Formation of Propane Clathrate Hydrates for Wastewater Treatment

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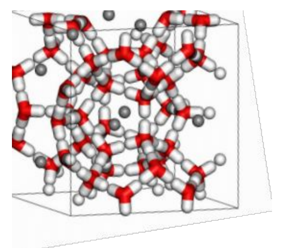
Abstract

Experimentation to test effective scaleup of propane hydrate formation for use in wastewater separation. A reactor system was designed and constructed, including a cooling tank and support system. Several cooling systems were examined, as well as the impact of agitation on nucleation time.

Introduction

Hydrates are cage-like crystals formed from hydrogen-bonded water molecules, enclosing a central "guest" molecule. These structures have several unique properties; their crystal packing structure allows for denser storage of certain guest molecules than in their natural gaseous state, and they can be formed at temperatures above water's native freezing point provided a sufficient pressure.

Gas-hydrates have promising use-cases in gas storage, as their crystal packing structures often allow a high gas density in solid form, as well as an effective de-watering technique for impure waters or waste.



Methods and Materials

In this research experiment, we conducted tests in both a large reactor and a small batch reactor. Experiments required propane gas, tap water, a Merlin Recirculating Chiller, a water bath, and the following reactors and their mechanical supports.

The Large Reactor: To begin, we fill the proprietary, glass reactor with 100mL of tap water. We then fill the cooling bath with tap water and place the cooling coil inside the water bath. Next, we flush the reactor with propane gas and purge the system three times to remove any atmosphere. The reactor is then pressurized with propane to 60 psi. The chiller is powered on, set to -5°C, and allowed to cool the water bath. When the operating temperature for hydrate formation is reached, the gas inlet is closed and the vessel is sealed. In experiments conducted with the large reactor, no visible hydrates were formed, there was no pressure drop signifying hydrate formation beyond the saturation of the solution, and we were largely unable to hit the hydrate formation temperature at 60 psi of +4°C, using external cooling.

The Batch Reactor: A Parr Instrument Series 4570 HP/HT 1000mL reactor with internal cooling coil and stirrer is filled with 100mL of tap water, then followed the same propane to purging method. The reactor was then pressurized with propane to 60 psi, leaving the gas inlet open. The stirrer was set to various rates (from 100-650 RPM) in various tests. We turned on the chiller, set to -5°C, and chilled the system, until the system reached +4°C, at which point the gas inlet was closed and pressure P1 was timestamped. Further data collection was taken in 5 minute intervals. When the pressure stabilizes, P2" is recorded. We saw immediate success in meeting the hydrate formation temperature of +4°C and forming hydrates.

Results

Figure 1 below demonstrates the gas uptake process as a function of time with sample data from stirred batch reactor. The guest propane is introduced in gaseous phase to water, and under pressure dissolves into the aqueous phase at the gas-liquid interface. The induction time, therefore, is the time between generating a supersaturated solution and the nucleation that spurs hydrate growth. In Fig. 1, point (I) marks the dissolution phase, where gas pressure equilibrates under the lower temperature and also enters the aqueous phase to form a supersaturated solution. Point (II) marks the end of induction time, and the beginning of nucleation. The start of hydrate growth is characterized by a rapid uptake in gas, as gas enters the hydrate phase, and by a temperature spike, because the formation reaction is an exothermic one. The former of which can also be observed qualitatively as a downward spike in gas pressure.

