Methane Hydrate Combustion

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1 Introduction

Methane hydrates are ice-like non-stoichiometric crystalline solids composed of water cages that are stabilized by the presence of a guest methane molecule. The methane molecule gets captured and sealed inside the surrounding water molecule structure by supporting the hydrogen-bonded water in a thermodynamically stable configuration. Methane hydrates occur naturally in the permafrost and in deep ocean sediments. They represent a potential mega-resource of energy and, at the same time, they can have a substantial potential impact on the environment. Forming a hydrate sample requires the thermodynamic conditions that encourage hydrate formation but it is also necessary to create sufficient interaction surface for the process to develop on a reasonable timescale. It is known that gas hydrates are formed at an elevated pressure and low temperature when the gas concentration exceeds the solubility limit [1-2], and various authors have explored methods to increase the rate of hydrate formation [3-6], mostly by combining gases or including surfactants in the water. Methane hydrates are being considered an alternative source of energy even though there have been only a few studies on the direct combustion of this ice-like fuel. For example, researchers in Japan tried to explain, using the classic Emmons problem configuration, some fundamental information on hydrate combustion [7-8]. They found that under flat-plate combustion conditions hydrates exhibit a self-healing process that is very similar to that seen in hydrates warmed in other ways [9].

In the present work, the formation process of methane hydrate samples is improved from previous work [10-11] to achieve reproducibility and high quality hydrates. A differential weight experiment is designed to measure the mass of hydrate, water melted, and gas released. The gas released is studied to determine the amount of water vapor that makes it to the flame along with the fuel released from the hydrate. Further calculations determined key properties of the combustion behavior. For the first time, the water content inside the flame is determined during the combustion of a methane hydrate.

2 Experiment

Hydrate formation is notoriously variable and so the first objective was to form uniform, equal and reproducible samples in order to compare the different experiments and have a better understanding of the combustion process. The combustion experiment consists of differential weight measurements of the hydrate sample and the water melted during combustion. The design is based on two load cells, a mesh where the sample burns, a beaker for the water melted, an isolation system to reduce vibrations and the data acquisition control. The hydrates in this study are produced using a modified version of the Stern group approach [3]. Starting at low temperatures, approximately 255-260 K, the chamber is first pressurized to between 7.5-10 MPa with methane. At this point, the temperature is increased at a

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constant rate of 5 K/hour and then held at 281 K for 8-12 hours. Then, the sample is cooled down to 265K so that it can be depressurized without instant decomposition of the hydrate. Methane hydrates are non-stoichiometric compounds. That means that the ratio of methane to water can vary. Hence, determining the real composition and the amount of methane introduced is important to know the quality of the sample and to ensure accuracy in any further calculations. When the hydrate is saturated, the maximum amount of methane trapped inside the clathrate structure has an effective molar composition of CH₄*5.75H₂O, or 87% water and 13% methane on a mass basis. If the methane hydrate is saturated, the clathration achieved is 100%. Therefore, the amount of methane trapped can be described as the percentage of clathration of the sample. To measure the clathration it is possible to do a direct mass balance. This technique consists of measuring the difference of the sample weight and the weight of water left after the sample has been melted. This difference of mass is the methane gas from the hydrate. The results show good reproducibility and fairly high levels of clathration. It is important to note that the measurement of the initial clathrate weight takes place approximately 3 minutes after starting the process of depressurization, losing a small but similar quantity of methane for all the experiments. Actually, the measurement accurately characterizes the initial state of the hydrate to be burned. The results show that the clathration is between 75% and 90% when the sample is ready for combustion. This level indicates a very high quality that certifies the repeatability and effectiveness of the formation process.

The combustion process consists of igniting the cylindrical hydrate from one side using a propane torch; the outer layer is melted first and the methane caged in that surface layer is released. The released gas proceeds to feed the flame and the heat of the flame melts the next layer of the hydrate. During fuel evaporation there is also water evaporating as it joins the fuel gas mixture and some of it remains as liquid water and drips down from the surfaces of the hydrate and filters through the mesh into the container. During the combustion process it is possible to appreciate different regimes with specific characteristics, as shown in Fig. 1.



