Development of a Self-Atomizing Form of Water

Next Generation Fire Suppression Technology Program
Project 4D/4/7

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Richard K. Lyon
EER, Inc.

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The goal of this project was to do a laboratory-scale proof of concept evaluation of the use of novel type of ice-like materials (carbon dioxide hydrate and/or other gas hydrates) as fire fighting agents. If carbon dioxide hydrate were an effective fire fighting agent, it would also have the advantages of being clean, environmentally friendly and user safe. Specific milestone goals were the demonstration that hydrates are capable of self atomization and that this self atomization could be delayed briefly. While the test results show that these milestones were achieved, carbon dioxide hydrate does not appear to be a promising fire fighting agent and no further development is recommended.

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EXECUTIVE SUMMARY

A OBJECTIVE

Broadly the goal of this project was to do a laboratory-scale proof of concept evaluation of the use of carbon dioxide hydrate and/or other gas hydrates as fire fighting agents. Specific milestone goals were the demonstration that hydrates are capable of self atomization and that this self atomization could be delayed briefly.

B BACKGROUND

Halons provide fire protection in many U.S. weapons systems currently in service but production of halons has been banned, making it necessary to find suitable replacements. Gas hydrates such as CO_2 hydrate are an unusual form of ice, stable only under high pressure. Since gas hydrates are unstable at ambient pressure, it was speculated that a gas hydrate, when suddenly discharged to ambient pressure, might undergo self atomization, might disintegrated into fine mist. It was further speculated that this fine mist would be an effective fire fighting agent and that the self atomization might be delayed, allowing particles of hydrate to be thrown substantial distance toward a fire. While this research project involved substantial risks that these speculations might be incorrect, there was the advantage that CO_2 hydrate is obviously user safe and environmentally friendly. Thus the risk of discovering an effective fire fighting agent and then being unable to use it is avoided.

C SCOPE

Section 1 provides background information. A brief theoretical examination of the use of fine mists to extinguish fires is given in Section 2. The experimental methods used in this research are summarized in Section 3. Sections 4 and 5 respectively summarizes and discuss the experimental results of this study. Section 6 reports the conclusion of this examination and makes recommendations.

D METHODOLOGY

Theoretical and experimental studies included heat transfer analysis video tape analysis of the hydrate discharge process, low temperature recovery and examination of hydrate samples at ambient pressure and testa with two types of obstructed fires.

E RESULTS

The low temperature recovery experiments graphically demonstrated that gas hydrates can be metastable, i.e. they can exist briefly at ambient pressure even though they are thermodynamically unstable at ambient pressure. The results of the video tape experiments indicated that CO_2 hydrate can undergo delayed self atomization, though the efficiency of this process was not determined. Tests with two types of obstructed fires did not show CO_2 hydrate to be an effective fire fighting agent.

F CONCLUSIONS AND RECOMMENDATIONS

The failure of CO_2 hydrate to extinguish fires even though it does appear to self atomize, may mean that the self atomization was poorly efficient. Alternatively it may mean that, for the test conditions used, the discharge process allowed the hydrate to produce fine mist in the general vicinity of the flame but did not provide momentum to carry the mist into the flame. Whatever the reason for the failure gas hydrates do not appear to be promising as potential replacements for halons. Further research based on this approach is not recommended.

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1. INTRODUCTION

1.1 BACKGROUND

1.1.1 DEFINITION OF THE PROBLEM

At one time the fact that halons were highly effective, clean, and user safe led to their acceptance as a virtually ideal method of extinguishing fires. While cost considerations limited the use of halons in some fire protection applications in the civilian sector, military acceptance of halons was common. Weapon systems were designed in which the use of halons for fire protection was assumed. This led to the construction and deployment of weapons systems in which retrofitting carbon dioxide or some other fire protection system would be difficult and expensive if not impossible.

The recognition that halons contributed to the destruction of the ozone layer led to an international treaty banning their production. Since the treaty did allow the use of existing stocks of halons, the impact of this ban on the U.S. military was, in the short term, quite manageable. All nonessential uses of halons were eliminated and halons were recovered and recycled whenever possible. Even with strict conservation, however, weapons and other systems presently in use will, during their useful lifetimes, need much larger amounts of halon than the existing stocks.

Thus the problem of finding a "suitable replacement" for halons involves a number of difficult requirements. The new fire extinguishing agent must be:

1) Effective, comparable to halons on both a weight and volume basis.

2) "Clean" in that the extinguishing agent must be harmless to valuable materials and supplies. Since damage to electrical/electronic equipment is a critical issue, the new extinguishing agent needs to be nonconducting. Avoiding damage to machinery such as jet engines is also important and hence the agent also needs to be nonabrasive.

3) Environmentally friendly, i.e. there must be a substantial body of evidence indicating, if not absolutely proving that the new fire extinguishing agent causes little or no harm to local ecosystems, and contributes virtually nothing to ozone depletion and global warming.

4) Nontoxic, i.e. the agent must not cause significant acute toxic effects when used properly and there must be a substantial body of information indicating little or no reason to be concerned about

the long term effects of exposure to the agent.

These are, of course, conflicting requirements. If, for example, a proposed new extinguishing agent is not chemically inert, it may be very difficult to prove that human exposure to the agent does not cause some unfavorable long term health effect. If it is chemically inert, then it will accumulate in the atmosphere and contribute to the Greenhouse Effect.

1.1.2 CURRENTLY AVAILABLE FINE MIST TECHNOLOGIES

The discussion above suggests that a new fire extinguishing agent will be unsuitable as a halon replacement if it is not chemically inert and if it is. One possible way around this dilemma might be to avoid "new" fire extinguishing agents, i.e. to limit the search to materials whose effects on people and the environment are well known. Distilled water, for example, is not electrically conductive, is nonabrasive, environmentally friendly, and nontoxic. Thus if one could find a way to greatly improve the effectiveness of water for extinguishing fires this could be a satisfactory solution to the problem.

