Combustion of Methane Hydrate

Melika Roshandell[1], Jordan Glassman[2], Matt Khalil[2],
Peter Taborek[2], and Derek Dunn-Rankin[1]
[1]Department of Mechanical and Aerospace Engineering, University of California,
Irvine, California, USA
[2]Department of Physics, University of California Irvine,
Irvine, California, USA

This paper examines the combustion behavior of methane as it is released from clathrate cages in a methane hydrate. Gas hydrates (clathrates) are ice-like crystalline solids that encapsulate guest gas molecules. It has become known that a significant methane storehouse is in the form of methane hydrates on the sea floor and in the arctic permafrost. While this methane represents a potential mega-resource of energy it also represents a potential source of strong greenhouse gas. To better understand the important implications of direct utilization of fuel clathrates, we describe the structure and the combustion behavior of methane hydrate samples. The combustion studies involve determining the rate of ice melt and water evaporation during the hydrate burn. Different geometries are studied, including powder and spherical shapes.

1 Introduction

Natural gas hydrates are crystalline solids composed of ice and gas, also known as clathrate. The gas molecules are trapped in ice cavities composed of hydrogen-bonded ice molecules.

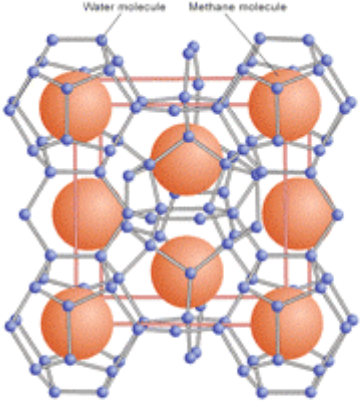

Figure 1. Structure of methane hydrate [5]; the methane is not bonded but caged by the surrounding water molecules.

Gas hydrates form at an elevated pressure and low temperature when the gas concentration exceeds the solubility limit [for example for methane hydrate, at 277 K, hydrate formation begins at pressures above 50 atmospheres] [1]. In an ideally saturated methane hydrate, the molar ratio of guest methane to water is approximately 1:5.7. The guest molecule in hydrates can be methane, ethane, propane, and carbon dioxide or their combinations [1,2], and the different guest molecules produce hydrates at different temperatures and pressures and with different molar ratios of guest-to-cage molecules.

Crude oil resources are finite, and an active search for alternative resources is in progress. One source of interest is the enormous quantity of methane gas hydrate found at the bottom of the ocean [3]. The study of gas hydrates has attracted researchers for many years in the oil and gas industry since hydrate formation in pipelines can hamper oil and gas recovery. More recently hydrate research has expanded to examine their stored energy content. There has also been a recognition that hydrates can concentrate methane with relatively little work (e.g., as compared to liquifaction or highly compressed

Correspondence to: mroshand@uci.edu

gas states) for fuel transport and that the methane contained in natural hydrate deposits represent a substantial energy reservoir [4]. The energy required for dissociation of the hydrate is far lower (< 15%) than that available from reacting the trapped methane.

Interestingly, although methane hydrates are being considered as an alternative source of energy, there have been few studies on the combustion of this ice-like fuel. In one of the few available studies, the propagation of a flame above a methane hydrate cake in an air laminar boundary layer was investigated [4]. By igniting the methane hydrate from the downstream side, the experiment showed flame propagation against the air flow and found it to be independent of free stream velocity. The work concluded that the propagation speed is determined by the dissociation rate of the methane hydrate [4].

The purpose of the present study is to investigate the burning of methane hydrate in a free-convection configuration and to examine experimentally the relationships between the burning behavior of hydrates and their size and shape. In particular, the work shows that the burning behavior depends significantly on the amount of water evaporated from the hydrate by the flame.

2 Experimental Procedure

To determine the effect of hydrate shape on the burning behavior of the methane released from the hydrate, two different geometries were studied, a packed sphere and loose powder. The methane hydrates for this experiment were made from fine ice powder. The ice powder was made by grinding droplets of nanopure water frozen with liquid nitrogen. The ice droplets were ground with a commercially available coffee grinder to yield particles with size on the order of hundreds of microns. For the packed sphere of methane hydrate, the ice powder was pressed using a custom aluminum mold of matching hemispheres. The sphere size was nominally 3 cm in diameter. The weight of the spherical balls or powder ice was obtained before placing them in the pressure cell for clathratization. The pressure cell was sealed using CF flanges and placed inside a commercially available freezer which maintained the temperature at about 260 K. The temperature inside the pressure cell was measured by a standard Pt RTD and the pressure was measured using an Omegadyne PX-309 pressure transducer. To increase the rate of hydrate formation, it is advantageous to raise the temperature inside the cell to temperatures just above freezing. This task is accomplished with a heating jacket made up of resistive heaters and controlled with a simple PID program. These techniques allowed for temperature control with precision below 1K.

