

Formation of Liquid Methane–Water Mixture during Combustion of a Laminar Methane Jet at Supercritical Pressures

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ABSTRACT: During the study of soot formation in laminar jet flames of methane at elevated pressures in a high-pressure combustion chamber, we have observed an anomalous occurrence at the chamber pressures of 6 MPa and higher. At pressures between 6 and 9 MPa, after the laminar methane jet flame had been stabilized on a co-flow circular nozzle-type burner, one of the following occurrences was observed: (a) the jet flame is completely extinguished without any external interference, and immediately after, a liquid material started to flow out of the fuel nozzle, and (b) the jet flame started flickering or changing its shape, and at the same time, a liquid stream started trickling out of the nozzle. This outflowing liquid influenced the jet flame by widening the flame near its base and decreasing the visible flame height. In consideration of the temperatures and the pressures involved, the liquid is believed to be a mixture of methane and water formed by the water vapor in the combustion products of the flame mixing with supercritical methane inside the nozzle.

1. INTRODUCTION

Most work-producing combustion devices, such as the power plants found in the land- and air-based transportation systems, as well as in the stationary power production plants, operate at pressures approaching and sometimes exceeding 10 MPa. For example, current aviation gas turbines operate at conditions approaching 4 MPa, and the pressures in the liquid propellant rocket engine combustion chambers may reach up to 20 MPa. These operating pressures are most of the time above the critical pressures of hydrocarbon fuels and air. Despite this fact, our understanding of high-pressure combustion and the governing mechanisms is very limited compared to the extensive knowledge-based understanding of combustion that we have at atmospheric conditions. Although projections have been made to use the combustion data obtained at atmospheric conditions to conditions at elevated pressures, there seems to be no reliable method to scale the extensive experimental data obtained at atmospheric pressure to elevated pressures. For example, combustion intensity, i.e., energy release per unit volume, scales with the square of the pressure, while soot formation rates in diffusion flames may increase an order of magnitude when pressure increases from 1 to 6 MPa.¹ Thus, the influence of pressure on combustion is not trivial.

The information on soot formation obtained from a non-smoking laminar diffusion flame at elevated pressures has the potential to shed some light on soot formation in turbulent diffusion flames at high pressures. This can be accomplished by exploiting the similarities between the laminar and turbulent flames.

Efforts to expand our understanding of the effect of pressure on soot formation rates in laminar diffusion flames have been focused on the investigation of the soot loading of laminar diffusion flames as a function of pressure.^{1–6} Previous studies on the effect of pressure on soot formation in laminar methane jet diffusion flames are available up to 4 MPa² and, more recently, to about 6 MPa.¹ During our efforts to extend the measurements above 6 MPa, we have observed some interesting occurrences. At pressures between 6 and 9 MPa,

after the laminar methane jet flame had been stabilized on a circular nozzle-type burner, one of the two following occurrences was observed: (a) the jet flame was completely extinguished without any external interference, and immediately after, a liquid material started to flow out of the fuel nozzle as either a clear liquid bubble growing with time or a slurry-like liquid flowing out of the nozzle, and (b) the jet flame started flickering or changing its shape, and at the same time, a liquid stream started trickling out of the nozzle. This was reported as a brief communication,⁷ and the observed liquid was inadvertently labeled as a liquid methane hydrate. The aim of this paper is to report this unexpected occurrence and discuss its nature.

2. EXPERIMENTAL SECTION

2.1. Apparatus. The high-pressure combustion chamber that is designed for 11 MPa was used to conduct all of the experiments at high pressures. The schematic drawing of the chamber is provided in Figure 1 and described in detail in refs 1, 3–5, and 8. The combustion chamber has an internal diameter and height of 0.24 and 0.6 m, respectively. The body of the chamber is a 10 in. schedule 160 stainless-steel pipe closed at both ends with flanges, with a mass of 200 kg. The combustion chamber is a continuous flow system, where the chamber pressure is controlled by the back-pressure regulator. Optical access into the chamber is achieved through three ports at 0°, 90°, and 180° locations, allowing for line-of-sight measurements, 90° scattering measurements, and imaging experiments. The optical ports are equipped with jet nozzles around the rim inside the chamber to blow away any water condensation on the quartz glass and provide an unobstructed view of the nozzle and the flame.

