Methane Flame Extinguishment with Layered Halon or Carbon Dioxide

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In quenching tests of downward propagation in stoichiometric methane-air mixtures based on flammability limits and flame speed data, Halon 1301 was about five times more effective, on a volumetric basis, than carbon dioxide as an extinguishant.

WHEN an extinguishant is applied to a flame, its concentration varies both spatially and temporally in the vicinity of the flame being quenched. Studies of flame inhibition and extinguishment in the past have usually been conducted with homogeneous mixtures of the combustible gas, oxidant, and extinguishant because of the lack of an appropriate technique for carrying out experiments under reproducible, nonhomogeneous conditions. Some investigators have used a burner flame method with a variable atmosphere of extinguishant, but this method does not simulate the extinguishing process encountered with nonstationary flames.

The present paper describes the application to this problem of an interferometric technique developed by Liebman et al.[9] for determining flammability limits and flame propagation rates. These authors investigated the characteristics of flame propagating in vertical tubes in the direction of steep methane-air concentration gradients. In the present study, similar interferometric techniques are used to examine the quenching of methane-air flames propagating in the direction of extinguishant concentration gradients. Halon 1301 and carbon dioxide served as the extinguishants. Particular emphasis is given to the effect of these extinguishants on the flame speed of methane-air mixtures.

EXPERIMENTAL APPARATUS AND PROCEDURES

The apparatus, as shown in Figure 1, consisted of an interferometer, a vertical transparent duct with a square cross section, a light source, and a motion picture camera. The interferometer, a Twyman* type with folded

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*Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

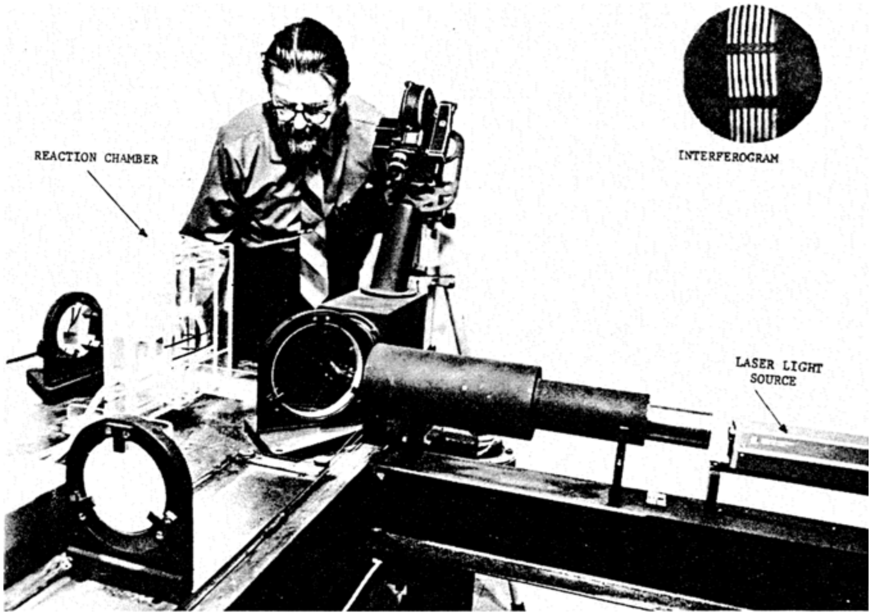

Figure 1. Experimental arrangement of interferometric apparatus.

light beams, had a beam diameter of about 11 cm. The light source was a low-power, helium-neon laser operating at a wavelength of 6,328 angstroms. The test mixtures were contained in the vertical transparent ducts, which were either 2.5 or 7.6 cm wide and 30 or 45 cm long, respectively, divided by a removable thin plastic sheet into upper and lower compartments. Optically flat windows positioned in line with the interferometer beam were mounted in the front and rear sections of the upper compartment. The motion picture camera, operating up to 500 frames per second, was used to photograph the changing interference light pattern.