There has been a substantial amount of R&D seeking to improve the effectiveness of water as a fire fighting agent. At the time that halons were developed it was recognized that fine mists of water were also a very effective fire fighting agent. As illustrated by the calculations shown in Figure 1, the evaporation time of a water droplet in a hot environment decreases with decreasing droplet diameter. The large droplets generated by the classic fire hose have an evaporation time that is much longer than the time they spend passing through a flame. Thus they do not remove heat directly from the flame but rather do so indirectly by cooling the flame's surroundings. This, of course, is inefficient and requires using large quantities of water. Conversely a flame is vulnerable to cooling by small droplets of water <u>provided one has a means of getting the mist into the flame</u>.

That, however, has been a problem. Figure 2 shows the calculated terminal velocity of droplets settling in air as a function of size. Comparing Figures 1 and 2 one sees that droplets small enough to effectively remove heat from a flame are also small enough that they settle quite slowly. Similarly the amount of momentum small droplets can be given is so small and the frictional forces acting on them so large that they can not be thrown any great distance.

As discussed by Tatem et. al.[1] a number of "fine mist" systems are commercially available for fire protection. Within these systems the

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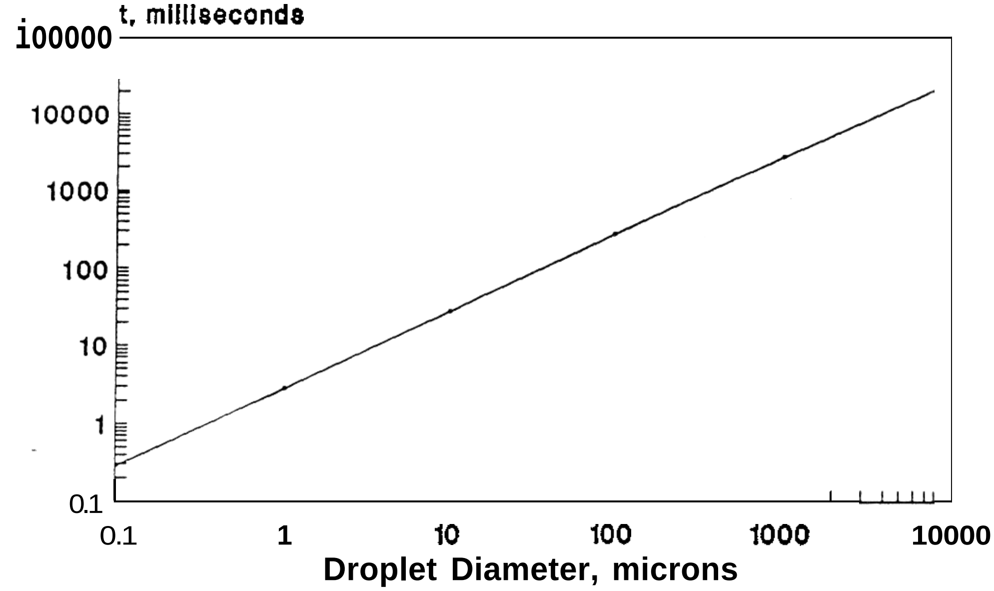
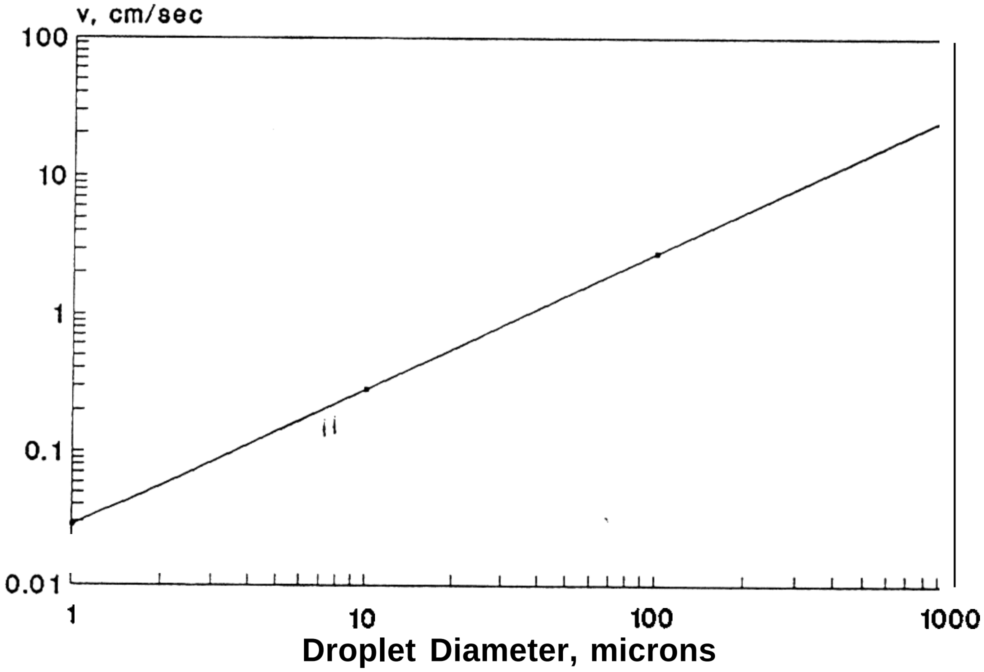
[1] P. A. Tatem, C. Beyler, P. J. DiNenno, E. K. Budnick, G. G. Back, S. E. Younis, A Review of Water Mist Technology for Fire Suppression, NRL/MR/6180--94-7624 (AD-A285 738)

Figure 1 Droplet Evaporation Time in 1100 C Gas



Heat Transfer Coefficient taken
as 0.0142 watts/cmsqu C

Figure 2 Droplet Terminal Velocity



solution commonly adapted to the problem of getting the fine mist to the fire is to generate a mixture of coarse and fine droplets. The former can be given enough momentum to carry them to the fire and they tend to drag the latter in their wake.

While this approach allows extinguishing fires with much less water than would be required with a conventional fire hose system, the amount of water used is still quite large compared with a halon system.