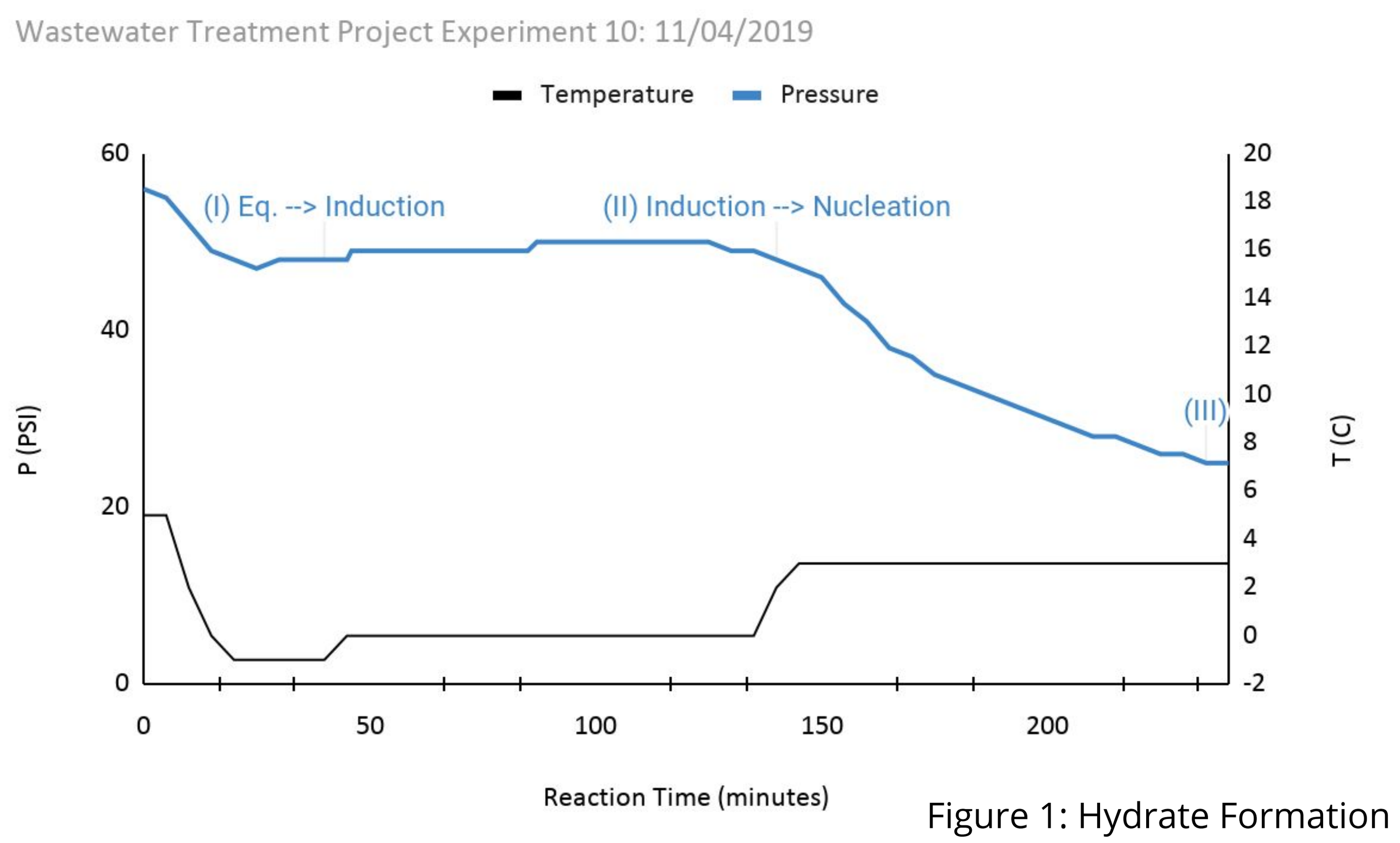


Figure 1: Hydrate Formation Curve

The formation of the supersaturated solution, followed by the nucleation phase, are key characteristics of hydrate formation supported by literature. This was further corroborated by visual confirmation of hydrate formation precipitated around the cooling coil, seen across multiple experiments, as pictured in Figure 2.

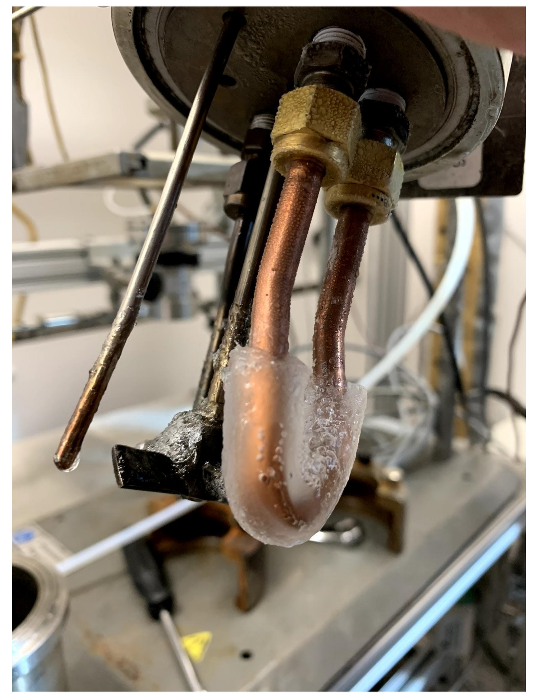


Figure 2: Hydrate Ice Formation

In Figure 3, the time T = 0 represents the point at which the reactor vessel reached the hydrate formation temperature for 60 psi, or 4° C. The reactor was filled with 100 mL of water, and pressurized with propane to 60 psi, until equilibrated at 4° C, after which the vessel was sealed and internal cooling continued consistently. This is a good qualitative representation of the pressure development as the hydrate formation reaction proceeds and gas is taken up. RPMs given are the average for each experiment.

