COMPARISON OF AGENT EXTINGUISHMENT OF HYDROGEN AND HYDROCARBON FLAMES USING A FID

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INTRODUCTION

The FID (flame ionisation detector), was modified and developed **as** a screening test by DERA for determination of extinguishing concentrations of potential halon replacement compounds. The modifications and method have been previously reported at HOTWC [I]. The test protocol is flexible and can facilitate the evaluation of both gaseous and liquid agents, with boiling points **up** to about 300 °C. With very small quantities of agent required for assessment, typically less than 2g (although this is dependent on the density of the agent), this method has significant economic benefits for indicative testing of novel compounds relative to the cup-bumer methods. The flame conditions are adaptable and can be modified to simulate different fuel-based fire scenarios.

EXPERIMENTAL

For the standard DERA FID methodology, the flame model employed consisted of a hydrogen/air diffusion flame, spiked with methane to impart hydrocarbon character. Based initially on stoichiometric fuel/air flame combustion chemistry, the precise **gas** flows were adjusted until an extinguishing concentration of 2.9% for Halon 1301 was achieved. This was the accepted result generated from cup-burner tests. The **gas** flows for the DERA FID that simulated this results were (I) 15 ml/min hydrogen, (2) 400 ml/min air (bottled), and (3) **38** ml/min methane. These are now considered to be the standard set of conditions for the DERA FID method for comparison with heptane cup-burner values.

An alternative set of flame conditions was employed for comparison of hydrogen and hydrocarbon based flames. Initially, this was done to confirm that the introduction of methane in the standard DERA FID flame conditions **was** imparting the desired hydrocarbon character to the fire model. For this purpose a limited number of compounds were to be assessed. However, the suppression of hydrogen flame fires is relevant for specific equipment and applications. One such rapidly developing technology area is that of fuel cells. **A** wide variety of analytical equipment, both stationary and portable, also have associated pressurised hydrogen cylinders. Due to the potential requirement for extinguishing hydrogen fires, it was decided to expand the study to investigate the efficiency of a range of compounds against a hydrogen flame scenario. The agents evaluated cover both gases and liquids, and include the DERA novel organic phosphorus containing compounds [1, 2], halogen containing hydrocarbon liquids, Halon 1301 **gas,** and some inert gases. The **gas** flow rates employed for these assessments were 40 ml/min hydrogen and 400 ml/min air (bottled). For both the hydrogen flame and standard DERA FID test conditions the FID temperature was maintained at 250 °C.

RESULTS

The percentage extinguishing concentrations by volume determined for the agents are detailed in the tables below. Results are presented for the standard DERA FID flame conditions ($H_2/CH_4/air$), for the hydrogen FID flame **(H_2/air),** for the cup burner, and against a hydrogen flame source. The latter two sets of values are quoted from literature, where available. Table 1 details the results for the phosphorus compounds, which are **all** liquids; however, cup-burner and hydrogen extinguishing results are not included, as values are not commonly available in the published literature. The exception to this is tris (2,2,2-trifluoroethyl) phosphite, whose cup-bumer extinguishing concentration is quoted as being 1.8%.*

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* Tapscott, R. E., personal communication, September 1998.

TABLE 1. FID EXTINGUISHING CONCENTRATIONS OF PHOSPHORUS COMPOUND LIQUID AGENTS AGAINST HYDROGEN AND HYDROCARBON FLAMES.

Compound		DERA FIDHC Flame	DERA FID H_2 Flame	HC to H_2 Flame Extinguishing Concentration Ratio
Trimethyl phosphate	TMP	1.9	3.0	1:1.6
Dimethylmethyl phosphonate	DMMP	0.7	3.0	1:4.3
Diethylmethyl phosphonate	DEMP	0.9	2.5	1:2.8
Dimethyl-2,2,2-trifluoroethyl phosphate		0.7	2.3	1:3.3
Diethyltrifluoroethyl phosphate		0.7	2.4	1:3.4
Diethylpentafluoropropyl phosphate		0.7	2.5	1:3.6
Diethylheptafluorobutyl phosphate		0.6	2.3	1:3.8
Diethyloctafluoropentyl phosphate		1.1	3.7	1:3.4
Bis (2,2,2-trifluoroethyl) 2,2,3,3,3-pentafluoropropyl phosphate		0.7	1.9	1:2.7
Tris (2,2,2-trifluoroethyl) phosphate		0.8	3.5	1:4.4
Tris (2,2,3,3,3-pentafluoro-1-propyl) phosphate		1.0	3.0	1:3
Tris (2,2,3,3,4,4,4-heptafluoro-1-butyl) phosphate		1.8	3.7	1:2.1
Tris (2,2,2-trifluoroethyl) phosphite	CB: 1.8%	1.0	4.3	1:4.3

Table 2 presents the results for the liquid halogenated hydrocarbon agents. Here cup-burner values are included; however, again no extinguishing concentrations against hydrogen fuel sources were found to have been reported.

