Resolving CO₂ and methane hydrate formation kinetics

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Abstract We analyse the kinetics of CO₂ and methane hydrate formation. The characteristic formation times are associated with different steps of the formation process. Conditions for minimising these rate times are identified while maintaining a regime where CO₂ hydrate is formed and methane remains predominantly gaseous. This involves a rapid pressurisation routine and accesses points well above the phase boundary in order to enable faster kinetics. Conditions for optimising rates and times, to obtain maximum CO₂ uptake with respect to CH₄, were identified as (1) stirring faster than 1,000 rpm, (2) rapid pressurisation to a partial pressure of around 50 bar for CO₂ and (3) re-use of contaminated as opposed to fresh water.

Keywords Natural gas · Contamination · CO₂ · Hydrates · Kinetics

Introduction

Concerns about CO₂ are currently driving the search for novel methods of separating it from either a natural gas or from an exhaust gas combustion effluent stream (“flue gas”). The classical method of solvent absorption is both energy

and capital intensive above ca. 15% v/v CO₂ in the gas (Kohl and Nielsen 1997). The most promising methods require a carbon capture method that uses phase separation to yield a CO₂ waste stream in a form where it can be sequestered by, e.g. reinjection. Such schemes include cryogenic methods that yield either a CO₂-rich liquid or a solid. The problem with these is the low temperature which is required.

An alternative method for doing a phase separation is to form a CO₂ hydrate. Although methane hydrates have been extensively studied, it is only recently that CO₂ hydrates have been a focus of interest and then overwhelmingly for cleaning up combustion exhaust products (Spencer 2005). The reason for this is easily seen from the phase diagram (Fig. 1). It is much easier to keep nitrogen purely in the gaseous phase while trapping CO₂—and thus exhaust gases would be easier to separate using hydrates. Figure 1 also shows the hydrate formation curve for another commonly occurring natural gas contaminant, H₂S. This also is well removed from methane. It is shown only as a reference because in this study we are concerned with CO₂ removal from methane.

On the other hand for the contaminated natural gas problem (Golombok and Nikolic 2008), the equilibrium lines (methane and CO₂) are rather close together. However, formation of hydrates is an easier option for the contaminated gas cleaning problem than for flue gas. Exhaust gases are generated at hot temperatures and generally low pressures, and even after heat exchange with, e.g. a steam turbine feed, the typical temperature and pressure will be 150°C and 1 bar, respectively. Contaminated natural gas on the other hand, emerges from the ground at temperatures around 50°C and with a pressure of 50–250 bar (although surface facility manifold pressures are restricted to 150 bar). There is thus more room for expansive cooling in the contaminated gas cleaning scenario.

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Fig. 1 Hydrate phase boundary for contaminated natural gas components

In contrast, the flue gas cleaning problem is clearly more universal and this may explain why it has till now been the focus of attention when looking at hydrate methods for removing CO₂. Another reason for the contaminated gas application is precisely the high pressures that enable faster kinetics (see below).

Close examination of the methane and CO₂ boundaries shows a region (for CO₂) between 0–10°C and 10–60 bar where in theory the methane is present as a gas but where the contaminant is expected to be in the solid (hydrate) state. The question then is whether the two gaseous components will behave independently when present as a mixture. Many workers (Lee et al. 1997) have assumed formation of a mixed hydrate. A previous study based on exhaust gas seemed to assume that mixed hydrates would be formed (Kang and Lee 2000). However, more recent work does indicate that “pure” hydrates would be formed (Kang et al. 2001). Dalmazzone et al. (2004) worked with methane and contaminated water—but they explicitly state that their results depend on the fact that methane is barely soluble in water. What is clear, however, is that there is a region between the methane and CO₂ pure hydrate boundaries where formation of CO₂ hydrate is more favoured although the end result will be an equilibrium composition between the two lines. However, it would be reasonable to assume differential rates of formation—if only on the basis that CO₂ is much more soluble than methane in water. Therefore, we seek to establish the different rate of formation of CO₂ hydrates as opposed to that for methane in order to provide a basis for a possible separation.

Experimental

We may break up the formation of hydrates from a gas feed into a number of steps.

Equation 1 describes the mixing of the incoming gas with water to give dispersed microbubbles of gas in the liquid phase. This is then followed by solvation of the gas molecules. These solvated molecules then interact with surrounding water molecules to form hydrate nuclei, which then grow either by diffusion of water and gas to the surface of the solid or by agglomeration. We have assumed the normal ca. 6 coordinated water clathrate structure associated with type 1 and type 2 hydrates.

The rate of reaction (3) is dependent on how much of the gas is dissolved in the water. This requires a good mixing system so that concentration in water is not simply determined by gas/liquid contacting. Provided that is the case then the rate of hydrate formation is purely dependent on the solubility of the gas in water. For CO₂ this is not a problem, as especially at elevated pressures it is highly soluble in water, however, methane is practically insoluble in water (Golombok 2003). We thus expect the hydrate formation rate for methane from Eq. 3 to be significantly lower than for CO₂ even if we are on the hydrate formation side of the phase boundary for both components. Our initial experiments have thus been concerned with measuring these different times of formation in order to see if it is possible to select a regime where CO₂ reacts to hydrate fast but methane is slow.

