a function of viscosity, interfacial tension, and shear rate. The model has been extended to represent gas hydrate particle size distributions in oil after conversion.

1. Introduction

In seafloor pipelines, conditions are often suitable for formation of clathrate hydrates of natural gases, potentially blocking oil production (Hammerschmidt, 1934). The thermodynamics of hydrate formation is well understood (Ballard and Sloan, 2004b), but understanding of hydrate growth mechanisms and associated rates has been elusive. Reasons for the dearth of hydrate formation data in production pipelines include the following:

1. hydrate formation thermodynamics were prerequisite to understanding hydrate formation driving forces controlling mass/heat transfer and kinetics,
2. the tools available for inspecting the hydrate phase *in situ* during growth have only recently become available, and
3. formation mechanisms are inherently very complex and system dependant, involving multiphase flow and possible limitations by mass transfer, heat transfer, or intrinsic kinetics.

Recent developments have now overcome the first two barriers to understanding hydrate formation. For the most part, hydrate thermodynamic models now have almost the same accuracy as experiments (Ballard and Sloan, 2004b) and so understanding of the thermodynamics of hydrate formation is now adequate for industrial purposes. Additionally, the recently developed focused beam reflectance method (FBRM) of particle size analysis (Ruf et al., 2000) provides a tool which now allows particle size distributions to be rapidly measured *in situ* in highly concentrated emulsions and suspensions.

It should be noted that Bishnoi's laboratory has defined the standard in hydrate kinetics over the last three decades. Bishnoi and coworkers have produced a paradigm-defining series of publications, commencing with the publication of Vysniauskus and Bishnoi (1983), progressing through the detailed modeling and experiments of Englezos et al. (1987a,b); and continuing recently in the same tradition with the work of Clarke and Bishnoi (2005) (to mention only a few). In their study of the formation of carbon dioxide hydrates in water, Clarke and Bishnoi (2005) demonstrated the usefulness of the FBRM probe for monitoring particle size evolution while measuring hydrate formation rates.

Due to the complexity of the problem, it has been difficult to measure and model hydrate formation in real hydrocarbon liquids for large amounts of hydrate formation by separating mass transfer, heat transfer, and hydrate intrinsic kinetics. The current work is another approach, considering the development of hydrate particles as they form in emulsified water in real oils. A FBRM particle size analyzer is used to examine hydrate particle growth mechanisms in highly concentrated water-in-crude oil dispersions, by monitoring water droplet and hydrate particle size distributions *in-situ*, as water is converted to methane hydrate at high pressure.

* Corresponding author.
E-mail address: esloan@mines.edu (E.D. Sloan).

0009-2509/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2009.08.013

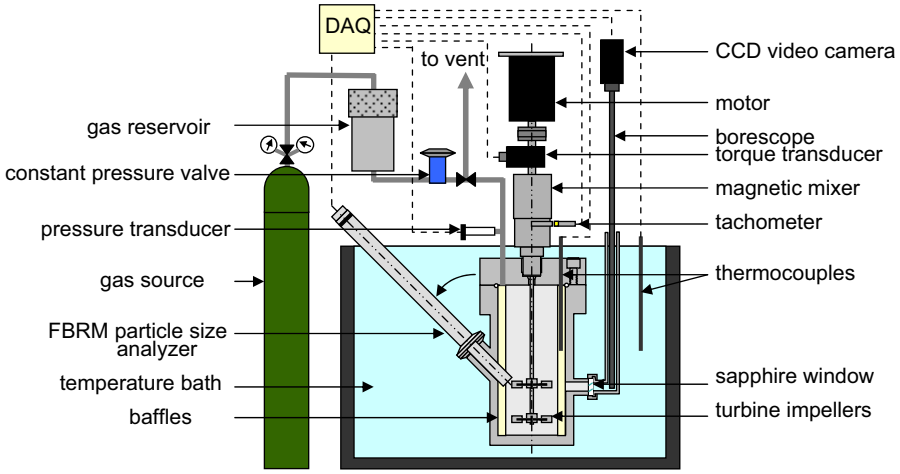

Fig. 1. Diagram of autoclave cell hydrate formation apparatus with particle size analyzer.