To conduct an experiment, the upper compartment was filled with a known, homogeneous, methane-air mixture prepared with calibrated rotameters. The lower compartment was filled either with pure extinguishant or with a mixture of extinguishant and the methane-air of the upper compartment. The thin plastic divider between the two sections was removed, and the gases were permitted to interdiffuse for a predetermined time to form the layered mixture. The methane-air was then ignited by a weak electrical spark from a Tesla coil vacuum tester near the top of the upper compartment, which was opened to the air immediately before ignition; the resultant flame propagated downward towards the closed duct end until it was extinguished. The present study was limited to downward propagation into the layered extinguishant mixtures because of the high density of both Halon 1301 and carbon dioxide and the consequent requirement of upward diffusion of the extinguishant into the lighter methane-air mixture.

The extinguishant concentration was measured by the lateral shift of the initially vertically oriented interference lines. Initial calibration was accomplished by counting the number of fringes moving past a given point as the concentration of extinguishant increased from 0 to 100 volume percent. For Halon 1301, one fringe shift corresponded to a change of 0.58 percent Halon in the 7.6-cm-square duct. Due to the uncertainty in the measurement of the fringe shift, the Halon concentration could only be determined to within ±0.2 volume percent. Flame position was determined at the locus of the discontinuity in the slopes of the interference fringes.

In a separate experiment, the diffusion coefficient of Halon 1301 was determined during diffusion into a stoichiometric methane-air mixture. Following removal of the thin plastic separator, the fringe shift was photographed at regular intervals of 1.8 seconds over a period of about 30 seconds. Because of existing thermal gradients, these measurements were only approximate, but serve to indicate the range of diffusion coefficients measurable with this apparatus.

RESULTS AND DISCUSSION

Flame Speeds of Methane-Air Mixtures

Figure 2 compares the flame speeds determined by Liebman in a 5-cm duct in a layered methane-air mixture under conditions of downward propagation with the values determined in the present study for homogeneous mixtures in the 7.6-cm duct. Also included for comparison is

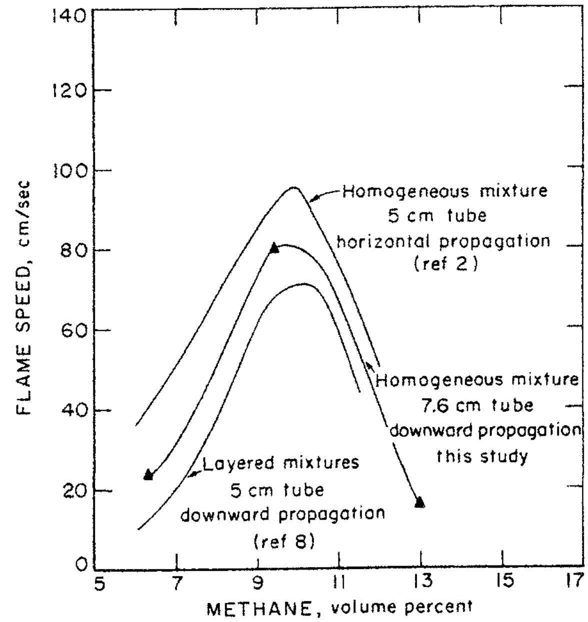

Figure 2. Flame speeds of methane-air mixtures.

the flame speed versus methane concentration curve produced in a horizontal 5-cm tube for homogeneous mixtures.[2] Flame speed in the 7.6-cm duct is higher than that in the 5-cm tube for all concentrations, being about 13 percent higher near the stoichiometric region. This is consistent with observations made by others, for example Coward et al.,[2] that flame speed increases with increased tube diameter. This trend is attributed to the increase in the ratio of flame area to tube cross section with increased tube diameter. These results agree qualitatively with Liebman's findings that flame speeds through layered mixtures are comparable to speeds in homogeneous mixtures for corresponding concentrations.