The co-flow circular nozzle-type burner was used to provide a laminar methane–air diffusion flame (Figure 2). The co-flow burner has a fuel nozzle exit diameter of 3.06 mm and an air nozzle diameter of 25 mm. Sintered metal foam elements are fitted into the fuel and air passages upstream of the nozzles to straighten and reduce the

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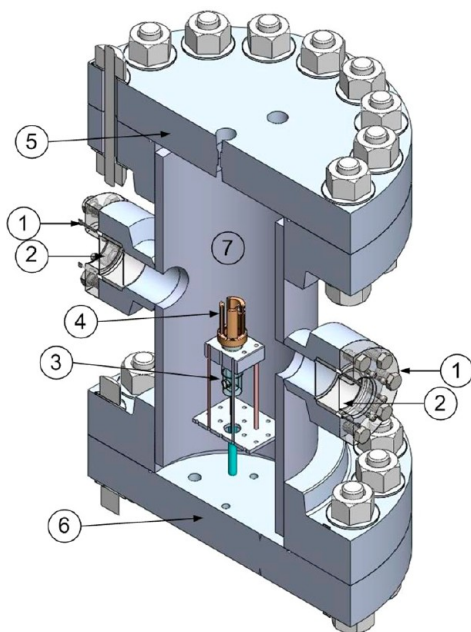


Figure 1. Cutaway view of the high-pressure chamber: 1, optical access ports; 2, quartz windows; 3, burner assembly; 4, chimney assembly; 5, upper flange housing the exhaust, safety valves, and pressure transducer; 6, lower flange housing air, fuel pipes, and wiring; and 7, combustion chamber.

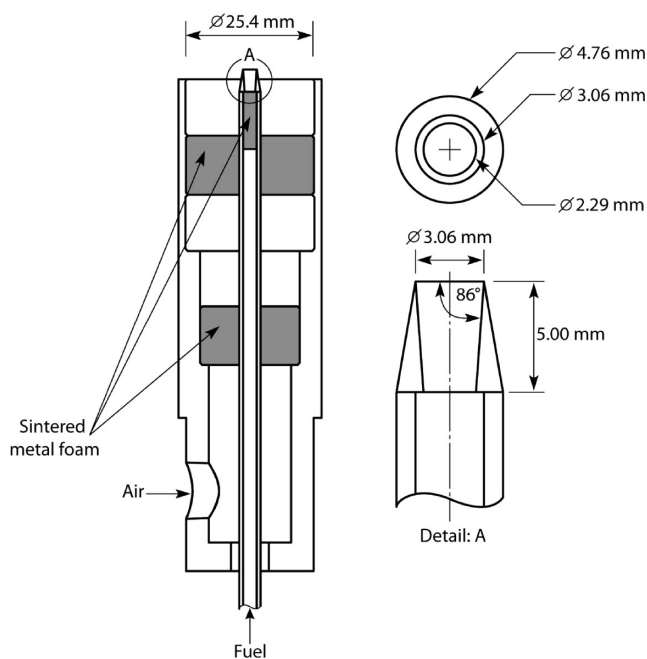


Figure 2. Details of the co-flow burner used in the high-pressure experiments.

instabilities in the flow and to create a top hat exit velocity profile as the gases leave the foam elements. The fuel nozzle surface was routinely examined and cleaned after use. A chimney was used to extend the length of the co-flow nozzle and to shield the flame from ambient fluid perturbations. A copper cooling coil with circulating chilled water is positioned just above the chimney to help condense the water in the combustion product onto the coil and keep the water from condensing on the quartz optical access windows.

2.2. Gas Flow. The fuel for the laminar diffusion flame was a 99% pure methane gas. The air used in the experiments was industrial extra-

dry air, and the nitrogen used in the experiments was better than 99.99% pure. All of the gases were delivered from compressed gas cylinders. The gas flow rates were controlled with thermal-based mass flow controllers (MFCs), and the pressure to each MFC was controlled by its own pressure regulators. The thermal-based MFCs are calibrated for high-pressure use and have a maximum total error of less than 2%.

The methane flow rate was selected to match the carbon mass flow rate of the studies conducted previously with propane,³ methane,^{1,5} and ethane⁹ diffusion jet flames at elevated pressures. A constant methane mass flow rate of 0.55 mg/s, which corresponds to 0.412 mg/s of carbon mass flow rate, was maintained at all pressures. The co-flow air flow rate was kept at about 0.4 g/s.