TABLE 2. EXTINGUISHING CONCENTRATIONS OF HALOGENATED HYDROCARBON LIQUID AGENTS AGAINST HYDROGEN AND HYDROCARBON FLAMES.

Compound		Cup Burner	DERA FID HC Flame	DERA FID H_2 Flame	HC to H_2 Flame Extinguishing Concentration Ratio
Bromochloromethane	Halon 1011	2.7 [1]	5.0	8.0	1:1.6
Dibromomethane		1.3 [1]	2.6	6.8	1:2.6
Dibromodifluoromethane	BFC-12B2	2.2 [1]	2.1	8.3	1:4.0
3-Bromo-1,1,1-trifluoropropanol		4.1 [1]	4.0	5.7	1:1.4
1,2,2-Trichloro-1,1,2-trifluoroethane	CFC 113	6.2 [1]	$6.9^{ind.}$	$26.2^{ind.}$	1:3.8
2-Bromo-3,3,3-trifluoro-1-propene	AAWG # 873	2.6 [1]	4.5	5.5	1:1.2
4-Bromo-3,3,4,4-tetrafluoro-1-butene	AAWG # 903	5.0 [3]	4.1	6.9	1:1.7
2-Bromo-3,3,3,4,4-pentafluoro-1-butene	AAWG # 1116	4.1 [1]	2.5	6.1	1:2.4

ind. = indicative result

Table 3 presents results for the gaseous agents. As some of these have been more extensively studied than many of the liquid compounds, data on cup-burner results and performance against hydrogen flame sources are available in the literature for some of the compounds.

The results given for the "other hydrogen flame" sources were generated by different apparatus, but both of the systems were based on diffusion flames, with the agent added into the air stream. The Halon 1301 result was achieved on "Creitz diffusion flame extinction apparatus," and the Halon 1211 value was generated on the ICI cup burner [4].

TABLE 3. EXTINGUISHING CONCENTRATIONS OF GASEOUS AGENTS AGAINST HYDROGEN AND HYDROCARBON FLAMES.

Compound		Cup Burner	**DERA** FID HC Flame	DERA FID H_2 Flame	Other H_2 Flame	HC to H_2 Flame Extinguishing Concentration Ratio
Bromotrifluoromethane	Halon 1301	2.9 [1]	2.8	**11.5**	17.7 [4]	1:4.1
Bromochlorodifluoromethane	Halon 1211	3.2 [1]	3.5	18.0^{ind}	15.0 [4]	
Carbon dioxide		**20.4** [1]	18.8	17.7		1:0.9
Nitrogen		28.0 [1]	26.9	25.9		1:1

ind. = indicative result

Quoted [5] values for flame temperatures are (1) hydrogen: 2045 °C and (2) methane: 1875 °C. However, with the low flow of hydrogen adding to the potential flame temperature in the standard DERA FID fire model, the resultant temperature difference would probably be negligible.

The energy output of the two FID flame conditions was calculated. Assuming complete combustion, over one minute the hydrogen/air flame model was calculated to generate 0.5 kJ, compared to 1.5 kJ produced by the hydrogen/methane/air flame conditions. This corresponds to approximately 8 W and 25 W, respectively.

DISCUSSION

The extinguishing concentrations measured experimentally for the inert gases against both hydrogen and hydrocarbon flames were very similar. This indicates that the flame inhibition mechanism and mode of activity is the same for these agents against carbon and non-carbon containing fuels, and is characteristic of an agent with only, or predominantly, physical mechanisms of action.

For physically acting agents, such as the inert gases, the difference in the energy produced by the two different sets of flame conditions should enable the dominant type of physical mechanism with each agent to be identified, for example, thermal effects, i.e., cooling, or dilution effects. As the energy evolved by the hydrogen flame was calculated to be much less than that of the methane flame, a thermally active agent where the main mechanism was cooling, would be expected to show a significantly lower extinguishing concentration against a hydrogen flame than a methane flame. In the case of nitrogen and carbon dioxide in this study, the results were very slightly lower against hydrogen than hydrocarbon flames, indicating that cooling is a minor mode of activity with these agents, and that the dominant mechanism is likely to be due to diluent properties.

For the phosphorus compounds the volume percentage of agent required to extinguish the FID hydrogen flame ranged between 1.6 and 4.4 times greater than that required to extinguish the FID methane flame. The majority of these compounds required 2.5 to 4 times more to extinguish the hydrogen flame than the methane flame.