FLAME SPEEDS OF METHANE-AIR-HALON 1301 MIXTURES

Initial experiments with layered mixtures of Halon 1301 extinguishants were carried out in a 2.5-cm, square cross section duct. Figure 3 represents the data of two experiments in which stoichiometric methane-air mixtures were used. In the first, the maximum flame speed obtained from the slope of the curve in Figure 3 was 63 cm/sec with a reduction down to 5 cm/sec after the flame had traveled 5.6 cm and was extinguished at a level of 2.2 percent overall Halon.

In comparison, subsequent experiments indicated that the average extinguishment level for the 7.6-cm tube was 2.5 percent with a maximum flame speed of 80 cm/sec. Figure 4 shows the effect of Halon 1301 concentration on flame speed that was obtained from the interferometric measurement in the 7.6-cm duct with stoichiometric methane-air mixtures. Note that the flame speed decreased to 5 cm/sec at a Halon concentration

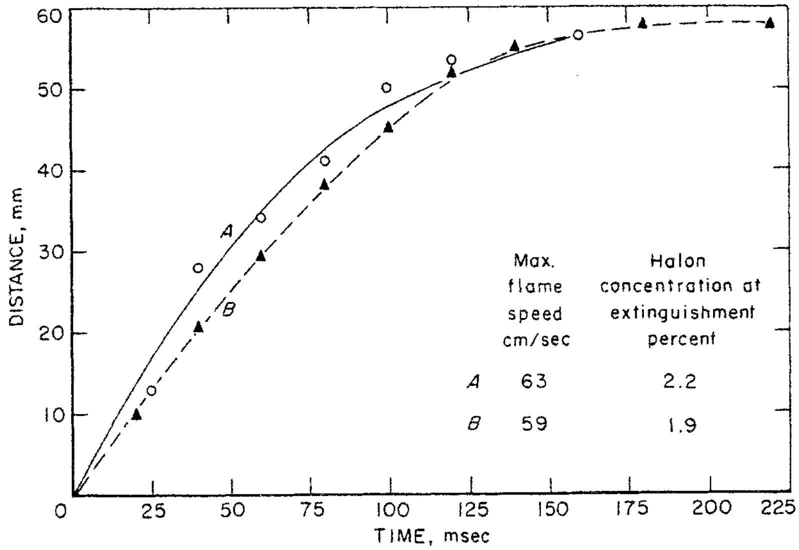

Figure 3. Flame travel in 2.5-cm square duct for stoichiometric methane-air flame propagating downward into layered Halon 1301 mixture.

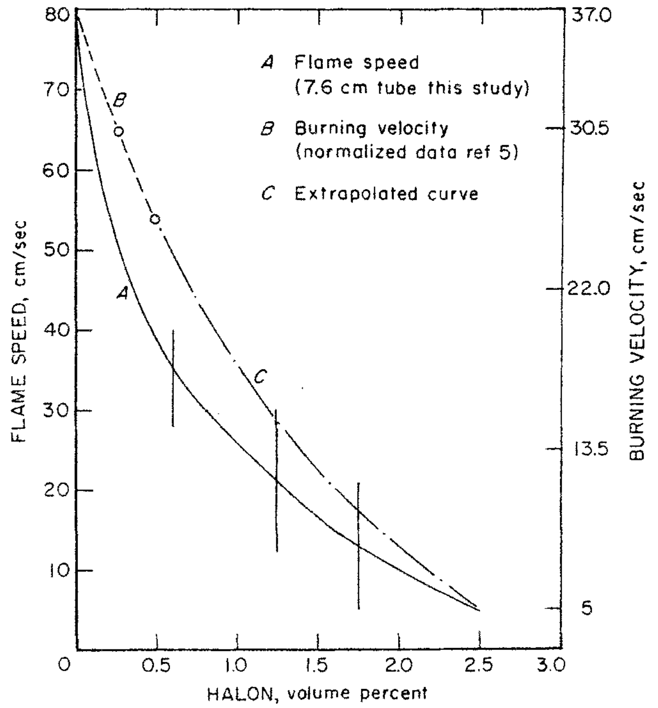

Figure 4. Effect of Halon 1301 concentration on flame speed and burning velocity of stoichiometric methane-air.