2.3. Procedure. Prior to starting any experiment, the gaseous contents of the combustion chamber are purged with dry air for the duration that is nominally equivalent to displacing at least three chamber volumes to remove any residual gases from the previous experiment. The flame is ignited using a glow plug inserted into the chimney that is located about 28 mm above the fuel nozzle. Once the flame is established at atmospheric pressure, the combustion chamber is pressurized rapidly by either introducing pure nitrogen or dry air directly into the chamber void space. The combustion chamber is allowed to reach thermal equilibrium with the surrounding environment, i.e., achieve steady combustion chamber wall temperature, for about 30 min prior to collecting any measurements. The soot and temperature measurement method used in this study is explained in detail in refs 1, 4, 5, and 9.

Still and motion pictures were captured using a single-lens reflex camera with a standard macro-lens and a video camera for all of the pressures from 6 to 10 MPa. The main purpose of the video recordings was to check the flame stability during the measurements. For all of the images, aperture and exposure time were adjusted to prevent image saturation, and thus, a relatively constant intensity was maintained for all of the images.

3. OBSERVATIONS AND DISCUSSION

At the chamber pressure of 6 MPa and above, two interesting occurrences were observed. After the chamber had been pressurized with nitrogen and the flame stabilized for about 30 min, the flame was suddenly extinguished and a clear and transparent liquid bubble emerged out of the fuel nozzle (Figure 3). At higher pressures, the flame was extinguished more readily and the visual appearance of the liquid substance was dark, opaque, and resembled a slurry-like material (Figure 4). The use of nitrogen as the pressurizing gas appeared to hasten the onset of flame extinction, and thus, it was not possible to sustain the laminar methane jet diffusion flame for an extended period of time at pressures higher than 6 MPa. The flame was extinguished often prior to reaching the set chamber pressure, and therefore, maintaining the flame above 6 MPa was very difficult. The use of dry air to pressurize the chamber, however, appeared to delay the onset of flame extinction and enabled the pressure to exceed 6 MPa relatively easily. The liquid material formed at 8 MPa is clear and transparent (Figure 4). Typical images depicting the time sequence of the flame extinction and the emergence of the liquid bubble in chronological order are shown in Figure 5. The images depicted in panels b and c of Figure 5 show a rapid increase in the visible flame height just before it is rapidly decreased to extinction, as shown in Figure 5e. Immediately, a clear liquid bubble emerged out of the nozzle and continued to grow in size (panels f–h of Figure 5). As the bubble continued to expand, free-floating particulates were observed to roam on the surface of the liquid bubble. With the fuel continuing to flow, the liquid bubble bursts and a new bubble emerged from the fuel nozzle. The cycle was repeated often several times or until the fuel flow



Figure 3. Liquid bubbles at 6.1 and 9.1 MPa. (a) $P = 6.1$ MPa. Clear and transparent liquid bubble with a diameter of approximately 6.5 mm. (b) $P = 9.1$ MPa. Small broken liquid bubbles spilled to the side of the fuel nozzle.

