Evaporation of Salt Water in a Mist Co-Flowing with Propane and Air

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Abstract—In this report we explore the concept of the creation and propagation of a repetitively pulsed or reignited plasma in a mist of co-flowing salt water, propane, and air. We were able to create a large volume plasma of Na(g), Cl(g), H₂O(vapor), and combusted propane and their ionic and radical products using a minimal quantity of propane. The concept is to aid in the evaporation of large volumes of polluted water. This plasma is spatially compact and has the potential for being easily superheated to very high temperature ~6000 K or higher using microwaves or RF. This approach may have applications in treating highly polluted water.

Index Terms—Electrical discharges, combustion, plasma chemistry, salt water

I. INTRODUCTION

In this study we examine the ignition and burn characteristics of co-flowing C₃H₈ (propane), air, and salt water mist mixtures under conditions of continuous pulsed reignition of the burn front as it is quenched by the salt water. There are some interesting aspects of ignition and spark propagation in a salt water spray due to the free ions released by the salt water droplets that are not seen in fresh water sprays.

Our primary result has been to demonstrate the concept that one can enhance the rate of evaporation of a water mist beyond the rate that would be obtained by merely spraying water into ambient air if one co-flows a small amount of flammable gas, e.g. propane or methane, in a mixing nozzle with the water. Instead of requiring several meters to evaporate the water can be evaporated in tens of centimeters.

Evaporation ponds and spraying are widely used for the disposal of waste water. They are typically used in the western US for produced and flowback water from wells and for mining operations [1-5]. Examples are the Powder River Basin in Wyoming that creates 400x10⁶ barrels (6.4x10¹⁰ liters) per year of produced water from oil and gas wells and the Sweetwater Basin, which is part of the greater Green River Basin, having oil, gas, coal, and uranium mining operations and numerous ponds [6]. Such water is typically high in total dissolved solids (TDS) and has a high electrolyte content. Sometimes the water is sprayed into the air using high volume devices such as the Land Shark™ wastewater evaporation sprayer [7]. The object of this research was to find out what it would take using an admixture of combustible gas and air-water spray to make the evaporation process more efficient than simply spraying the waste water into the ambient air.

There is a sizable literature having to do with the combustion of co-flowing mixtures of a flammable gas, water, and air. Such studies appear to have begun in the 1920s [8-10]. Much of the research has had to do with the effects of water vapor density and droplet size or the spark ignition energy, flame propagation speed, and flame quenching. Most of the published studies of the ignition properties of co-flowing combustible gas and water use propane (C₃H₈) or methane (CH₄) and water vapor or mist ignited by a single spark at a point in the flow [9-15]. Some experiments have used a salt water mist [9]. Flammable gases do not easily ignite and burn with a heavy water loading and point ignition but we found that in a salt-water mist we could ignite the mixture over a line between well separated electrodes due to the electrical conductivity of propane/air/salt-water mist. Propane and
methane have similar burn characteristics. We used propane in our experiments because it was more readily available to us and is somewhat more safe to work with. A sketch of the geometry of the kind of experimental device that we are discussing here is shown in Fig. 1.

II. THE PHENOMENOLOGY OF SPARK IGNITION AND BURNING OF GAS IN A SALT WATER SPRAY

The ignition and burn characteristics of flammable gases in air and with various diluents including water vapor have been systematically studied phenomenologically for many decades [8-10]. The ignition energies and quenching distances as functions of pressure and gas mixture were tabulated long ago. In recent years there has been a lot of research on spark ignition and burn characteristics of flammable gases, primarily methane or natural gas, in a water mist [9-15]. Quantities such as flame temperature, burn velocity, and evaporation rate arising from ignition by a single spark have been measured and modeled as functions of water loading, droplet size, and equivalence ratio. Some of the results of others [2] are shown in Fig. 2. This spray mist in those experiments was not diverging as in our experiments. Our divergent spray has a major effect upon the process as discussed below.

Whereas most of the published research is related to the topic of fire and explosion mitigation, our research was more concerned with how much gas is required in a pulsed flame from a mixture of flammable gas, air, and salt water mist to efficiently turn a water mist to steam in less time and in a shorter distance than it would take the spray to evaporate in the ambient air. The use of salt water allows for the possibility of superheating the steam, which is essentially a plasma afterglow laden with Na+ and Cl- ions, further downstream using RF or microwaves [16].

How rapidly a water drop falling through the air at some temperature $T_{\text{air}}$ and relative humidity $\phi_{\text{air}}$ evaporates has been a standard textbook problem since the 19th century [17]. The virga that we see falling from clouds in the summer sky is an obvious example of this phenomenon. The description of droplet evaporation involves the usual transport coefficients such as diffusion coefficients and thermal conductivities, specific heats, and a driving force that is proportional to the difference between the ambient partial pressure of water vapor and the vapor pressure of the water drops. Fig. 3 shows the calculated $R(t)$ for evaporation of a 25 $\mu$m diameter droplet at various ambient temperatures. A fine water mist of
water at 20°C in air at 20°C can project several meters vertically before evaporating.