Experiments are carried out in a stainless steel autoclave with a maximum process pressure of 100 bar. The autoclave has a total volume of 380 ml, contains 100 ml distilled water and is immersed in a perspex container bath through which is circulated a distilled water mixture, which is cooled by a temperature regulated chiller. Gas is fed via

a Brooks mass flow and pressure control systems into the autoclave and is added to the system on the second time scale—i.e. much shorter than the subsequent hydrate formation times. Gas is fed into the autoclave via an on-axis gas liquid mixer. This is a gas injector stirrer manufactured by Premeg Reactor AG, Lengnau, Switzerland. This is connected via a flexible magnetic coupling to an external shaft driven by a variable speed electric motor. The gas pressure is recorded by a Keller digital manometer.

This hydrate formation path consists of rapid pressurisation of a pre-cooled system and thus follows a different route (Fig. 2) from that usually followed for hydrate creation. The standard method for observing hydrate formation is to cool a pressurised gas/water mixture (Fig. 2a). A slight pressure decrease is then observed due to contraction effects as well as enhanced solubility in water as a result of temperature decrease. When the hydrate boundary is reached, a more rapid decrease in pressure is observed.

The problem with the last discussed previous formation pathway is twofold:

1. It only gives an indication of hydrate formation kinetics on the phase boundary line and not at pressures elevated above this. An ideal experiment requires that temperature lowering stop the moment the hydrate boundary is reached—this is difficult to

determine so in fact the measured hydrate formation rate is effectively smeared out over a range of p , T values along the phase boundary line.

2. It requires a time consuming pseudo steady state lowering of temperature. This is not realistic compared to a real continuous process where pressure increase can be imposed much more quickly and efficiently than a temperature decrease (see [discussion](#) for the elevated pressures associated with natural gas in the introduction).

In our case, to avoid ambiguous solvation effects, the system is initially pressurised to a level below the hydrate phase boundary line. Once this is stabilised the pressure is raised to various levels above the phase boundary line. Typical responses (Fig. 3) display the characteristic response times associated with hydrate formation in Eqs. 1–3: there is an induction time τ_{ind} associated with mixing and solvation and a pressure decay time associated with hydrate formation. The latter is defined as τ_{dec} —the time for the pressure to decay from its peak value half way to its ultimate stable equilibrium value. Clearly for any industrial process that we wish to operate, we will require τ_{ind} and τ_{dec} for CO_2 to be small whereas the corresponding values for methane should be long. To find this regime, we have to characterise the behaviour of each of the two species separately.

Fig. 2 Two different pathways for hydrate formation in a batch autoclave. **a** Cooling with temperature contraction followed by hydrate formation on the phase boundary line. **b** Fixed temperature with rapid excess pressurisation above the phase boundary line

Results and discussion

A well-known phenomenon in kinetic studies of hydrate formation is the problem of poor result reproducibility in characteristic reaction time measurements, which has been related to the thermal “history” of the water, i.e. whether it

Fig. 3 Graph showing typical pressure time response for hydrate formation using Fig. 2b. The graph shows the characteristic long induction time expected with a non-dissolving gas (methane) in distilled water

has previously been used for hydrate formation and the purity of the water which is utilised. We observe this in measurements of τ_{ind} , which show a large spread round the mean value as measured by the standard deviation as recently shown by McCallum et al. (2007). However, in our experiments this spread (as measured by the standard deviation) decreased with the stirring rate although the values themselves are in agreement with those obtained from previous studies (Sloan 1990).

Some previous result inconsistency may have arisen because the hydrate formation process was limited by insufficient mixing. The kinetic effects associated with mixing can be ruled out by carrying out measurements at varied stirring rates and looking at the associated values of the induction time τ_{ind} . The induction times also show a dependence on stirring rate. Figure 4 shows that induction times can be brought down by increasing the stirring rates but that a higher stirring rate is required for methane. This relates to the mechanism we have described in Eqs. 1–3. Equation 2 has an equilibrium constant much more to the right for CO_2 than for methane (as evidenced by the greater solubility of CO_2). The result is that we need to physically disperse the methane much more intensely so that the transfer to the limited solubility phase is maximised and no longer depends on the axial stirring dispersion. This is the reason that much higher stirring rates are required to obtain the lowest induction times. The sensitivity with increased stirring (as measured by slope) is lower for CH_4 than for CO_2 .

Contaminated water or water that has shortly before been used for hydrate formation appears to be most favourable for rapid hydrate formation (Sloan 1990). This would make sense within the context of a continuous reactive flow loop which aimed to extract gas contaminants using hydrate formation. In such a scheme, the

Fig. 4 Induction time as a function of stirring rate for methane and CO_2 in distilled water

contaminants would be removed as a slurry while the cleaned-up natural gas emerges from the gas/liquid contactor. Clean water would then be regenerated from the slurry by a regenerative process rather similar to that used for the amine treater. The regenerated water thus is “reused” and not fresh.