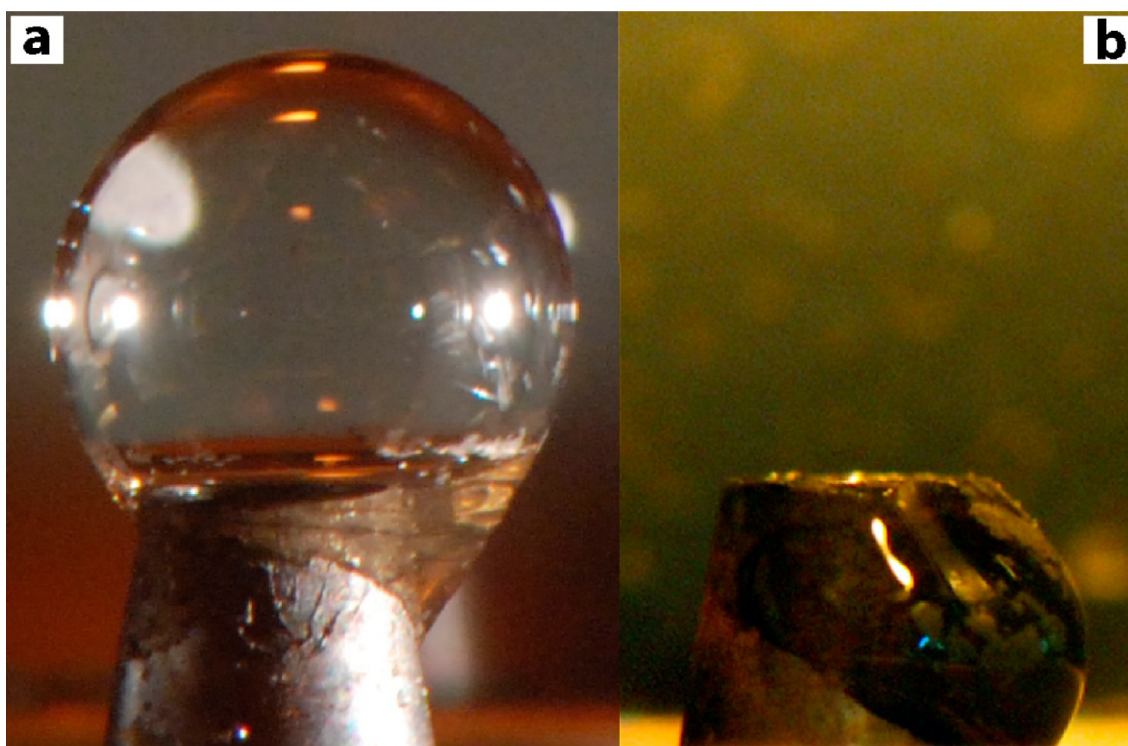


Figure 4. Liquid material at 8.1 MPa. (a) Low nitrogen concentration in the vessel using dry air as the pressurizing gas. Clear and transparent liquid bubble with a diameter of approximately 6.8 mm. (b) Higher nitrogen concentration in the vessel using pure nitrogen as the pressurizing gas. The liquid material is dark and opaque.

was stopped. When the pressure was decreased to atmospheric pressure, the liquid was evaporated completely, regardless of the gas used to pressurize the chamber, and solid deposits on the surfaces of the fuel nozzle were observed.

The second interesting occurrence was the simultaneous observation of the liquid substance and the flame. The typical physical appearance of the laminar diffusion flame at high pressure is a stretched or elongated flame. The flame is wide

close to the nozzle rim, but immediately downstream of the nozzle, the flame narrows into a slender shape, which gives the appearance of an elongated flame. For the diffusion flame experiment at 9 MPa, the combustion chamber was pressurized with air. At 9 MPa, however, the overall geometrical structure of the flame was affected by the liquid material emerging from the same nozzle (Figure 6). A typical image of the laminar methane jet diffusion flame at 9 MPa is slim, as described above

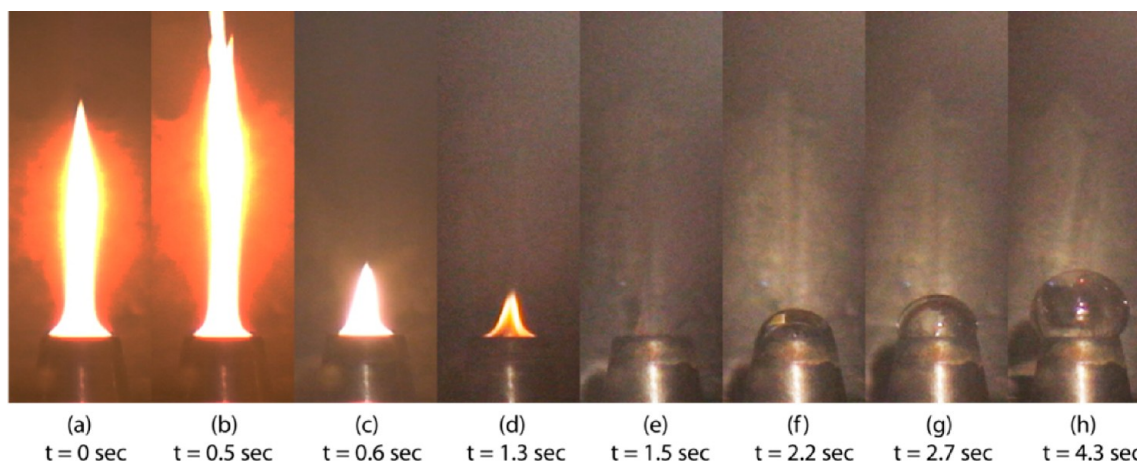


Figure 5. Sequence of images showing the development of the liquid bubble at 8.1 MPa. (a) The diffusion flame at 8.1 MPa with the visible flame height of about 9 mm. (b and c) Rapid increase and then decrease in the flame height. (d and e) Flame extinction. (f–h) Formation of liquid bubble and its growth.