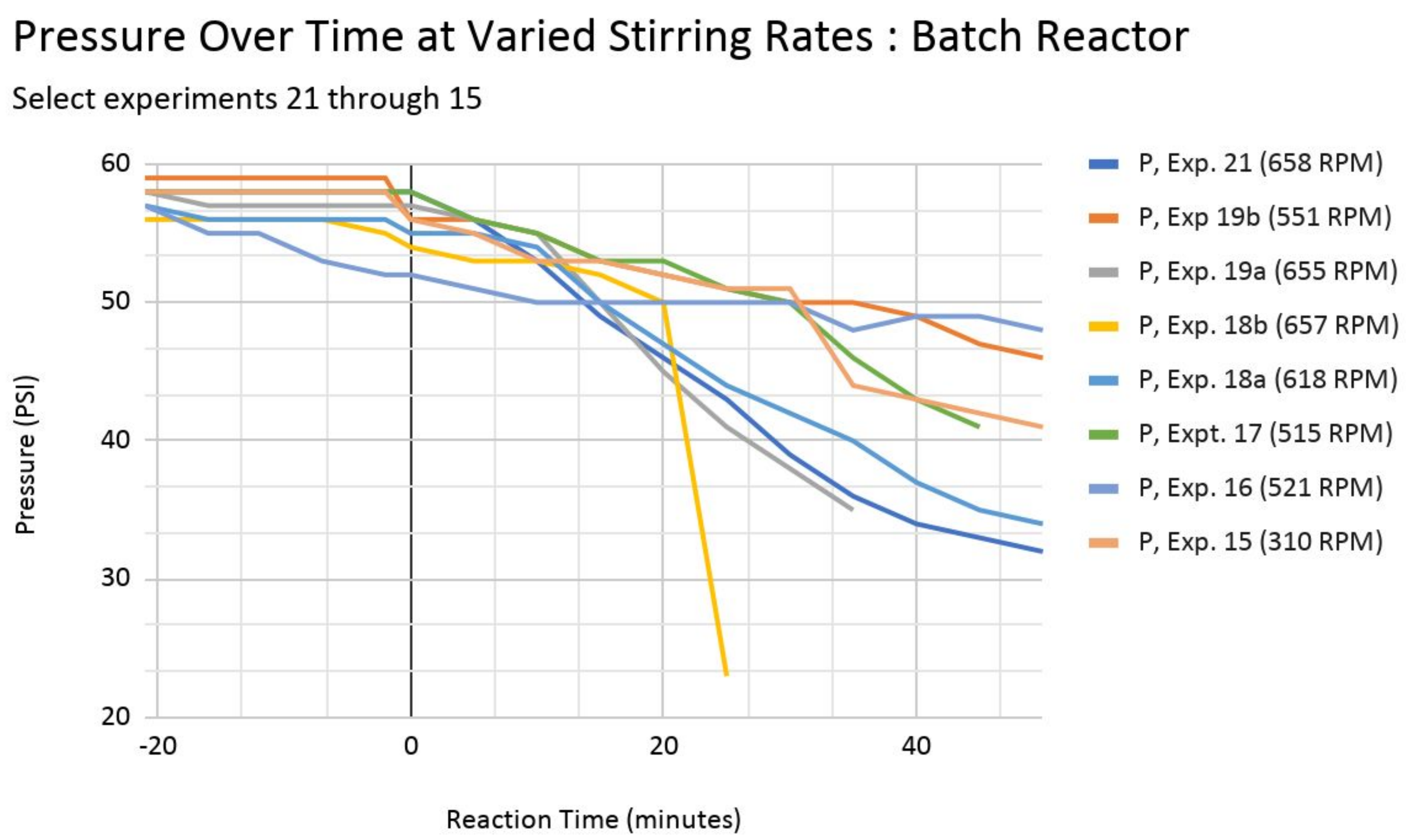


Figure 3: Hydrate formation Curves as a Function of Stirring

Conclusions

Large reactor vessel saw minimal hydrate formation beyond supersaturated solution. Glass vessel was insufficiently cooled to reach our operating temperature.

Batch reactor vessel served as proof of concept of hydrate formation and separation. Nucleation was most effective with increased agitation.

Future research will study the achievability of using propane hydrates to separate water and contaminants on a larger scale, using a 2L reactor and the external cooling method. The larger reactor will require internal stirring methods and additional chilling to reduce the temperature to reach hydrate formation temperature.