of about 2.5 percent. Also included in Figure 4 is a curve for the results reported by Halpern;[6] who used a Bunsen burner technique to determine the burning velocity (S_u) of stoichiometric methane-air mixed with Halon 1301. Reported S_u values ranged from 37 to 26 cm/sec for Halon concentrations of 0.0 to 0.5 percent. Since their measurement was of S_u and not flame speed (S_f), the results were normalized and also extended to the minimum Halon quenching concentration of 2.5 percent. This was done on the basis of the following two premises.

(1) During flame propagation in a short duct towards the closed end, S_f is approximately equal to $(A/a)S_u$, where A/a equals the ratio of flame area to duct cross sectional area.

(2) During downward flame propagation in a duct through progressively decreasing S_u mixtures, the flame shape changes, resulting in a continuing decrease in A/a. In the present experiments, this would correspond to a near hemispherical flame front ($A/a \simeq 2$) at 0 percent Halon and a near flat flame front ($A/a \simeq 1$) at 2.5 percent Halon.

For convenience, S_u is plotted on the right ordinate of Figure 4, so that the maximum S_u value of 37 cm/sec is at the same level as the maximum S_f value of 80 cm/sec. A minimum value of S_u of 5 cm/sec would then also correspond to the same level of minimum flame speed of 5 cm/sec ($A/a \simeq 1$). By the use of premise 1, A/a values of 2.16 and 2.04 were calculated using Halpern's S_u values of 37 and 26 cm/sec, respectively. A smooth curve extending the normalized S_u data was then plotted on Figure 4 in conformity with premise 2. Table 1 shows the results obtained for this plot. With this extrapolation, it is thus possible to estimate burning velocities of the stoichiometric methane-air mixed with as much as 2.5 percent Halon.

QUENCHING BY HALON 1301

Figure 5 shows the Halon 1301 required to quench flame propagation by the upward and downward modes for various methane-air mixtures. It compares data obtained in the present layered Halon experiments for downward flame propagation in the 7.6-cm duct (A) with data obtained by Burgess and Kuchta[1] in the Bureau of Mines flammability apparatus (F-11) for premixed mixtures of Halon-methane-air and upward flame propagation in a 10-cm-diameter tube (B). The increased Halon requirement (4.7 percent) for upward flame propagation is believed to be due largely to preferential diffusion, which results in dilution of the Halon in the vicinity of the flame zone. An analogous effect is observed in the combustion of heavy hydrocarbons. For example, the rich limit of pentane in air is 8.0 and 4.64 percent pentane by volume for upward and downward propagation respectively.[3]

TABLE 1. *Flame Speed and Burning Velocity of Stoichiometric Methane-Air Mixtures with Halon 1301.*

Halon concentration (volume percent)	*Flame speed (cm/sec)*	*Burning velocity (cm/sec)*	*A/a*
0	80	37.0*	2.16
0.3	65	30.5*	2.13
0.5	53	26.0*	2.04
1.0	35	17.5†	2.00
1.5	22.5	12.5†	1.80
2.0	12.5	8.4†	1.49
2.5	5.0	5.0†	1.00

*Data from Reference 6.

†Extrapolated.

Downing et al,[5] also studied the effectiveness of Halon 1301 as a quenching agent for methane-air flames in a standard 100-cc explosion pipette (about 2.5 cm in diameter and 33 cm long.) For downward flame propagation, they found that 1.1 percent Halon premixed in a 9.9 percent methane-air mixture prevented flame propagation. This low Halon quenching requirement is even less than the present finding of 2 percent in the 2.5-cm duct. It can, therefore, be assumed that the quenchant requirements for layered mixtures are not necessarily less than those for premixed mixtures, but that they are more dependent upon whether the propagation is in the upward or downward mode. It is interesting to note that the minimum design concentration of Halon 1301 for flame extinguish-