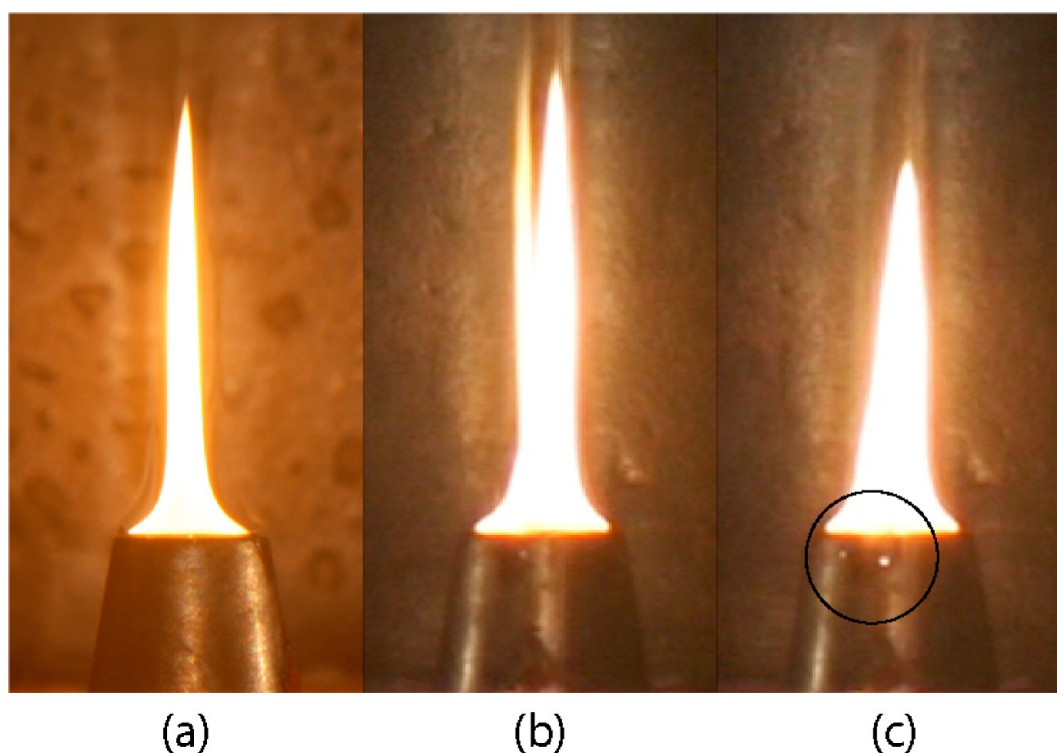


Figure 6. Coexistence of laminar methane–air diffusion flame and liquid substance at 9.1 MPa. (a) Gaseous only flame at $P = 9.1$ MPa with the flame about 9 mm ($t = -30$ min). (b) Onset of liquid formation and burnoff ($t = 0$ s). (c) Liquid droplet on the side of the nozzle (indicated by the circle) and change in flame geometry ($t < 10$ s).

(before flame shape change), and it is depicted in Figure 6a. About 30 min later, however, some liquid material emerged out of the fuel nozzle and disturbed the flame stability by causing the flame to flicker randomly and sway side-to-side. Then, some liquid was then burned off to give an appearance of a small secondary flame from the same nozzle (Figure 6b). The liquid material continued to flow out of the nozzle, and a few seconds later, enough liquid material was collected on the side of the fuel nozzle to form a small droplet. Then, the visible flame height decreased, and the flame widened near its base (Figure 6c). The liquid was then evaporated, and the flame regained its original shape only until a new liquid droplet was formed to repeat the process.