Figure 1. Combustion of a 15g cylindrical sample. Image (a) is the ignition instant, (b) and (c) are the flame propagation, (d), (e) and (f) are the initial moments of the combustion, (g), (h) and (i) are the steady-state region and finally (j) is the extinguishment moment. The flame is unsteady and heterogeneous, the maximum height (25 cm) is at the beginning (b), and the total time combustion is 56.63 seconds

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The flame surrounds the circumference of the hydrate and starts propagating along the cylindrical column. After 0.6 seconds the flame propagates along the entire cylinder enclosing the hydrate. Therefore, the bulk flame spread velocity of the hydrate is approximately 0.1 m/s. This velocity is comparable to that found in hydrate flame spread studies [8]. After the propagation, the flame is characterized by a bright yellow color and unsteadiness due to the jets of methane released that induce an expansion of the flame. By the end of this regime, the brightness of the flame diminishes and the intensity in blue increases, but it still conserves some bright yellow flame. After 5 seconds, the quasisteady state burning starts. During this regime the flame recedes toward the top of the clathrate sample and the bright color disappears. The length of the cylinder decreases very slowly while its radius decreases more quickly, which means that the flame is primarily heating the top of the sample. Heat transport from the flame to the hydrate occurs mainly due to diffusion and not radiation, and that is the main reason of the linear regression of the diameter of the sample and not the length. The flame intensity decreases until all the methane is released and there is no heat to maintain the flame, at which point it extinguishes. What is remarkable about this final process is that even with the large quantities of water in the hydrate fuel, the sample burns completely and no residual ice is left on the mesh.

3 Calculations

The results and calculations presented in this paper come from 7 representative experiments which had the desirable characteristics needed to draw conclusions. Those are cases that had a complete combustion, good level of clathration with little gas popping (i.e., little trapped gas pockets that were not hydrated). With a 95% confidence interval, the average molar ratio of water to methane is 7.3 ± 1.0 , representing an average clathration of $81.8 \pm 3.4\%$. With the readings of the weights, the water drained and the mass of the sample are calculated with a polynomial interpolation of third order to smooth the data and simplify the calculations. The gas released, which is the methane released from the hydrate and water evaporated due to the heat of the flame, is calculated by the difference between the initial mass of the sample minus the two readings of the load cells.

To compare samples with different mass, the experiments are divided by the surface area, which can be approximated by a linear regression line. The results show an average dissociation rate of 0.125 kg/s m², average burning rate of 0.25 kg/s m², average draining rate of 1 kg/sm², average flow rate of methane released of 1.25 ± 0.25 mg/s cm² and average flow rate of water evaporated of 1.25 ± 0.25 mg/s cm² and average flow rate of water evaporated of 1.25 ± 0.25 mg/s cm² and average flow rate of water to methane of 0.88, inside the limits of sustainability compared to other work [12]. During the first seconds of the combustion, the water content in the flame is around 90% of the total content, above the level of sustainability of the adiabatic flame temperature, suggesting that the ignition and initial temperature is fairly insensitive to the water content.



Figure 2. Results of experiments. Left: Flow rate water evaporated per unit surface area. Right: Molar ratio of water/methane during combustion of the hydrates.

4 Energy model

There is an important relationship between heat flux from the flame, the amount of water that was released, and the ratio of water evaporated to methane released. In order to understand that process better a simplified planar one-dimensional steady-state energy balance of hydrate combustion is created to account for these behaviors. The schematic of the model illustrated in Fig.3.



Figure 3. Schematic 1-D planar model of the methane hydrate heat transfer.

The flame provides heat flux to the surroundings Q_{fs} and transmits the rest toward the hydrate Q_{fh} . This heat flux goes through the gas layer, that has thickness t_l , to the liquid layer Q_{gl} and finally into the hydrate Q_{ls} . The solid hydrate phase is assumed to be semi-infinite for this analysis. There are three interfaces: the flame sheet at temperature T_f , the gas-liquid boundary with water boiling temperature T_{gl} , and the liquid-solid boundary, with hydrate dissociation temperature T_{ls} , which is the water melting temperature. The governing equations are energy and mass balances at each interface. Starting from the solid/liquid interface, it is assumed that the hydrate has a constant dissociation temperature T_{ls} and latent heat of fusion L_{f} . The heat flux per unit area into the hydrate Q_{ls} includes the heat of fusion and the sensible heat of increasing the temperature of the hydrate from its initial temperature T_i to the dissociation temperature, where c_{ps} is the specific heat of the hydrate, and \dot{m}_s is the dissociation rate of the hydrate per surface area. It is assumed that the liquid phase has a constant thermal conductivity k_l and the thickness of the layer is very thin, therefore heat transfer through the liquid can be considered to occur only by conduction. Regarding the liquid/gas interface, the heat flux per unit area incorporates the latent heat of vaporization h_{fg} , the sensible heat to increase the temperature of the liquid that is evaporating to the boiling point T_{gb} and the liquid that is draining to the draining temperature T_d . Adding the heat flux into the hydrate solid, the heat flux per unit area of the liquid/gas interface is obtained, where c_{pl} is the specific heat of water, \dot{m}_g is the burning rate of the hydrate per surface area, \dot{m}_d is the draining rate per surface area and α is the mass fraction of the gas released that is vapor, since the methane has no latent heat associated with it. The heat transfer from the flame into the liquid layer is estimated to occur by convection only, where h_g is the effective convective heat transfer coefficient. Finally, for the flame/gas interface, the sensible heat to increase the gas from the boiling point to the flame temperature T_f is added to the heat flux into the liquid layer to get the heat flux per unit area of the flame/gas interface, where c_{pg} is the specific heat of the gas. The heat generated by the flame is determined by the mass portion of methane that goes into the flame and the heat of combustion for methane and air ΔH_c . This combustion heat is diffusing outward toward the surroundings to heat the incoming oxidizer and inward toward the hydrate to heat the fuel and vapor, along with that heat required to dissociate the hydrate. The mass balance is defined so that all the mass that is dissociated from the hydrate goes into gas or liquid water.