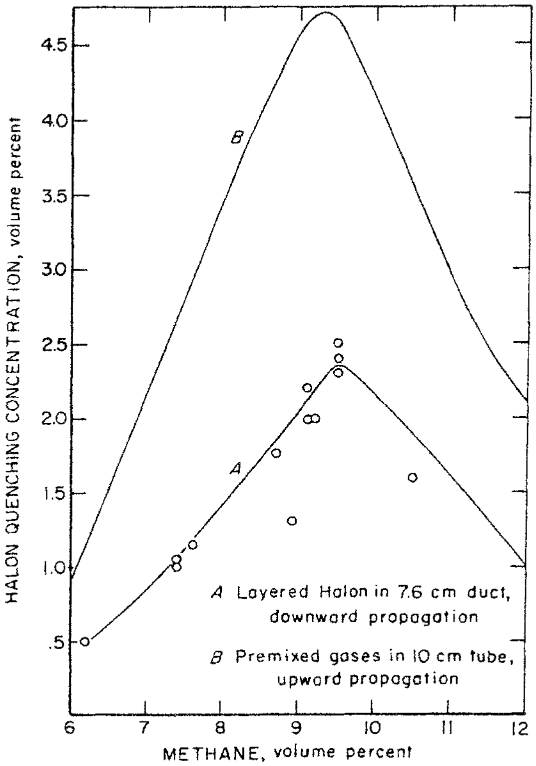

Figure 5. Halon 1301 quenching concentrations for flame propagation with layered and premixed methane-air-Halon mixture.

ment or inerting is 2 percent by volume as cited by the National Fire Protection Association.[11] This would agree with the data obtained in this report for downward propagating flames. However, in accordance with the findings of Burgess and Kuchta, the safe level of Halon 1301 concentration should be above 4.7 percent.

Figure 4 shows that a relatively small amount of Halon results in a significant reduction in flame speed. For example, only 0.5 percent Halon or one-fifth of the requirements for flame extinguishment reduces flame speed by one-half. This suggests that small quantities of Halon act as chemical inhibitors, whereas increased amounts serve mainly as thermal sinks. This reasoning is consistent with that of Rosser et al.[12] who examined the effect of metal salts on hydrocarbon flames.

Work with diffusion flames by others is also of interest, since most fires behave like diffusion flames. Creitz[4] determined that Halon 1301 added to the air side of a methane-air diffusion flame extinguished it at the 1.5 percent Halon level, but it required 22.9 percent Halon added to the fuel side for extinguishment. The former required Halon level is similar to our observation. Due to mixing, the latter percentage is reduced from 22.9 percent to approximately 2.2 percent (0.229 × 0.096) in the stoichiometric fuel-air region (9.6 percent methane). The Halon concentration in this region would be even further reduced because of the relatively slow diffusion rate of Halon. Simmons and Wolfhard[13] also noted that extinguishment of propane diffusion flames by methyl bromide was more readily achieved when the inhibitor was supplied to the air side of the reaction zone than when it was added to the fuel side.

QUENCHING BY CARBON DIOXIDE

A limited number of experiments were conducted with carbon dioxide as the quenching agent. As shown in Figure 6, reduction in flame speed to 5 cm/sec would require more than 12 percent carbon dioxide with stoichiometric methane-air, as compared to 2.5 percent with Halon 1301. This would indicate that the Halon 1301 is about five times as effective on a volumetric basis as carbon dioxide in reducing the flame speed of methane-air mixtures. This result is compatible with that found by Miller et al.,[10] who studied the effect of various inhibitors on hydrogen-air. They found that 2.17 percent added Halon 1301 reduced the hydrogen-air flame speed by 42 percent, while the addition of 3.96 percent carbon dioxide reduced flame speed by 15 percent. Thus, again the Halon is apparently five times as effective as carbon dioxide in its ability to reduce the flame speed of flammable mixtures. Halon 1301 is also found to be five times more effective than carbon dioxide with upward propagation in view of the reported quenching concentration requirements of 4.7 percent versus 22 percent.[14]