Further improvement seems possible in light of the experiments of B.J. McCaffrey[2]. In these experiments the effect of fine water mist on a natural gas diffusion flame was examined. The problem of getting the mist to the flame was avoided by placing the atomizer at the base of the flame. Since the natural gas into which the mist was injected all went into the flame so did the mist. Mass flow rates of mist approximately equal to the flow rate of the fuel were found sufficient to extinguish the flame, i.e. in this instance fine mist was fully as effective as a halon.

1.1.3 OTHER APPROACHES TO FINE MIST PRODUCTION

One possible approach to the problem of getting the fine mist to the flame is to generate the mist electrostatically. Since flames are electrically conductive, they tend to ground themselves, causing the electrically charge mist to be attracted to them. Work along these lines is currently being done by Dr. Kelly and coworkers at ZYW Corp, Princeton, NJ and by Dr. Berman at AeroChem Princeton, NJ.

1.1.4 THE APPROACH TO FINE MIST PRODUCTION FOLLOWED IN THIS RESEARCH

Gas hydrates can form with either of two structures. In both of these structures the essential unit is a pentagonal dodechedron of water molecules, the gas molecule occupying the space in the center of the dodechedron. This structure owes its stability to the fact that each of the twenty apices is occupied by an oxygen atom bonded to four hydrogen atoms at close to tetrahedral angles, i.e. it maximizes hydrogen bonding.

In the type I structure there are 2 smaller (a_1 = 3.94A) and 6 larger cavities (a_2 = 4.30A) for every 46 water molecules. For type II there are 16 smaller cavities (a_1 = 3.91A) and 8 larger cavities (a_2 = 4.73A) for every 136 water molecules. The type II hydrate forms only with gas molecules that are too large for the cavities in the type I structure. While the number of cavities has a definite stoichiometry, the extent to which gas molecules occupy those cavities can vary over a significant range. Furthermore mixed hydrates with two or more different types of gas molecules filling the cavities can readily be formed. For the case of a mixed hydrate of a large molecule such as

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[2] B.J. McCaffrey, Combust. Sci. and Tech., 63, 315-335 (19889)

$CHCl_3$ and a small molecule such as CO_2, the large molecule occupies some of the large cavities and none of the small cavities while the small molecule occupies some of both.

At 0°C a pressure of **12.9** atmospheres is necessary to form the CO_2 hydrate from pure water. With increasing temperature the CO_2 pressure needed to form the hydrate increases. At 9.9°C 43.5 atmospheres is needed and at greater temperatures no hydrate can be formed by CO_2 alone. Mixed hydrates containing substantial amounts of CO_2 can, however, be formed at higher temperatures by using a second gas with a hydrate forming ability greater than CO_2.

There do not appear to be any reports in the literature as to what happens when a gas hydrate is suddenly depressurized. It is, however, interesting to note that water under extreme pressure can form 5 solid phases in addition to the familiar ice. One of these, Ice 111, is blue. While Ice III is thermodynamically stable only at pressures in excess of 2040 atmospheres, it can be cooled to liquid nitrogen temperature, and then be depressurized. At one atmosphere and very low temperature, Ice III is metastable. It can last for an extended period of time if kept cold but it disintegrates into a fine powder of ordinary ice on contact with anything warm.

From a thermodynamic viewpoint the decomposition of a CO_2 hydrate offers two quite different cases. The heat of forming a CO_2 hydrate from gaseous CO_2 and liquid water is almost exactly the same as the heat for forming ice from the water. Thus, if a pure CO_2 hydrate at an initial temperature below 0°C is adiabatically depressurized, it becomes unstable with respect to decomposition to ordinary ice and gaseous CO_2 with very little temperature change occurring during this decomposition. This case would appear to be quite similar to the case of Ice III in which considerable metastability was possible, i.e. both involve the conversion of one solid to another without the formation of a liquid phase.

If, however, the initial temperature is greater than 0°C, the hydrate becomes unstable with respect to adiabatic decomposition to gaseous CO_2 and a mixture of liquid water and ice, the temperature falling during the decomposition to 0°C. Since the liquid water can act as a catalyst for the conversion of the solid hydrate to ordinary ice the hydrate seems less likely to be metastable in this case.

1.2 OBJECTIVE

The goals of this project was to demonstrate that hydrates are capable of delayed self atomization and that they are consequently potentially useful as replacements for halons in fire fighting.

1.3 SCOPE

Section 1 provides background information. A brief theoretical examination of the use of fine mists to extinguish fires is given in Section 2. The experimental methods used in this research are summarized in Section 3. Section 4 summarizes the experimental results of this study. Section 5 examines the scientific and engineering implications of these results.

Section 6 reports the conclusion of this examination and makes recommendations. While no further work along these lines appears justified a possible alternative approach is suggested.

2. THEORETICAL ANALYSIS

The theory of evaporation of small droplets in the vicinity of a flame involves a complex set of issues that are beyond the scope of this report. There is, however, some useful insight to be gained by going beyond the very simplified discussion given above. Let us assume the following situation: a droplet of diameter D and initial diameter D_o travels toward a flame at a velocity of v. Initially the gas through which the droplet travels is cool. The flame has a temperature of 1400°C. As the droplet approaches the flame it passes through a region of thickness a in which the temperature rises from 100°C to 1400°C. While the droplet passes though this region, it evaporates, its diameter decreasing at a rate of

1) $$-dD/dt = 2K\Delta T/\Delta H$$

where K is the heat transfer coefficient, typically **0.0142** watts/cm^2°C, AT is the difference between the local temperature and 100°C, and AH is the heat of evaporation of water, 2410 joules/cc.

combustion gases. While the evaporation of the droplet removes heat from the precombustion gases in the temperature gradient region, from postcombustion gases leaving the flame, and from the flame reaction zone itself, in first approximation only the latter is useful for extinguishing the flame, i.e. the effectiveness of the droplet in extinguishing the flame will be proportional to the fraction of total heat it removes which comes from the reaction zone.