2. Experimental section

Hydrate formation in water-in-oil dispersions was studied in an autoclave reactor by monitoring the water droplet size distribution during the water-to-hydrate conversion process. Particle size distributions were measured at elevated pressure as a function of time using a FBRM particle size analyzer capable of measuring particle widths (chords) between 0.5 and 1000 microns.

2.1. Experimental setup

The hydrate formation experimental apparatus is shown in Fig. 1. The hydrate formation cell was a cylindrical autoclave cell with 10.16 cm inner diameter and 22.86 cm inner depth. A combination of two six-blade squared-pitch turbine impellers (diameters = 5.08 cm) and baffles (width = 1.90 cm) promoted radial and axial flow over centripetal flow. This flow pattern maximized droplet and particle entrainment, while minimizing gas bubble entrainment.

An FBRM particle size analyzer (Lasentec, Model D600X) was used in this study. This instrument utilizes a 795 nm wavelength laser that scans rapidly (4 m/s) across a sample of particles. As the laser intersects a particle, light is reflected back to the probe. The product of reflectance time and scan speed give the chord length, which is the measured length across a particle (Underwood, 1970).

The probe was inserted into the autoclave cell at a 45° angle facing the upper turbine blade, causing droplets and particles that were expelled radially outward from the blade to deflect off the probe window. This effectively allowed sampling of all particles present in the cell, while preventing a buildup of particles on the probe window. Hydrate formation experiments were conducted at constant gas pressure, analogous to an oil-producing pipeline. Constant pressure was maintained by a Tescom pressure-regulating valve, which separated the hydrate formation cell from a gas reservoir. This valve allowed for gas stored in the reservoir to be passed to the cell, replacing gas consumed during hydrate formation. The gas reservoir was filled with 99.99% pure methane gas at ~13.8 MPa. Gas consumption was determined from the pressure decrease in the reservoir.

Impeller speed was measured by a tachometer during operation, so that the shear rate in the system could be estimated. Experimental impeller speeds could be varied from 0 to 800 rpm, but were typically kept at 400 or 500 rpm. The entire autoclave cell was inserted into a temperature-controlled bath, maintained at 277.2 K.

2.2. Experimental procedure

Droplet size distributions were measured for water in four different crude oils, namely (with suppliers), Albacora Leste (Petrobras), Conroe (ExxonMobil), Petronius (Chevron), and a West African crude with proprietary label (ExxonMobil).

Relevant physical properties of each of the oils were measured in the laboratory. The viscosity of each oil was measured as a function of shear rate using a Fann model 35A viscometer with concentric cylinder arrangement (Fann Instrument Company 1996), the interfacial tension of each oil with water was measured using a droplet buoyancy force-balance technique (Wilkinson, 1972) and the densities were measured gravimetrically.

All experiments were performed at 277.2 K, which is the approximate value of the worldwide seafloor temperature below 900 m (Sloan, 2000, p. 5).

Each experiment was performed by filling the autoclave cell with a fresh sample of deionized water and oil in respective volume fractions, 0.35 and 0.65, of the total sample liquid volume, 1.18 liters. The autoclave cell was allowed to cool overnight to 277.2 K to ensure that thermal equilibrium was achieved.

The impeller was set to the desired speed and the water droplet distribution was monitored until the distribution remained steady with time. Typically, a steady-state distribution was achieved after 2–3 h.

A hydrate equilibrium prediction program, CSMGem (Ballard and Sloan, 2004a), predicted that the mixture of 99.99% methane gas and Conroe oil at 277.2 K would form sI methane hydrate above an equilibrium pressure of 3.88 MPa. Experiments were performed at one of two pressures by setting the constant pressure valve to 4.35 or 4.92 MPa.

Two events, coincident within each experiment, were used to identify hydrate nucleation in the autoclave cell:

1. the onset of rapid gas consumption after cessation of absorption, and
2. a sudden drop in the number of particles registered by the FBRM instrument (presumably corresponding to a change in the reflective properties of the droplet in the oil experiments).

The droplet size distribution and pressure in the reservoir were monitored through the process of hydrate nucleation and growth, until significant growth was no longer apparent. The time required for each experiment was on the order of one week.