INITIAL INVESTIGATION OF COMBINED FIRE EXTINGUISHING EFFICIENCY OF NOVEL PHOSPHORUS CONTAINING COMPOUNDS IN POTENTIAL DELIVERY MEDIA.

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INTRODUCTION

A suite of novel phosphorus containing compounds have been designed and synthesised through QinetiQ research. These have been evaluated for extinguishing concentration on the FID, a screening method of measuring extinguishing concentration to simulate the cup burner, developed by QinetiQ, and found to be very efficient extinguishing compounds [1,2,3]. Results showed that 1-2% by volume of agent was sufficient to extinguish the FID hydrocarbon / air diffusion flame, whereas 3% by volume of Halon 1301 was required. The extinguishing concentrations for some compounds previously measured are summarised in Table 1. The phosphorus compounds are liquids with boiling points between about 180-280°C, compared with Halon 1301, which has a boiling point of –57.8°C, i.e. is a gas at room temperature. This means that in order to progress the phosphorus compounds from novel chemicals towards marketable agents, a method for delivery & dispersion of the compounds needs to be developed.

Table 1. Summary of extinguishing concentrations for some compounds previously reported

Compound	Cup Burner	FID
Bromotrifluoromethane (Halon 1301)	2.9	3.0
Bromochlorodifluoromethane (Halon 1211)	3.2	3.5
Bromochloromethane (Halon 1011)	2.7	5.0
Carbon dioxide	20.4	18.8
Nitrogen	28.0	26.9
Dimethyl-2,2,2-trifluoroethyl phosphate		0.7
Diethyltrifluoroethyl phosphate		0.7
Diethylpentafluoropropyl phosphate		0.7
Diethylheptafluorobutyl phosphate		0.6
Diethyloctafluoropentyl phosphate		1.1
Bis (2,2,2-trifluoroethyl) 2,2,3,3,3-pentafluoropropyl phosphate		0.7
Tris (2,2,2-trifluoroethyl) phosphate		0.8
Tris (2,2,3,3,3-pentafluoro-1-propyl) phosphate		1.0
Tris (2,2,3,3,4,4,4-heptafluoro-1-butyl) phosphate		1.8
2-Bromo-3,3,3-trifluoro-1-propene (# 873)	2.6	4.5
4-Bromo-3,3,4,4-tetrafluoro-1-butene (# 903)	5.0 [5]	4.1
2-Bromo-3,3,3,4,4-pentafluoro-1-butene (# 1116)	4.1	2.5

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].

PRELIMINARY SOLUBILITY STUDY

A preliminary study was performed [6] on the solubility of three of the phosphorus compounds in carbon dioxide (CO_2) and 1,1,1,2-tetrafluoroethane (R134a), a HFC compound, under supercritical conditions, with the prospect of using supercritical fluids as carrier and delivery media. The critical temperatures are 31°C and 101°C for CO_2 and R134a, respectively. The extraction experiments were performed in a stainless steel reaction vessel within an oven, with the samples dispersed on sand to improve contact. The extractions were performed for 10 minutes under each set of conditions, and in triplicate where the quantity of sample permitted. The effluent from the reaction cell was trapped in 2 vials containing dichloromethane, and the solutions were then blown down under nitrogen, and the residues weighed. The results are presented in Table 2.

Table 2. Comparison of solubility of selected phosphorus compounds in CO_2 and R134a under non-supercritical and supercritical fluid conditions

Solvent	Temp. (°C)	Pressure (bar)	Density (kgm^{-3})	State	Solubility (mass %)
Bis (2,2,2-trifluoroethyl) 2,2,3,3,3-pentafluoropropyl phosphate					
CO_2	25	100	818	Liquid	0.343
CO_2	35	60	159	Supercritical	0.092
CO_2	35	100	713	Supercritical	1.028
CO_2	60	60	125	Supercritical	0.175
CO_2	60	100	290	Supercritical	4.510
R134a	25	50	1206	Liquid	1.832
R134a	105	50	727	Supercritical	1.803
Tris (2,2,2-trifluoroethyl) phosphate					
CO_2	25	100	818	Liquid	0.403
CO_2	35	60	159	Supercritical	0.234
CO_2	35	100	713	Supercritical	1.311
CO_2	60	60	125	Supercritical	0.150
CO_2	60	100	290	Supercritical	2.413
R134a	25	50	1206	Liquid	1.127
R134a	105	50	727	Supercritical	2.179
Tris (2,2,3,3,3-pentafluoro-1-propyl) phosphate					
CO_2	25	100	818	Liquid	1.339
CO_2	35	60	159	Supercritical	0.232
CO_2	35	100	713	Supercritical	2.318
CO_2	60	60	125	Supercritical	0.060
CO_2	60	100	290	Supercritical	2.021
R134a	25	50	1206	Liquid	1.355
R134a	105	50	727	Supercritical	1.979