Figure 3 shows the results of a set of calculations done with this model with the assumption that r/a = **0.01.**

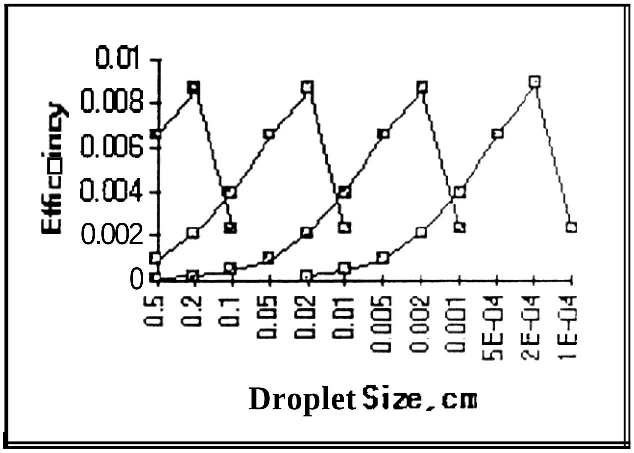


Figure 3 Efficiency of droplets for removing heat from a flame's reaction zone, v/a = 10, 1, .1, .01 seconds

For any given value of v/a, the time for the droplets to pass through the temperature gradient, there is a droplet diameter which maximized efficiency of droplets for removing heat from the flame's reaction zone. Droplets much smaller than this optimum value never reach the reaction zone and hence are completely ineffective. Those much larger have some effect but spend most of their cooling power uselessly in the postcombustion gases.

Thus the problem of making droplets effective for extinguishing fires does not appear to be a simple question of getting droplets of some "right" size, but rather a matter of getting the droplet's size and the speed with which it enters the flame to match. Large droplets fail because they move much more rapidly than their optimum velocity while with small droplets it is difficult to get them to move at a velocity as high as their optimum.

3. EXPERIMENTAL PROCEDURES

3.1 SAMPLE PREPARATION

500cc stainless steel sample bombs which were equipped with 1/4" ball valves (i.e. valves with Cv = 1.4).were used to prepare CO_2/water mixtures which were converted to hydrate. To prepare these mixtures the sample bomb was weighed, distilled water was transferred into it and it was reweighed. It was then attached to a vacuum line and evacuated briefly to remove air. The sample bomb valve was then close and the bomb was connected to a CO_2 cylinder that was equipped with a dip leg. After liquid CO_2 was added to the bomb, it was reweighed and placed in a refrigerator to convert the CO_2/water mixture to hydrate.

3.2 VIDEO CAMERA STUDIES

During tests the sample cylinders were held vertically with the valve pointed down. A length of 1/4" OD stainless steel tubing on the outlet of the ball valve bent to a right angle or to a U shape was attached to the outlet end of the ball valve. This allowed the discharge to be directed vertically or upward. A video camera was used to record what occurred. During subsequent analysis of the video tape the discharge time was measured with a stop watch while playing the tape at slow speed. Playing speed was measured by comparing stop watch readings with time as recorded on the tape by the video camera's clock. Distances were measured on the tape by using the PI's height as a reference length.