The full range of halogenated hydrocarbon liquids gave results showing requirements of 1.2 to 4 times more agent for extinguishment of the hydrogen FID flame compared to the methane FID flame. The majority of these results fell in the range of 1.0 to 3.0 times more agent required to extinguish the hydrogen than the methane flame. Although this is a tentative measure, this would seem to indicate that proportionally less additional halogenated hydrocarbon agent is required than phosphorus compound agent, to extinguish a hydrogen flame relative to a methane flame. However, the potential significance of this is tempered by the fact that the actual percentage concentrations against both methane and hydrogen flames are notably lower for phosphorus compounds than for halogenated hydrocarbons. Actual percentage extinguishing concentration values for phosphorus compounds against hydrogen flames compared favourably against the equivalent halogenated hydrocarbon agent percentage extinguishing concentration results against methane flame conditions.

The fact that phosphorus containing agents are proportionally less efficient at extinguishing hydrogen compared to methane flames could be due to the carbon content of the methane flame. Phosphorus compounds as flame retardants are known to act in both the condensed and vapour phases.

In organic phosphorus compounds, the condensed phase mechanism proceeds via degradation of the P-O-C bond, which allows formation of phosphorus acid derivatives in the substrate volatilisation and thermal decomposition zone. These species participate in phosphorylation reactions. Phosphorus acids also catalyse dehydration, thus facilitating char formation in the presence of carbon containing compounds [6]. The carbon source with flame retarded materials is usually small, thermally decomposed fragments of the polymer, which would otherwise act in the vapour phase as the fuel for combustion when they progressed to the flaming combustion zone. However, other sources, such as the methane fuel in the standard DERA **FID** conditions, could provide a similar source of carbon in a volatilised state, prior to the flame combustion zone. Such a mechanism of char formation is supported by experimental observations of a greed black deposit forming on the jet nozzle of the FID, in the region that the methane fuel is introduced.

The vapour phase mechanism of phosphorus activity is believed to be through breakdown to small molecular species, e.g., PO, PO,, and HPO,, in the flame zone, with consequent reduction of the hydrogen radical concentration in the flame. This effectively inhibits the rate controlling branching step of combustion [7].

$$H\bullet + O_2 \rightarrow HO\bullet + O \qquad (1)$$

And associated combustion reactions [8]

$$O + H_2 \rightarrow OH + H \qquad (2)$$

$$OH + H_2 \rightarrow H_2O + H \qquad (3)$$

Promotion of hydrogen radical recombination (Eq. 4-7), and scavenging of oxygen radicals by molecular phosphorus (Eq. **8-9),** have also been proposed as vapour phase mechanisms of action for phosphorus compounds [6].

$$R_3PO \rightarrow PO\bullet, P\bullet, P, \qquad (4)$$

$$H\bullet + PO\bullet + M \rightarrow HPO + M \qquad (5)$$

$$HO\bullet + PO\bullet \rightarrow HPO + \bullet O\bullet \qquad (6)$$

$$HPO + H\bullet \rightarrow H, + PO\bullet \qquad (7)$$

$$P_2 + \bullet O\bullet \rightarrow P. + PO\bullet \qquad (8)$$

$$P\bullet + HO\bullet \rightarrow PO\bullet + H\bullet \qquad (9)$$

The promotion of hydrogen radical recombination and scavenging of oxygen radicals also helps to inhibit the rate controlling vapour phase combustion step and promotes incomplete combustion [7]. The promotion of incomplete combustion has also been observed experimentally **in** the production of significant quantities of smoke, particularly as the extinction concentration of the agent is approached.

These catalytic vapour phase mechanisms will be active in both hydrogen and hydrocarbon flames. The more efficient extinction of hydrocarbon flames by phosphorus compounds is likely to be due to the additional chemical mechanisms of promotion of carbonisation (char formation).

CONCLUSIONS

The inert gases tested gave similar extinguishing concentrations for hydrogen and hydrocarbon tlames, which indicates the same mechanism of interaction with the flame. The mechanism is likely to be dilution, as a lower extinguishing concentration against the hydrogen flame would be expected, due to the lower flame energy generation, if the mechanism was thermal (cooling).

The extinguishing concentrations against hydrogen flames were higher than against hydrocarbon flames for both phosphorus compounds and halogenated hydrocarbons.

As with extinguishment of methane flames, the percentage concentrations of phosphorus compounds required to extinguish hydrogen flames were less than those measured for halogenated hydrocarbons

Phosphorus compounds were effective at extinguishing hydrogen flames at low concentration levels

Proportionally, larger increases in extinguishing concentration were measured for phosphorus compounds against hydrogen, compared with hydrocarbon flames, than were required for the halogenated hydrocarbon agents. This is thought to be due to the additional mechanism of promotion of carbonisation, which can occur with phosphorus compounds. As this requires a source of carbon (present in the hydrocarbon, but not the hydrogen flame), the absence of this mechanism in the hydrogen flame conditions could account for this difference.

The “promotion of carbonization” mechanism observed supports the enhanced effectiveness of phosphorus agents against hydrocarbon flames that has previously been measured experimentally using the standard DERA FID apparatus.

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