The results showed that for relatively high molecular weight compounds, the phosphorus agents are very soluble in both CO_2 and R134a. CO_2 is known to have an affinity for fluorinated compounds. The solubilities of the agents in CO_2 and R134a are similar, and all three of the agents selected for test showed similar solubility in these two media. The investigation showed that supercritical conditions were not required to achieve good solubility of the phosphorus compounds in these media. Non-supercritical fluid based systems would allow significant cost savings compared to the maintaining the temperature and pressure conditions required to store and use the agents in fire extinguishing systems using supercritical fluids.

COMBINED AGENTS/CARRIER MEDIA STUDY

Following the solubility results presented in Table 2, an experimental study was designed to investigate the novel phosphorus compounds in gaseous carrier media under non-supercritical conditions in order to determine the optimum concentration combinations of novel agents to carrier media. This study is currently in the early stages of experimental work, but the rationale, the method design, its experimental validation with standard liquid agents, and the initial testing of novel liquid agents is described here.

APPARATUS

Initial work focussed on modifying existing apparatus that had been designed to measure the extinguishing concentrations on very small quantities of novel agents. The apparatus used was the FID (flame ionisation detector), which was developed as a screening test for determination of extinguishing concentrations of potential halon replacement compounds. The apparatus and method have been previously reported [7,8,9]. 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 burner methods. The flame conditions are adaptable, and can be modified to simulate different fuel-based fire scenarios.

For the standard FID methodology the flame model employed consisted of a hydrogen/air diffusion flame, spiked with methane in order to impart hydrocarbon character. This flame model may show some premixed characteristics, due to the very small scale of the apparatus. Based initially on stoichiometric fuel/air flame combustion chemistry, the precise gas flows were adjusted until an extinguishing concentration of 3.0% for Halon 1301 was achieved. This was the accepted result generated from cup burner tests. The gas flows for the FID that simulated these results were 15ml/min hydrogen, 400ml/min air (bottled) and 38ml/min methane. These are now considered to be the standard set of conditions for the FID method for comparison with heptane cup burner values. The FID detector block temperature was maintained at 250°C during all tests.

Although the FID method was capable of evaluating the extinguishing concentrations of liquid or gaseous agents in its standard configuration, liquid and gaseous agents had not been introduced simultaneously. There were two main modifications to the apparatus for this experimental study. The first was the introduction of a gaseous carrier medium through a mass flow controller to combine with the air stream, instead of a gaseous agent. The second was the addition of an injection port shortly after the point where the air and carrier gas combine for introduction of the liquid agents. Using this technique both the gaseous and liquid additives were introduced to the flame zone primarily by diffusion. This method was successful for the agents tested with boiling points below 100°C. However, for the agents with higher boiling points, the combined air and gaseous carrier medium stream flow proved insufficient to transport these agents in volatilised or aerosol form, so further modifications were required. For these agents the set up used was similar to that for evaluating liquid agents only. The gaseous carrier medium was still combined into the air stream using a mass flow controller. However, the liquid agent was combined into this stream at a slightly later point, in the oven of the GC, which was set to 200°C, a temperature close to the boiling point of the agents, to aid volatilisation, and hence delivery to the flame zone.

EXPERIMENTAL

The carrier media compounds, carbon dioxide (CO_2) and nitrogen (N_2) were selected as a starting point for this experimental study for their potential dual role. They are commonly used in fire extinguisher cylinders, both as extinguishing agents, and as pressurising agents for other extinguishing compounds. Also CO_2 was one of the solutes considered in the preliminary supercritical fluid solubility study, where it was shown that supercritical fluid conditions were not required for good solubility of the phosphorus compounds evaluated.