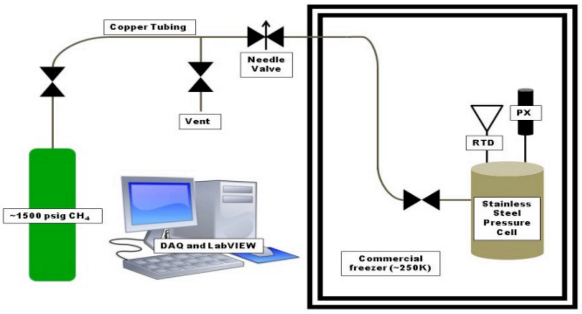

Figure 2. Schematic of the hydrate formation system

A sample run consists of pumping down the entire sealed system using a standard rotary-vane vacuum pump to remove air and other gases, and then slowly pressurizing the system with methane to minimize any thermal transients. The PID is activated and a program of temperature control at around 276-278K is implemented to achieve 80% or more clathration in 72-96 hours. Clathration is monitored by measuring the pressure drop inside the cell as the guest molecule gas is absorbed inside the recrystallizing ice. An estimate of the extent of clathration can be made from the original mass of ice and the overall temperature corrected pressure drop. Figure 3 shows a typical approximately spherical methane hydrate sample.

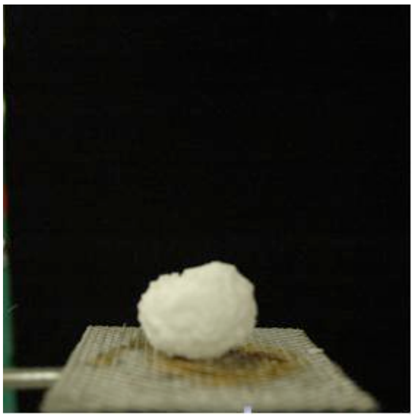

Figure 3. Approximately spherical methane hydrate sample with 3 cm diameter.

After creating the methane hydrates, a simple experiment was conducted to measure the ratio of water melting and water evaporating from the hydrate. For this experiment, both spherical methane hydrates, and loose powder methane hydrates were tested, as shown in Figures 4 and 5.

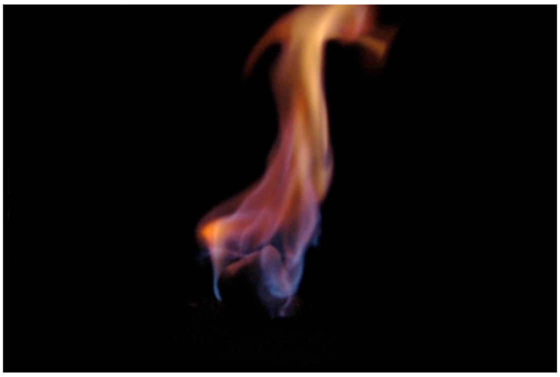

Figure 4. Spherical methane hydrate burn

Figure 5. Powder methane hydrate burn

Methane hydrate was placed on the mesh with a beaker beneath the mesh stand. The hydrate was ignited using a small propane torch, and the burn was monitored using a digital video camera (Casio DX-F1). During the burn the amount of water melt was collected using beaker below the mesh. In addition, photographs of the flame during the key periods of the burn were taken using a Nikon D70 digital SLR camera. After the flame self-extinguished, the mass of the remaining ice or hydrate and the collected water from the burn was measured, in order to determine the amount of evaporated water into the flame, the normalized results from the spherical methane hydrate experiments are presented in Table 1 and from the powder methane hydrate in Table 2.

Table 1. Spherical Methane hydrate

Mass of Original Sample	Hydrate Fraction	Water mass in original sample	methane mass in original sample	ice remaining	water remaining	water evaporated	water vapor/methane molar ratio
53.3	0.3	51.1	2.2	32.9	17.1	1.1	0.5
49.6	0.8	44.6	5	12.4	30.5	1.7	0.3
50.1	0.4	47.2	2.9	29.4	15.3	2.5	0.8

Table 2. Powder Methane hydrate

Mass of Original Sample	Hydrate Fraction	Water mass in original sample	methane mass in original sample	Ice remaining	water remaining	water evaporated	water vapor/methane molar ratio
35.2	0.87	31	4.2	5.2	10.5	5.3	3.3
57.9	0.86	51.2	6.7	5.9	36.4	8.9	1.2
37.6	0.87	33.2	4.4	5	9.6	18.6	3.7

3. Discussion

As mentioned above, Figure 4 shows the burning of the spherical methane hydrate and Figure 5 shows the powder burn of the methane hydrate. The images were selected to highlight the significant qualitative differences between the burning of these two forms of hydrate. In both cases, during the burning process, the surface layer of the hydrate melts which releases the caged methane in that layer of hydrate. The released gas feeds the flame, and heat from the flame melts the next layer of hydrate. During this process some of the water evaporates and joins the fuel gas and some of it remains as liquid water and drips from the surfaces of the hydrate. The more water that evaporates, the cooler the flame. If all the water were to evaporate (i.e., none drips as liquid) the molar ratio of water to fuel would be greater than 5 and the adiabatic flame temperature of such a mixture is so low (1300K) that it seems unlikely that a flame could be self-sustained. It appears, therefore, that the combustion process proceeds so as to ensure a reasonable division between melted and evaporated water.