To our knowledge, this is the first reported observation of liquid material from a laminar diffusion jet flame at elevated pressures. In the present study, experiments suffered from water vapor retention and condensation on the viewport glass. Considering that the fuel and air flow rates were kept as a constant throughout the experiment and the exhaust products mix with the ambient gas, the steady-state mole fraction of water vapor will increase with the total chamber pressure.¹⁰ The increase in water vapor with pressure invariably poses a problem of formation of water droplets and water condensation in cool downstream momentum of the jets and on viewport glass. The water droplets that are described as what appears to be a very fine mist that circulates in the chamber can cause poor

visibility and momentarily interfere with the flame, causing an unstable flame structure. Although every attempt has been made to minimize the effect and lower the concentration of water vapor, complete removal of water vapor through condensation was unsuccessful. In view of strong air entrainment into the flame near the burner tip and into the fuel stream with increasing pressure,¹¹ it is possible that water vapor can be entrained strongly into the methane fuel tube at the flame base. Although the temperature of the fuel nozzle rim can be high because of radiative heating from a highly sooting flame, there may be a significant upstream temperature gradient sufficient enough to yield a lower temperature region in the fuel tube and form some liquid material at elevated pressures. In view of the phase diagram of the methane–water system in Figure 7, it is

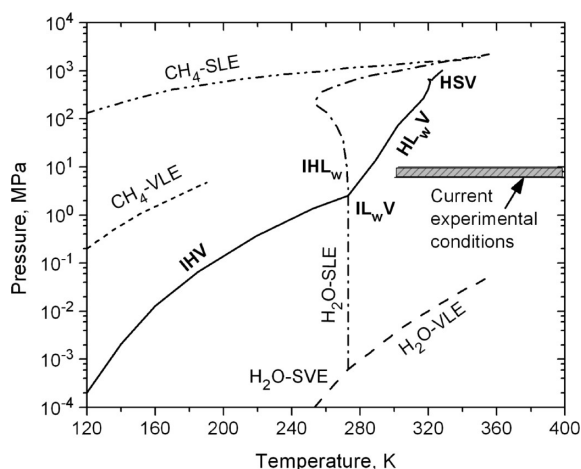


Figure 7. Univariant three-phase lines for the methane–water system.¹⁴ Solid lines correspond to calculations by an equation of state by Yokozeki. IHV, ice/hydrate/vapor; HL_wV, hydrate/water-rich liquid/vapor; IL_wV, ice/water-rich liquid/vapor; IHL_w, ice/hydrate/water-rich liquid; and HSV, hydrate/solid solution/vapor. Broken lines are the three-phase behaviors of pure water^{15,16} and pure methane.¹⁷ SLE, solid–liquid equilibrium; SVE, solid–vapor equilibrium; and VLE, vapor–liquid equilibrium. The pressure and approximate temperature range of the current experimental conditions is shown by the cross-hatched area on the graph.

suspected that the liquid material is a mixture of water and methane. The current experimental conditions are indicated in the phase diagram of the methane–water system (Figure 7). Methane, in these experimental conditions, is above the critical point values of the temperature and pressure, and thus, it is defined as a supercritical methane fluid (Table 1). It is believed that relatively cool temperature and high pressure in the presence of water transforms the supercritical methane fluid to the liquid methane–water mixture in the fuel tube, which has been observed during the experiments.

Once the liquid substance is formed, its movement and growth of the liquid bubble loosens the soot deposited on the

Table 1. Critical Properties of Methane, Oxygen, and Nitrogen¹⁹

gas	formula	molar mass (g/mol)	critical pressure (MPa)	critical temperature (K)
methane	CH ₄	16.04	4.64	190.8
oxygen	O ₂	32.00	5.09	154.6
nitrogen	N ₂	28.01	3.40	126.3

annular surface of the fuel nozzle tip. The fuel nozzle tip may be an attractive place for soot deposits. The deposition of soot on the nozzle surface is enhanced with pressure because of the fact that the soot formation zone moves toward the burner tip with increasing pressure. Then, at a high enough pressure, it is possible that this zone moves further down into the fuel nozzle. Because the fuel nozzle temperature is significantly less than the gas temperature, where soot forms, the soot particles are attracted toward the nozzle surface to form annular soot aggregates.¹² The emergence of the liquid substance then breaks the soot deposits and appears as free-floating particles on the bubble surface. Then, it is possible that the dark color of the liquid could be the result of dissolved soot from increased soot loading at elevated pressures.¹² In the supercritical environment, the ambient water solubility in the methane fluid is quite significant and increases with the temperature. For instance, water solubility in the supercritical methane fluid can be more than 35% by mole at 6 MPa and 478 K, as shown in Figure 8. It seems that this condition is ideally set in the fuel