$$Q_{ls} = \dot{m}_{s}(L_{f} + c_{ps}(T_{ls} - T_{i}))$$

$$Q_{ls} = k_{l} \frac{(T_{gl} - T_{ls})}{t_{l}}$$

$$Q_{gl} = \dot{m}_{g}\alpha(h_{fg} + c_{pl}(T_{gl} - T_{ls}) + \dot{m}_{d}c_{pl}(T_{d} - T_{ls}) + Q_{ls})$$

$$Q_{gl} = h_{g}(T_{f} - T_{gl})$$

$$Q_{g} = \dot{m}_{g}(c_{pg}(T_{f} - T_{ls}) + Q_{gl})$$

$$Q_{f} = (1 - \alpha)\dot{m}_{g}\Delta H_{c}$$

The values used for the hydrate heat of fusion and the specific heat are the values of ice, which are very close to the hydrate properties and the flame temperature is estimated to be 1750 K, from other studies [12]. The initial temperature of the hydrate is the temperature of the hydrate when is taken out from the formation vessel, 265 K, and the temperature of the water drained is measured to be 300 K. Based on the results from the experiments, the heat flux from the flame is 62.7 kW/m^2 and the heat flux to the surroundings is approximately 47 kW/m^2 , therefore only 25% of the combustion heat is needed to maintain the steady release of methane and a steady burn. The energy balance analysis confirms that the experiments sustain the steady-state and the flame through the drainage of water. The hydrate could ideally and theoretically produce 470 kW/m^2 from the methane released which gives an indication of how much of the energy is used in water phase changes. These results are not exact for every experiment, and are only a reference using the average of the experiments. Hence, the validity of the results is more qualitative rather than quantitative.

Finally, the temperature of the flame can be estimated by modelling the flame as a constant-pressure flame and calculating the adiabatic flame temperature under the assumptions that the combustion is complete; the flame temperature is estimated to be 75% of the adiabatic flame temperature, Figure 4 shows the transient flame temperature during the combustion process for each experiment. there is a difference between a minimum of 1550 K to 2050 K, with an average of 1822 K at the peak temperature. The big range shows the high dependency on the water content in the gas released and the difference by the assumption that the temperature of the flame is the fraction of the heat combustion needed for dissociating.



Figure 4. Adiabatic flame temperature based on water content of experiments.

6 Conclusions

Methane hydrates are an interesting field of study and they may be a promising fuel due to the large amounts of methane they contain. Their direct combustion behavior is studied in this work and their

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unique structure makes them a very challenging fuel problem due to their multi-phase characteristics. In this work it is shown that it is possible to form methane hydrates in the laboratory that burn completely and that are reproducible, with the same shape and internal structure. This is the most difficult aspect of the hydrate combustion experiments. The clathration achieved (i.e., the amount of methane trapped relative to the theoretical maximum), is above 90% of the ideal saturated methane hydrate, based on the inverse regression of the dissociation. For the cylindrical samples (2 cm diameter 6 cm long) tested, the combustion reaches a quasi-steady state regime 10 seconds after ignition during which the key combustion characteristics are determined. Analysis of the data determined the dissociation rate to be approximately 12.5 mg/s cm² and 20% of the dissociated mass is released as a gas, giving a burning rate of 2.5 mg/s cm². Estimates from the differential mass measurements, and assuming the hydrates are homogenous, show that the gas composition released from the hydrate has a molar ratio of methane to water between 0.5 and 1.5, inside the limits of flame stability determined in other work. The energy balance model showed that during steady-state burning around 25% of the energy released by the flame is needed for dissociating the methane hydrate and that the regression rate is 0.14 mm/s. The energy from the hydrate flame to the environment is approximately 470 kW/m². Finally, calculating the flame temperature with corrections for the real losses yields estimates between 1550-2050 K, showing the high dependency of the flame temperature on the water vapor content.

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