It is to our advantage that waste water tends to have a high electrolyte content. It has been well known since the time of Rayleigh in the 1880s that salt water droplets are likely to be charged and that as they evaporate they release free ions into the surrounding gas [18-24]. We have discussed this in detail in Ref. [25]. The presence of free ions in the propane/air/salt water mixture enhances the spark ignition of the gas.

The combustion chemistry of propane is well understood [26-30]. The presence of water vapor should not change the chemistry very much because H₂O is a final product of C₃H₈ combustion and OH, HO₂, and numerous CₓHᵧOz species are intermediate products.

The addition of Na(g), Cl(g), Na⁺, and Cl⁻ alters the chemistry high in the flame, as shown in a photograph of our experiment Fig. 4 due to the Na⁺ and Cl⁻ ions released into the combusting gas as the salt water drops evaporate. We discussed the plasma chemistry of a salt water flame in detail in Ref. [25].

III. “BACK OF THE ENVELOPE” THERMODYNAMICS OF THE BURNING AND EVAPORATION PROCESS

In our best experiment, described in Section IV, the salt water (0.1 Molar solution) flow rate was F₉H₂O = 3 cm³/s and the propane flow rate was Fₐ₀ = 15 cm³/s. This is shown in Fig. 4, where the water was evaporated in about 1/2 meter rather 2-3 meters at 20°C. Typically we used a propane flow rate of from 15 cm³/sec to about 45 cm³/sec. It is difficult to estimate the total volumetric air flow rate. We had several cm³/sec of air mixed with propane but there was also the air that pressurized the water, and the air educted up through the diffuser. Observe in Fig. 5 that this is far less propane than would be required to simply evaporate the same mass of water in a pan. The flow rate of the propane was much greater than the air flow rate through the nozzle. As in a propane torch, the propane gas flow entrains ambient air into the flame from the sides at the base of the diffuser via eduction, i.e. the Venturi effect. The presence of the air co-flowing with the propane through the mixing nozzle was to aid in the ignition of the propane, which then drew more air in through the bottom of the diffuser.

The nozzle diameter is D_nozzle = 0.05 cm. The water flow velocity exiting the nozzle was then \( v_{H₂O} = 1500 \text{ cm/sec} \). The half-angle of the spray cone is \( \theta_u = 16^\circ \). So the volume of a plug of mist and gas of thickness \( \Delta z \) flowing upward in the spray cone would be \( V_{plug} = \pi z^2 \tan^2 \theta_u \Delta z \) where \( z \) is the height above the nozzle. The average droplet diameter is 25 \( \mu \)m based on the specifications of the nozzle manufacturer. A water flow rate of 3 cm³/sec amounts to \( F_{drops} \sim 3 \times 10^8 \) drops/sec flowing from the nozzle.

As the water drops make their more or less ballistic flight upward the flux of drops, neglecting for now the evaporation and the slowing due to gravity and dynamic drag, is

\[
\Gamma_{drops} (z) = \frac{F_{drops}}{\pi z^2 \tan^2 \theta_u} \quad (\text{cm}^2 \text{s}^{-1})
\]

The number of water drops per cm³ is then

\[
N_{drops} (z) = \frac{(F_{drops}/\pi z^2 \tan^2 \theta_u)}{v_{H₂O}}
\]
\[ V_{\text{sphere}}(z) = \pi z^2 \tan^2 \theta_o / A_{\text{nipple}} \text{ cm}^3 = A_{\text{nipple}} / \pi z^2 \tan^2 \theta_o \]

The average radius of the spherical volume, \( V_{\text{sphere}}(z) \) which we will call the droplet sphere radius in analogy to the "ion sphere radius" of plasma physics, encompassing each water drop is then

\[ R_{\text{sphere}}(z) = \left[ \left( \frac{3}{4\pi} \right) \left( \frac{\pi z^2 \tan^2 \theta_o}{N_{\text{drops}} (z)} \right) \right]^{1/3} \text{ (cm)} \]

The ratio of the volume of the droplet sphere to the initial drop volume is then

\[ \frac{V_{\text{sphere}}(z)}{V_{\text{drop}}} = \left( \frac{A_{\text{nipple}} / \pi z^2 \tan^2 \theta_o}{\pi D^3_{\text{drop}} / 6} \right) \]

This relationship is graphed in Fig. 6. This neglects the reduction in \( V_{\text{drop}}(z) \) due to evaporation.

The enthalpy of vaporization of water is about 2270 J/g and the initial mass of a 25 \( \mu \)m water drop is \( 8.2 \times 10^{-9} \) g so that \( \Delta H_{\text{vap}} = 19 \) \( \mu \)J/drop.