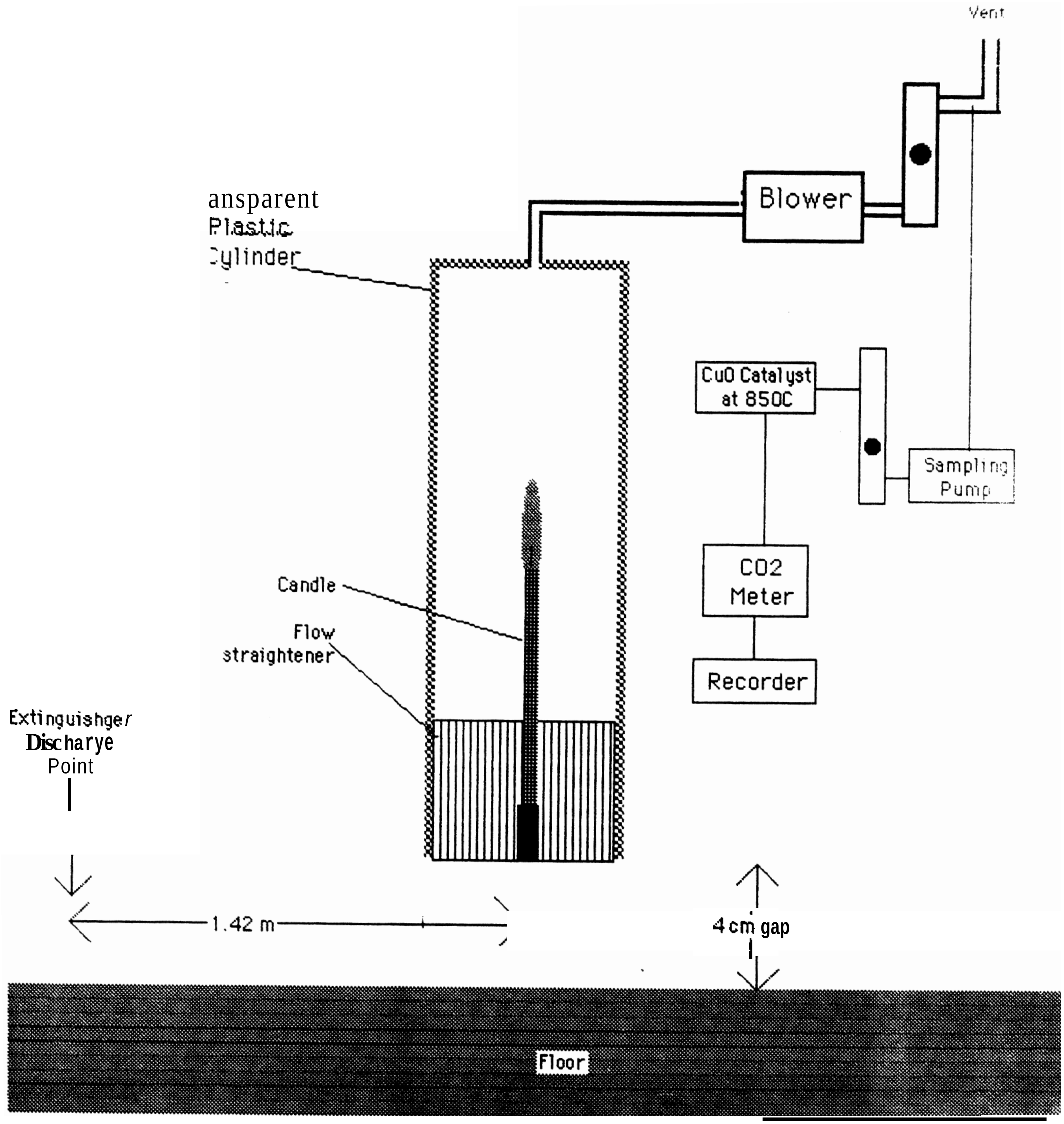
3.3 CANDLE IN THE WIND EXPERIMENTS

Figure 4 shows the experimental setup used in this series of tests. In this setup an 0.875" diameter candle is placed inside a transparent plastic tube, 24" long by 4" in diameter. The top of this plastic tube was connected to a blower while the bottom was filled with vertical 4" lengths of pyrex tubing, 6mm OD, 4mm ID. The blower was used to pull a flow of air through this tube at a rate of 7.5 cfm, i.e. at a velocity of 1.43 ft/sec. The 4" lengths pyrex tubing served as flow straighteners.

While the bulk of this air flow is vented, some of it is extracted by a sample pump and send first through a rotameter then to a Fuji

FIGURE 4

Experimental Setup for Testing the Relative Effectiveness of Fire Extinguishing Agents



NDIR CO_2 meter whose output was recorded. Thus the CO_2 content of the gases exiting the blower could be monitored. For comparison experiments with Halon 1211, the sample was passed through a bed of an oxidation catalyst at 800°C (CuO on high surface area alumina) to convert the halon to CO_2. Previous EER studies have shown that this catalyst is quite efficient for oxidizing halons.

3.4 TESTS WITH AN OBSTRUCTED FIRE

In a literature survey Tatem et. al.[3] discussed tests of the commercially available fine water mist fire extinguishing systems. Some test procedures are uninformative, all systems being highly effective or highly ineffective. Tests with obstructed flames, however, proved quite informative, the percentage effectiveness of different systems varying over a substantial range. In one obstructed flame test setup a 1' by 1' square obstruction plate was placed 1' above a 6 cm diameter pan filled with diesel fuel. The pan was under the center of the obstruction plate and the extinguisher discharge point was directly over the center of the obstruction plate.

The experimental setup shown in Figure 5 duplicates this description, although, of course, the tests reviewed by Tatem et. al. involve a continuous discharge system while the Figure 5 setup was used for sample which discharged in a single burst.

In tests done with the Figure 5 setup the following procedure was used: a paper wick and 75 cc of diesel fuel were placed in the 6 cm cup. After igniting the wick the fire was allowed to burn for 3 minutes, the ball valve was opened, and the result observed.

3.5 AMBIENT PRESSURE RECOVERY OF HYDRATES

To recover CO_2 hydrate a 1" OD stainless steel tube with swagelok fittings on its ends was used instead of the 500 cc sample bomb. Hydrate was prepared as above but then the sample was cooled to -15°C, depressurized, the swagelok fittings were undone, and the hydrate removed.

To prepare and recover C_3F_8 hydrate the same procedure was used except that the preparation was done in a Fischer-Porter glass sample bomb.

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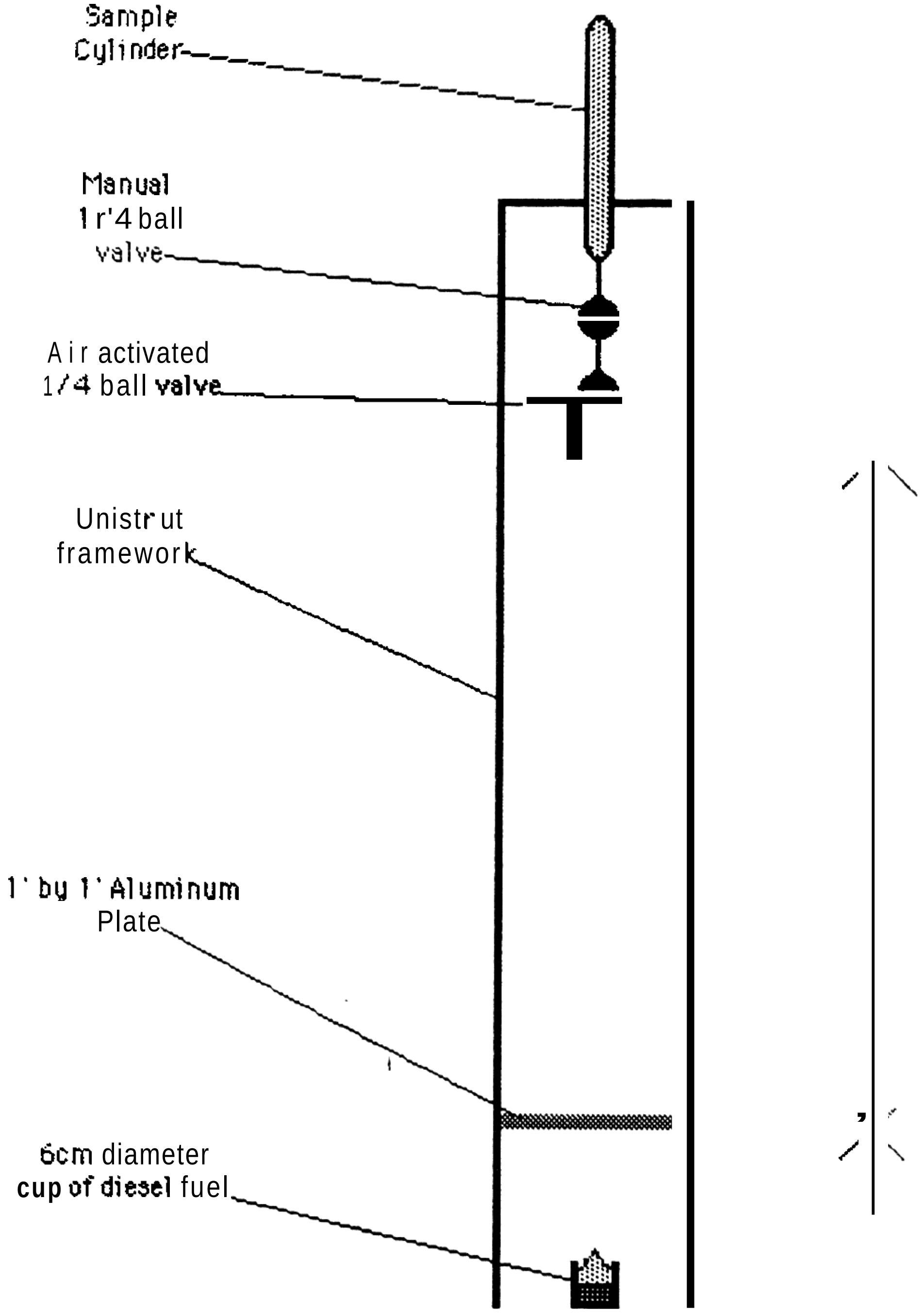
[3] P. A. Tatem, C. Beyler, P. J. DiNenno, E. K. Budnick, G. G. Back, S. E. Younis, A Review of Water Mist Technology.for Fire Suppression, NRL/MR/6180--94-7624 (AD-A285 738)