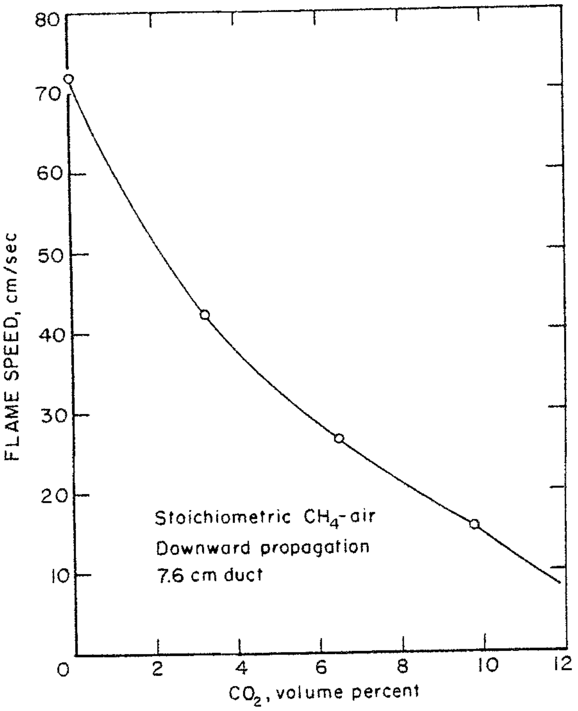

Figure 6. Effect of carbon dioxide concentration on flame speed of stoichiometric methane-air.

DIFFUSION COEFFICIENT OF HALON 1301

The diffusion coefficient of Halon 1301 was determined from the diffusion equation[7] using results of experiments in which Halon concentration was determined as a function of time and distance from the initial separation barrier between the Halon and the stoichiometric methane-air mixture. Table 2 indicates the values of the coefficient obtained at various distances from the barrier and at the indicated elapsed time interval. The average value of the diffusion coefficient is 0.027 cm^2/sec. These values can be useful in comparing the effectiveness of the extinguishants where diffusion of the species is a controlling factor. It is interesting that the diffusion coefficient of carbon dioxide (approximately 0.16 cm^2 per sec for diffusion in air[8]) is considerably higher than that of Halon, yet on a volumetric basis, carbon dioxide is much less effective as an inhibitor.

TABLE 2. *Diffusion Coefficient of Halon 1301 into Stoichiometric Methane-Air at 25° C and Atmospheric Pressure.*

Halon concentration (%)	*Distances from barrier (mm)*	*Diffusion time (sec)*	*Diffusion coefficient (cm^2/sec)*
1.8	15.4	7.2	0.036
	18.1	9.0	0.041
	18.1	10.8	0.035
	16.7	12.6	0.025
	17.3	14.4	0.024
3.6	11.7	7.2	0.029
	13.7	9.0	0.032
	13.5	10.8	0.026
	11.9	12.6	0.017
5.4	9.0	7.2	0.021
	10.4	9.0	0.024
	10.0	10.8	0.018
			Average 0.027 ± 0.007

SUMMARY

The extinguishment of methane-air flames by layered mixtures of Halon 1301 and carbon dioxide was studied by means of an interferometric technique. In a 2.5-cm duct, stoichiometric methane-air flames were quenched in their downward progress at a Halon 1301 concentration of 2 percent; whereas in a 7.6-cm duct, the concentration needed for quenching increased to 2.5 percent. Under similar conditions in the 7.6-cm duct, 12 percent carbon dioxide was required to quench the flame. Similarly, Halon 1301 was about five times more effective in reducing flame speed than carbon dioxide. Comparison of quenching data indicated that flames propagating upward require more quenchant than the downward propagating flames, and, therefore, the former should be relied upon in determining safety requirements. Additional data from this research includes a determination of 0.027 cm^2/sec as the diffusion coefficient of Halon 1301 into stoichiometric methane-air.

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