If we take the specific heat of the gas, which will be mostly air, propane, and its combustion products in the sphere surrounding the water drop to be \( C_v = 5/2 \) k per molecule then the total heat capacity in the sphere having a gas density of \( N_{\text{gas}} (p, T) \) is

\[ C_{v,\text{sphere}}(z) = \left( \frac{\pi z^2 \tan^2 \theta_o}{N_{\text{gas}} (p, T)} \right) / A_{\text{nipple}} \]

It can be seen from the calculations shown in Fig. 7 that for \( z > 1 \) mm there is much more heat contained in the droplet sphere than is needed to evaporate the water drop.

IV. EXPERIMENTAL DESIGN

Figure 4 above shows one of our experimental devices in operation with the laboratory lights on. It is clear that, for the most part, the lower part of the flame of burning propane is optically thin to visible light. Also of interest is the time or distance from the nozzle for the sodium emission from the flame to become prominent. The sodium flame is optically thick.

We used a stainless steel liquid-gas internal mixing nozzle (Exair #SR102055) having water driven by compressed air flowing in one port and the pre-mixed \( \text{C}_3\text{H}_8 \) and air flowing in the other port. A conical spray pattern was produced by the nozzle. As shown in the photos and sketch it was oriented vertically. The nozzle opening was 20 mils \( \approx 0.5 \) mm. For air pressures of 1.4 – 4.1 Bar (i.e., 20-60 psi) the cone half angle was \( \theta \approx 16^\circ \). We experimented with a number of electrode configurations ranging from merely a pair of tungsten electrodes sticking into a ceramic cylinder to a prototype gliding arc. Flammable gases do not easily ignite and burn with a heavy water loading and point ignition but we found that in a salt-water mist we could ignite the mixture over a line between well separated electrodes due to the electrical conductivity of propane/air/salt-water mist.

The experiment that we are describing here, however, i.e. that shown in Fig. 4, used two rim fire spark plugs (Pulsar) driven by two capacitive discharge ignition (CD) units (MSD) and coils (Mallory) that were triggered by a square wave from
Fig. 8. Oscilloscope traces of $V(t)$ and $I(t)$ for CD ignition

a standard pulse generator. An oscilloscope trace of a typical pulse train is shown in Fig. 8.

Co-flowing propane, air, and salt water we found that pulsing the igniter at 800-900 Hz allowed us to produce a continuous stable flame with minimal propane gas usage. When the igniters were shut off the flame would be extinguished. So we had what amounted to a pulsed flame having the appearance of being continuous.

V. SUMMARY AND CONCLUSIONS

Our primary result has been to demonstrate the concept that one can enhance the rate of evaporation of a water mist beyond the rate that would be obtained by merely spraying water into ambient air if one co-flows a small amount of flammable gas, e.g. propane or methane, in a mixing nozzle with the water. Instead of requiring several meters to evaporate the water can be evaporated in tens of centimeters.

The keys to the process are using a nozzle with a reasonable spray cone, the eduction and entrainment of the ambient air through a diffuser located below the nozzle, as shown in Figs 1 and 5, and a pulsed ignition system for continuous reignition of the gas-water mix on approximately the quenching time scale.

The use of salt water enhances the ignition process due to its electrical conductivity but also provides a plasma further up the flame that could be superheated using RF or a flowing microwave torch configuration. As shown in the photo in Fig. 9 we tested the concept of post-heating of the flame using a dielectric barrier discharge (DBD). The center electrode can be seen in the left-hand photograph. This device did indeed heat the flame further but the heat load on the quartz tube was excessive and we broke tubes after a short time. An alumina tube may have worked better but RF or microwave heating, which may have fewer materials, issues, are probably the best approaches to post-heating of the flame. Temperature of 5000-6000 K might be attained which would dissociate all the molecular constituents of the plasma. Depending upon how one cooled the plasma and what additives may be flowed into it, one might be able to tailor the product species. Such a device may have applications in treating polluted water on a large scale.

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REFERENCES


Louis A. Rosocha (’94) earned the B.S. degree in physics from the University of Arkansas (Fayetteville) in 1972, and the M.S. and Ph.D. degrees in physics (minor in chemistry) from the University of Wisconsin (Madison) in 1975 and 1979, respectively. From 1978-1981, he was at the National Research Group of Madison, WI, developing pulsed ultraviolet lasers, fast pulsed-power switchgear, and modeling commercial ozone generators. From October 1981 – January 2008, he was a technical staff member and manager at the Los Alamos National Laboratory (LANL). After an early retirement from LANL in 2008, Dr. Rosocha became an independent consultant, focusing his R&D interests on CO2 sequestration/global warming, national energy security, and water/air pollution abatement.

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