FIGURE 5

Experimental Setup for testing Agents against an obstrcuted flame



4. RESULTS

4.1 DISCHARGE CHARACTERISTIC OF CO_2 HYDRATE

Samples in which the ratio of CO_2 to water was low enough to leave a significant portion of the water unconverted to hydrate had reasonably satisfactory discharge characteristics, i.e. when the ball valve was opened the hydrate/water mixture was discharged in a more or less continuous flow. Samples in which the ratio of CO_2 to water was high enough to leave little or no water unconverted did not show satisfactory discharge characteristics, i.e. when the ball valve was opened the hydrate was discharged in discontinuous spurts.

4.2 VISUAL OBSERVATIONS

A blank experiments was done with 400 cc samples of water in 1000 cc sample bombs pressurized with He at 1500psi. This produced a spray jet with a 0.35 second discharge time, 5m tall and roughly 15 cm wide at its peak. The droplets formed by this jet showed a readily observable settling rate indicating that they were relatively coarse. Qualitatively similar behavior was observed at He pressurization of 1000 and 550 psi. At **228** psi He pressurization, however, the discharge resembled that of a common garden hose with little or no atomization.

For a solution of **20** wt% $CaCl_2$ in water saturated with CO_2 at ambient temperature and 845 psi, the spray jet pattern was clearly different, 3m tall and 50 cm wide. The droplets formed by this jet did not show an observable settling rate indicating that they were the desired fine mist.

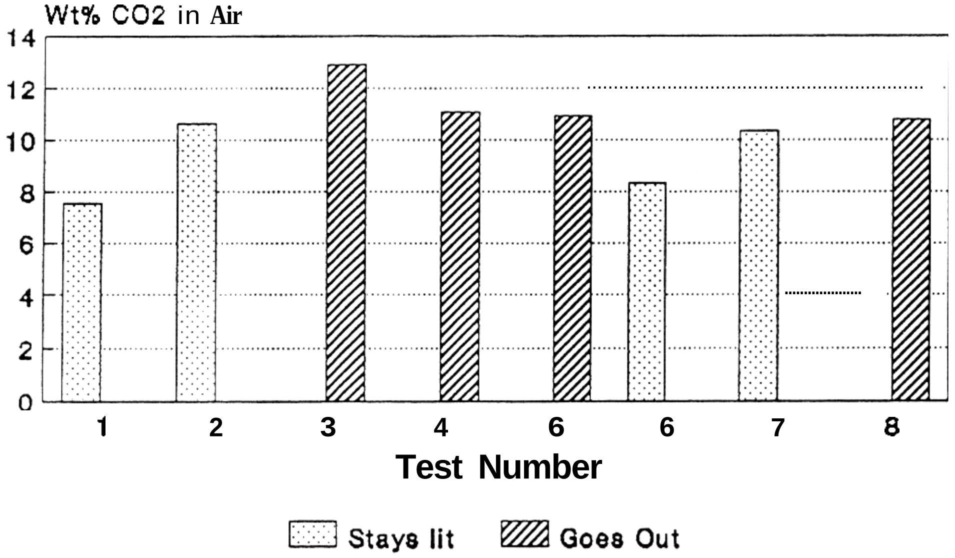
For samples of CO_2 hydratelwater mixture with an initial pressurization of **220** psi the discharge was similar in length and width to that of the sample which was pressurized with helium to 228 but the discharge produced a mist with no observable tendency to settle.

4.3 RESULTS OF THE CANDLE EXPERIMENTS

Experiments were done with the Figure 4 setup to determine the threshold for extinguishing candle flames by CO_2, Halon **1211**, and fine mists generated by CO_2 hydrate/water mixtures. The results in Figures 5 and 6 show, these experiments gave a threshold for CO_2 between 6.8 and 7.1 vol % and a threshold for Halon 1211 between 1.57 and 1.74 vol%. No thresholds were determined for fine mists generated by the CO_2 hydrate/water mixtures since under all conditions tested these mists were not able to extinguish the candle flame.