Before testing of the novel agents commenced the system was trialled with standard liquid agents. Bromochloromethane (Halon 1011), was used in order to prove the modified apparatus and establish a baseline experimental protocol. In addition 2-bromo-3,3,3-trifluoropropene, a tropodegradable bromocarbon being studied by the AAWG (Advanced Agents Working Group) was also used. This was due to the very limited availability and higher synthesis cost of the novel phosphorus compounds, so 2-bromo-3,3,3-trifluoropropene, with higher relative availability, was the first test compound evaluated.

The extinguishing agents selected were two of the most efficient novel phosphorus compounds from earlier studies, tris(2,2,2-trifluoroethyl) phosphate and bis(2,2,2-trifluoroethyl)2,2,3,3,3-pentafluoropropyl phosphate, see Table 1.

For each set of test runs the concentration of the carrier medium was set at a level below its extinguishing concentration, which was then fixed for that set of tests, the extinguishing agent was added at different concentrations for each run, and the extinguishing efficiency assessed. For example, 20ml/min (4.76%) CO_2 carrier medium with agent (Halon 1011) at progressively increasing syringe pump flow rates 10 (0.58%), 20 (1.16%), 30 (1.73%), 40 (2.29%), etc. would constitute one set of test runs. The carrier medium level would then be changed for the next set of tests, for example 30ml/min (6.98%) CO_2 with agent (Halon 1011), again with at progressively increasing flow rates of 10 (0.58%), 20 (1.16%), 30 (1.73%), 40 (2.29%), etc. The time to flame extinction, if extinction occurred, was recorded for each run. At least three test runs were performed at each agent/carrier medium concentration combination.

The experimental work to date has covered Halon 1011 and 2-bromo-3,3,3-trifluoropropene in CO_2 and limited runs with tris(2,2,2-trifluoroethyl) phosphate in CO_2.

RESULTS

The results are presented in both tabulated and graphical format, to facilitate identification of the optimal concentration combinations for progression to larger scale assessment. The results for Halon 1011 are presented as Table 3 and Figure 1, and the results for 2-bromo-3,3,3-trifluoropropene are presented as Table 4 and Figure 2.

Table 3. Mean time to flameout for Halon 1011 in carbon dioxide

Halon 1011 concentration (%)	**Mean time to flameout (s)**					
	in 4.96% CO_2	**in 6.98% CO_2**	**in 9.09% CO_2**	**in 11.11% CO_2**	**in 13.04% CO_2**	**in 14.98% CO_2**
0.58	>300	>300	134	26.7	23.7	7.7
1.16	>300	28.7	19.3	16.7	15.0	5.7
1.73	35	19.0	12.7	12.3	11.0	5.3
2.29	18.7	14.0	11.3	9.3	9.0	5.3
2.84	15.7	12.0	9.0	9.0	9.0	5.3
3.39	14.3	11.7	8.7	8.0	7.3	5.0
3.94	12.7	9.7	8.0	8.0	7.3	4.7
4.48	11.7	9.3	8.0	7.0	6.7	4.7
5.01	11.7	10.0	7.3	7.0	6.7	4.7

Table 4. Mean time to flameout for 2-bromo-3,3,3-trifluoropropene in carbon dioxide

2-bromo-3,3,3-trifluoropropene concentration (%)	**Mean time to flameout (s)**					
	in 4.96% CO_2	**in 6.98% CO_2**	**in 9.09% CO_2**	**in 11.11% CO_2**	**in 13.04% CO_2**	**in 14.98% CO_2**
0.73	>300	>300	109.7	43.5	20.0	16.3
1.44	>300	26.7	21.3	12.7	11.3	8.3
2.15	17.3	16.7	13.7	12.7	9.7	7.3
2.85	12.7	13.0	13.7	9.0	8.7	5.7
3.54	11.3	11.3	12.7	8.7	8.0	4.7

From the tables and graphs it is clear that the 0.58% Halon 1011 in 4.96% and 6.98% CO_2 and 1.16% Halon 1011 in 4.96% CO_2 combinations did not effectively extinguish the fire. This was also the case for 0.73% 2-bromo-3,3,3-trifluoropropene in 4.96% and 6.98% CO_2 and 1.44% 2-bromo-3,3,3-trifluoropropene in 4.96% CO_2. None of these six combinations were able to extinguish the FID flame within the 5 minute maximum test duration.