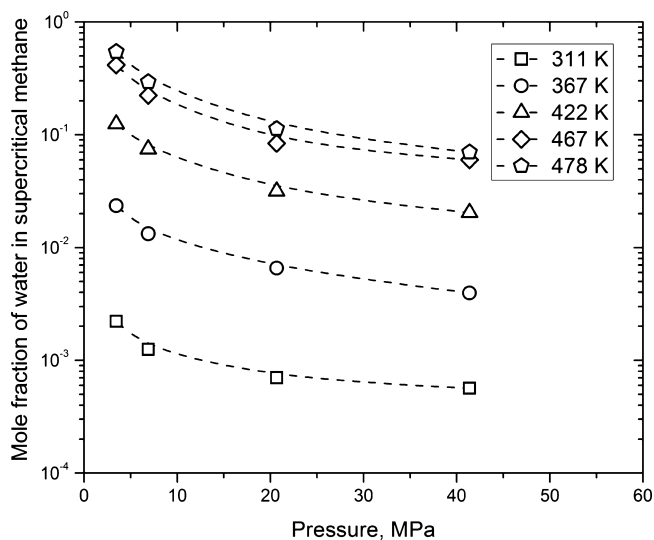


Figure 8. Solubility of water in supercritical methane.¹⁸

tube, where the phase change occurs. In Figure 5, the flame retracts rapidly toward the fuel nozzle to extinction and, immediately, the liquid substance emerges from the fuel tube. This seems to indicate that, as the cool liquid is pushed through the fuel nozzle by upstream methane, a cooler temperature and insufficient rate of methane release from the liquid fails to support the chemical reaction to sustain the flame.

It seems that molecular diffusivities play an important role in the formation of the liquid substance. At low to moderate pressures, defined here as when the reduced pressure, P_r (the ratio of actual pressure to the critical pressure of the gas) is below about 0.5, the molecular diffusivity is inversely proportional to pressure, so that the product of diffusivity and pressure is essentially constant.¹³ At higher pressures ($P_r > 0.5$), the inverse dependence of molecular diffusivity upon pressure deviates from the inverse relationship and the product of diffusivity and pressure decreases with an increasing pressure up to the critical point. At supercritical pressures, it appears that diffusivity is proportional to $P_r^{1/2}$.¹³ The critical pressures of methane, oxygen, and nitrogen are listed in Table 1. At 5 MPa and higher, methane, oxygen, and nitrogen are in supercritical conditions. The gas phase can deviate significantly from an ideal

gas, and the absolute concentrations become important in the diffusion of fluids. Experimental data strongly imply that molecular diffusivities are influenced significantly by the absolute concentrations at supercritical pressures.¹³ Considering that the critical pressure of nitrogen is 33% lower than oxygen, it seems that a higher concentration of nitrogen in the chamber (in the case of using nitrogen to pressurize the chamber) leads to significantly higher nitrogen diffusion at supercritical pressures. In the view that water vapor can enter the supercritical methane fluid at the flame base, it is possible that higher nitrogen diffusion can induce a greater flow of water vapor into the fuel tube. At 6 MPa and higher, it appears that increased diffusion of nitrogen enhances the water vapor entrainment into the supercritical methane fluid and increases the formation rate of the liquid methane–water mixture, and thus, this results in hastened flame extinction.

4. CONCLUDING REMARKS

The study was conducted experimentally in the high-pressure combustion chamber up to 10 MPa. To our knowledge, this work presents the first reported occurrence of the formation of the liquid substance during a study of soot formation from a laminar methane jet at supercritical pressures. During the combustion of the methane jet, it was determined that the supercritical methane fluid was transformed to the liquid methane–water mixture at 6 MPa and above. The liquid was clear and transparent but, on an occasion, appeared as a black and opaque liquid because of dissolved soot. The increase in molecular diffusion of nitrogen is considered to generate an induced flow and enhanced the entrainment of water vapor and ambient gas into the fuel tube to increase the liquid formation rate. The liquid is formed in the fuel tube in the presence of a high concentration of water vapor at supercritical pressures. The liquid is unstable and transitions to the gas phase when the pressure is decreased to atmospheric pressure.

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Notes

The authors declare no competing financial interest.

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