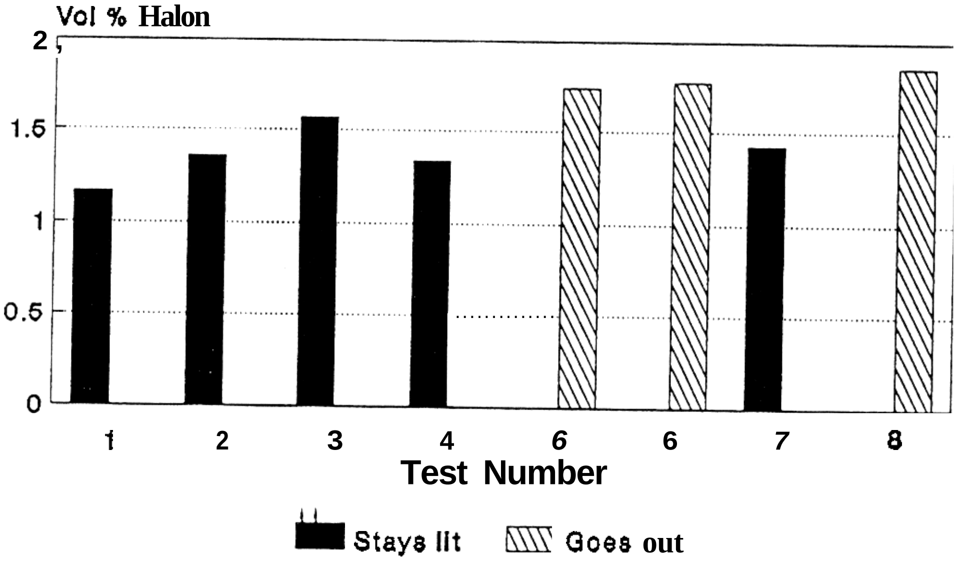
In another experiment a red laser beam was sent through the transparent plastic cylinder. Initially the beam was invisible but

Figure 6 Extinction of a Candle Flame by C02



Cylinder cross section ▪ 0.09 squ ft
Updraft ▪ 1.43 ft/sec.

Figure 7 Extinction of Candle Flame by Halon 1211



Cylinder cross section ▪ 0.09 squ ft
Updraft ▪ 1.43 ft/sec.

particles of $Ca(OH)_2$ (20 to 40 micron size) were scattered in front of the plastic cylinder the beam became evident.

4.4 RESULTS FOR OBSTRUCTED FLAMES

Three tests were done with CO_2 hydrate/water mixtures and in all three tests the obstructed flame was not extinguished.

4.5 OBSERVATIONS ON HYDRATE SAMPLES RECOVERED AT AMBIENT PRESSURE

Samples of the CO_2 hydrate looked very much like ice. When they were placed on the surface of a hot plate (surface temperature of 260°C), they acted much as did samples ice, i.e. they melted and boiled with little or no wetting of the surface.

A sample of the CO_2 hydrate placed on an ambient temperature aluminum plate initially melted with bubbling but without producing mist, then suddenly exploded. After the explosion some fragments of the sample remained on the aluminum plate. They melted with bubbling but without further explosion.

A sample of the C_3F_8 hydrate placed on an ambient temperature aluminum plate melted without explosion or mist production but with bubbling and a continuous snapping sound.

5. DISCUSSION

5.1 METASTABILITY OF GAS HYDRATES

As discussed above gas hydrates <u>might</u> be an effective fire fighting agent <u>if</u> they undergo delayed self atomization, which in turn might occur <u>if</u> the hydrate were metastable at ambient pressure. One might expect that metastability would or would not lead to self atomization depending on the circumstance. If a particle of hydrate is traveling through the air at a high velocity, its surface is subject to high shear. As that surface begins to convert to liquid water and gaseous carbon dioxide, any bubbles forming will be broken into fine droplets. Thus for a hydrate particle in flight metastability seems likely to lead to atomization. For a particle at rest, however, the situation is less clear. If the particle can store sufficient strain energy for self atomization, then it might do so. If the stored strain energy is not this large, it could still be sufficient to cause the hydrate particle to explode into coarse fragments or make snapping sounds as it melts.

While the observations with the recovered hydrate samples are consistent with these expectations, the only thing they unambiguously show is that the hydrates are capable of metastability.

5.2 ANALYSIS OF VISUAL OBSERVATIONS

Figures 8 and 9 are quoted from a review article by Faeth[4]. Figure 7 shows the different kinds of spray patterns which occur when a liquid is discharge through a hole at various flow rates. Figure 8 shows a map of the spray process, i.e. this figure shows ranges of Ohnesorge and Weber numbers in which different types of sprays will occur. Figure 8 also shows the results of calculations for the experiments done with water pressurized with helium. Consistent with the observation that samples with helium pressurizations of 1500, 1000 and 550 psi atomized, the calculations show that these pressurizations correspond to the atomization range. The fourth sample, which was observed not to atomize, is calculated to be in the wind-induced range.

The theory of spraying presented in the Faeth article does not consider the possibility that the liquid being sprayed may contain a dissolved gas. Given that helium is only very slightly soluble in water, it is not surprising that the experiments with helium pressurized samples were quite consistent with this theory. The solubility of CO_2 in water at 21°C and 845 psi is, however, 34 cc STP gas per cc of liquid. The decrease in height, the increase in width and the fact that the droplets did not show observable settling are all consistent with the assumption that the discharge produced coarse droplets which the dissolve CO_2 subsequently or concurrently atomized into fine mist.

There is, however, the problem that droplets of fine mist are far more readily visible that an equal mass of coarse droplets. While the visual observations indicate that spray water saturated with CO_2 at high pressure does indeed produce fine mist, they do not reveal how efficiently this happened.

Since the discharge hydrate/water mixture occurred in the wind induced region, had a similar appearance to the helium pressurized discharge in this region, but still produced a mist that showed no observable settling, the indication of the visual observations is that after a delay the hydrate atomized itself into a fine mist. Here again, however, the data do not tell us how efficient the atomization was.