A further complication, however, is that the rate of methane release is also a function of methane hydrate shape. According to the experimental results, the remaining ice in the powder form is, on average, 4 times lower than the amount of ice left in the spherical form. This is probably because the larger surface area available in the loose powder allows a more rapid hydrate melt and a concomitant increase in methane release to keep the flame burning. In the case of the spherical methane hydrate, the hydrate ignites, and for the first 5 seconds, the flame starts from the bottom of the sphere to the top. After this time, the flame moves to the top of the sphere as shown in Figure 6.

A significant experimental challenge was the variability in the clathrate samples and the determination of the amount of clathrate in each sample. As shown in Table 1, in spherical form, the estimates based on residual ice mass showed that only 30% of the initial water used was clathrated. As for the powder form, 90% of the initial water used was clathrated, but even in this case the amount that evaporated versus melted was highly variable. It is clear that producing a reliable clathrate sample will be an important part of future work on this project.

Figure 6. The Spherical methane burn after approximately 5 seconds

It is a subject of continuing study, but it appears that with the spherical hydrate, a melting/refreezing process seals part of the hydrate surface so that gas is released only from the top surface, sustaining a candle-like flame. We saw the same behavior using cylindrically shaped hydrate samples [6]. Figure 6 also shows a small blue jet flame. We presume that this is caused by the release of trapped methane in an ice pocket rather than smooth release from the hydrate. Again, it is difficult to confirm all of the structures in this complex hydrate, but there is a clear difference between jets of fuel burning and the steady burn of the hydrate.

Another interesting result from the experiments was the variation in flame temperature for the different hydrate forms. We determined the temperature using optical pyrometry. As mentioned earlier, photographs of the hydrate flame were taken with a Nikon D70, ensuring that the image was not saturated. The relative intensity of the red, green, and blue from this camera had been calibrated with a gray body source. Qualitatively, when the flame has a reddish color this indicates a relatively low flame temperature. As the flame color shifts toward orange and then yellow, the temperature is rising. Other hydrate combustion studies also showed images characteristic of fairly low temperatures. The quantitative analysis of the images was accomplished using MAXIM Dl software, but amounted essentially to determining the ratio of red to green and red to blue intensity over a window of the image representative of the flame color. Because the flame was buoyancy driven, it was difficult to create a uniform temperature region so typical areas were selected by eye.

Based on the pyrometry system, the temperature of the flame from the powder methane hydrate was approximately 1320 K and for the spherical methane hydrate it was determine approximately 50 K higher. These temperatures are quite low, and we are continuing to develop confirmatory results. Assuming adiabatic flame behavior, these temperatures would indicate conditions where all of the hydrate water evaporated. We know this is not true, and using the experimental estimate of water vapor ratio, we would obtain an adiabatic flame temperature approximately 300 K higher. The difference can be due to radiative loss, incomplete combustion, and entrainment, in addition to potential uncertainty in the pyrometry. It is clear, however, that the spherical geometry produces a somewhat higher temperature flame consistent with the fact that less water evaporates with this geometry (as determined in the experiment).

In order to further understand the relationship between water vapor content and flame temperature, we also conducted a computational study using CHEMKIN-Pro (Reaction Design) for a counterflow diffusion flame configuration with the GRI Mechanism 3.1. A low counterflow flame velocity (10 cm/sec) and small separation distance (1 cm) was used. The results showed that the maximum counterflow flame temperature is approximately 200 K lower than the adiabatic result over a range of water vapor/fuel molar ratios. Since the CHEMKIN calculation did not include radiative loss, it appears that the 300 K difference between the experiments and adiabatic results is not unreasonable. It is clear, however, that a detailed analysis of this difference in the flame temperature is needed as part of the future work on this project.

4 Conclusion

Hydrates are complex fuels because the amount of water evaporated depends on flame behavior and the flame characteristics then depend on the amount of evaporated water. The geometry of the methane hydrate plays a significant role in the amount of methane released from the hydrate and the amount of evaporating water in flame.

5 Acknowledgments

This research at University of California, Irvine, was supported by NSF CBET-0932415. The authors appreciate the assistance of Jennifer Menasha and Guillermo Gomez.

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