Whereas the induction times had different behaviours with stirring rates for methane and CO_2 (Fig. 4), the pressure decay times τ_{dec} are identical. These observations make sense within our modified mechanism model based on Eqs. 1–3. Once the molecules are solvated in water, any subsequent stirring maximises the chance of hydrate aggregation and this is what τ_{dec} is measuring. τ_{dec} decreases quickly with stirring rate so that it is clear that above ca. 1,000 rpm that we are looking at Eq. 3 and not simply at the mixing limit—although we have shown above that we need to be somewhat higher to minimise the induction times. This stirring rate is at the top end of the range observed by previous workers. The times do agree well with the reverse process, i.e. the break-up of gas hydrates back to the gas/liquid side of the phase boundary as observed by Rehder et al. (2004) and also correlates with times for water and liquid CO_2 as reactants to hydrate formation when CO_2 dispersion is optimised (Warzinski et al. 2008). Figure 5 clearly indicates that once the gas molecules have been hydrated then the ordering of the water structure around the “guest” molecules seems independent of the species.

These time response results fall within the context of previous observations where rapid hydrate formation was observed in water that had shortly before been used for hydrate formation (Sloan 1990). If applied to a continuous reactive flow loop contaminants would be removed as a slurry while the cleaned-up natural gas emerges from the gas/liquid contactor. Clean water would then be regenerated from the slurry by a regenerative process rather similar to that used for the amine treater. The regenerated water thus is “reused” and not fresh to ensure optimum rapid high hydrate formation rates. These high rates can be

Fig. 5 Effect of stirring rate on pressure decay half time τ_{dec} of methane and CO_2

further optimised by ensuring effective supersaturation of the water by overpressurising above the hydrate phase boundary. This utilises our alternative pathway identified in the discussion of Fig. 2.

The foregoing mixing-dependent experiments were carried out at moderate start pressures (ca. 30 bar). However as indicated above (Fig. 2 and associated discussion), a realistic process will involve contacting a pressurised gas stream with water. In particular, one would wish to apply a hydrate cleaning process at a pressure corresponding to the typical operating pressure of a gas processing plant—the so-called “surface facilities manifold pressure”. This is typically in the range 80–150 bar—dependent on the life of the gas field whose output is being processed: well-head pressures typically decay over time. The relevant pressure for a pure component is the partial pressure in the well gas stream. Assuming a 50/50 mixture as a representative contaminated natural gas, one then would be looking at partial pressures in the range 40–75 bar for the pure components. Accordingly, we have looked at the induction times for take-up of pure components as gas hydrates over this range. Figure 6 shows the effect of varying the gas pressure on the induction times for pure component gas hydrates in water. The starting conditions were 3°C and the system was overpressurised to the value given on the *x*-axis (Fig. 2b). The time τ_{ind} for hydrate induction is then measured and reported on the *y*-axis.

The main result is that $\tau_{\text{ind}}(\text{CO}_2) < \tau_{\text{ind}}(\text{CH}_4)$. There is thus a pressurisation regime where CO_2 hydrates form quickly and methane hydrates hardly form at all. Such effects during oversaturation of gases in liquid for hydrate formation have previously been observed by supercooling. However for our purposes, temperature lowering is too slow and energetically consuming a process compared to rapid pressurisation, especially given the already high facility manifold pressures mentioned above. Overpressurisation is

Fig. 6 Induction time τ_{ind} for formation of gas hydrates as a function of the initial pressurisation for pure CO_2 and methane gas in an autoclave. All measurements were carried out at 3°C, at maximum mixing rates for CO_2 and methane. The hydrate formation process was that illustrated in Fig. 2b

thus the preferred hydrate formation process option. A comparison of the two curves for CO_2 and CH_4 indicates a pressure regime where selective formation of CO_2 hydrate occurs. Of course in a gas mixture then (to a first approximation) these are the corresponding partial pressures. This indicates the optimal operating pressures for a variety of mixed gas compositions currently being studied.

Conclusion

In this study, we have demonstrated that there is a pressure regime where CO_2 hydrates form much faster than methane hydrates. Increasing the initial pressure decreases the hydrate induction time τ_{ind} , i.e. the nucleation time. This is basically supersaturation of a crystallising solution system as the times for CO_2 remain shorter than for methane due to the differential solubility.

Pressure decay times for methane and CO_2 decrease identically with stirring rate reaching minima around 1,000 rpm for the gas injector system. This suggests that the mechanism is bringing (post-induction) hydrate nuclei into contact with supersaturated volumes of the solution.

Current work is aimed at a continuous separation process. This study used distilled water to study the origin of fundamental differential kinetic effects which happen on a shorter time scale in contaminated systems. In practical applications one prefers to use, e.g. contaminated brines and the differential effects between CO_2 and methane are currently being assessed in those systems.

This study has not addressed another natural gas contaminant—namely H_2S , which for obvious reasons cannot be the subject of such a simple lab study. This will be much more easy to differentiate from methane because the phase boundary lines are much more distant from methane than that of CO_2 . This is the subject of ongoing study.

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