5.3 FIRE EXTINGUISHING TESTS

In a previous research project EER examine the ability of water saturated with CO_2 at high pressure to extinguish fires. While the results showed that this was indeed an effective way of extinguishing fires, the mechanism for extinguishing the fires was not clear. Perhaps the fine mist produced by the CO_2 saturated water extinguish the flame by cooling it or perhaps the jet of CO_2/mist was simply

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[4] G. M. Faeth, 23rd Symposium (int.) on Comb., 1345-1352, **(1990)**

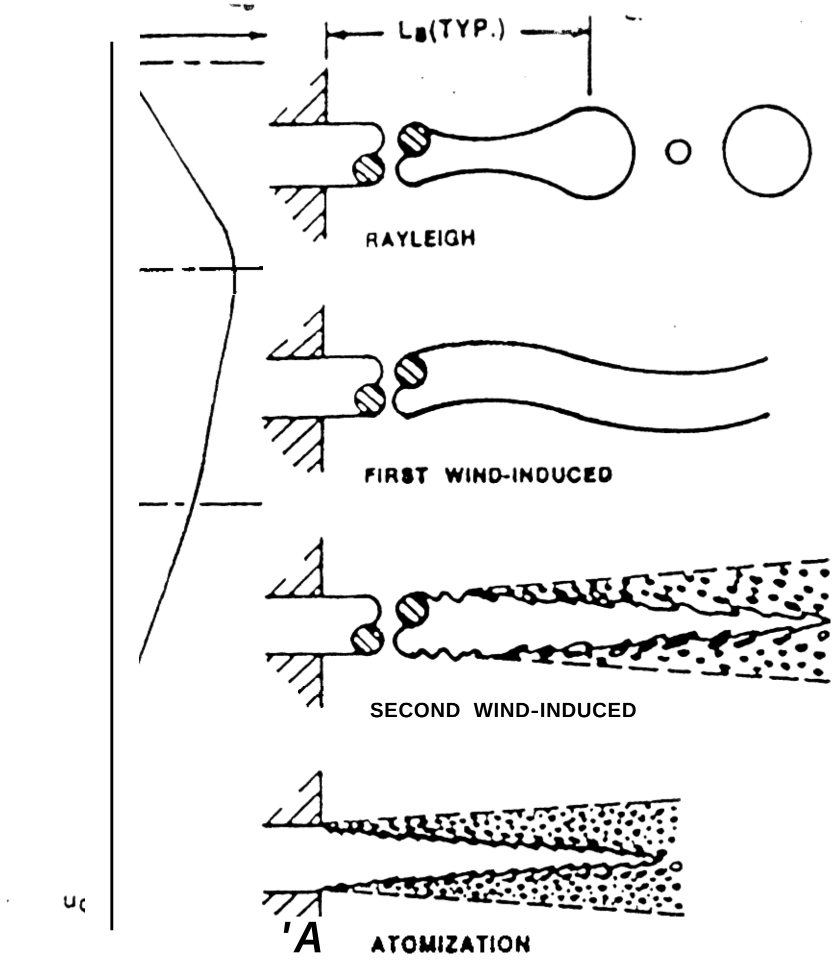

Figure 8 Spray breakup lenghts and regimes for nonturblent round liquid jets in still gas.

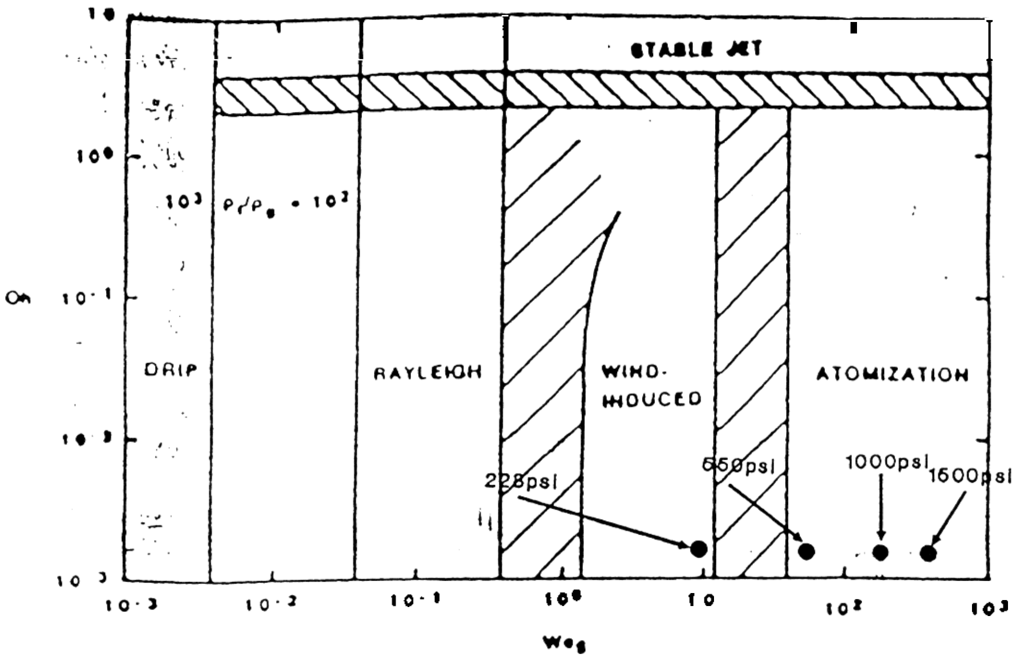

Figure 9 Spray breakup regime transitions

blowing out the flame.

Both sets of experiments reported above were designed to avoid this ambiguity. In both cases the flame was protected from the discharge of the hydrate so that mist from the hydrate arrived in the general vicinity of the flame, but without momentum from the discharge to carry it into the flame itself. Under this condition the mist from the hydrate was not effective for extinguishing the flame.

While the reasons for this failure are not completely clear, two possibilities are obvious. The present results suggest that CO_2 hydrate does undergo delayed self atomization but they do not show the efficiency of this process. If the efficiency of mist production is poor, the hydrate will not be an effective extinguishing agent. Secondly there is the question of the velocity at which the mist enters the flame. Droplets of mist have a diffusion coefficient that is very close to zero. For an ideal diffusion flame this would give them a near zero velocity of approaching the flame and for a real diffusion flame the velocity would be quite low. As the analysis in Section 2 shows, fine mist might be ineffective in this situation.

6 CONCLUSIONS AND RECOMMENDATIONS

The goal of this research was to demonstrate that gas hydrates, especially CO_2 hydrate, can undergo delayed self atomization and that this property makes them potentially useful replacements for the halons. While the data indicate the former, the latter now appears to be a remote possibility. Accordingly further research along this line is not recommended.