The results indicate a requirement for only low concentrations of the agents when used in combination with the higher levels of CO_2. The concentrations of agent needed to achieve flame extinction can be seen to increase progressively as the levels of CO_2 into which the agents are combined are systematically reduced. Hence the results provided confirmation of an expected trend.

With the exception of the combinations of the lowest levels of both agents and CO_2 carrier medium, where flame extinction was not achieved within 5 minutes, in most test scenarios there was no clear boundary where a change from efficient to inefficient fire extinguishing capability could be readily identified. The results in the Tables 3 and 4 have been zoned and coloured to aid in identification of bands showing similar levels of flame extinguishing efficiency.

The turquoise areas show rapid mean time to flame extinction, indicating that these agent/carrier medium combinations were the most efficient. Those results shaded pink show combinations where the extinguishing efficiency was only slightly reduced from the maximum measured under these test conditions. The results in the red and dark blue areas show where flame out was not achieved and where significantly extended times to flame extinction were indicated, respectively. The results coloured green do show a notable extension to the mean time to flame out over the most efficient results measured (shaded turquoise), however, the mean times to flame extinction are not excessively increased so these results still represent viable potential fire extinguishing agent and carrier medium combinations. It would be undesirable to select an agent & carrier medium combination from the red or dark blue zones, as the fire extinguishing efficiency is clearly compromised.

Testing has begun on tris(2,2,2-trifluoroethyl) phosphate, starting in levels of CO_2. The results are presented in Table 5. The difference from the results for the non-phosphorus containing agents that is immediately apparent is that even in the lowest agent and carrier medium combination, flame extinction was achieved, albeit after an extended period of time. While most of the agent concentration levels in 4.96% CO_2 cannot be considered to be efficient fire extinguishing combinations, several of the combinations (≥ 0.63% tris(2,2,2-trifluoroethyl) phosphate), show viable potential fire extinguishing agent and carrier medium combinations. All of the agent concentrations in 14.98% CO_2 showed effective fire extinguishing capacity, although the most efficient combinations were those containing the highest agent concentrations, as would be expected.

Table 5. Time to flameout for tris(2,2,2-trifluoroethyl) phosphate in CO_2

tris(2,2,2-trifluoroethyl) phosphate conc. (%)	Mean time to flameout (s)					
	in 4.96% CO_2	in 6.98% CO_2	in 9.09% CO_2	in 11.11% CO_2	in 13.04% CO_2	in 14.98% CO_2
0.18	283	nt	nt	nt	nt	24 (ind)
0.27	55	nt	nt	nt	nt	17 (ind)
0.36	35	nt	nt	nt	nt	13 (ind)
0.45	29	nt	nt	nt	nt	11 (ind)
0.54	26	nt	nt	nt	nt	10 (ind)
0.63	21	nt	nt	nt	nt	8 (ind)
0.72	18	nt	nt	nt	nt	7 (ind)

nt = not yet tested.
ind = indicative result

DISCUSSION

Although the phosphorus containing compounds have previously shown very low extinguishing concentrations (Table 1), a trend towards slower extinguishing times with the phosphorus compound (Table 5) compared to the other liquid agents tested (Tables 3 and 4) appears to be emerging. However, at this early stage of testing this can only be considered to be an indicative trend. The most likely reason for the apparent extended time to flame extinction shown by the tris(2,2,2-trifluoroethyl) phosphate is its mechanism of flame suppression action. Potential phosphorus fire extinguishing mechanisms were presented and discussed at HOTWC 2001 [10], by reference to published mechanisms of flame retardant activity. Phosphorus compounds 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 then participate in phosphorylation reactions. Phosphorus acids also catalyse dehydration, facilitating char formation in the presence of carbon containing compounds [11]. 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. However, other sources, such as the methane fuel in the FID flame, could provide a similar source of carbon in a volatilised state, prior to the flame combustion zone.

The vapour phase mechanism of phosphorus activity is believed to be through breakdown to small molecular species, such as PO, PO_2 and HPO_2 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 [12], and associated combustion reactions [13]. Promotion of hydrogen radical recombination and scavenging of oxygen radicals by molecular phosphorus have also been proposed as vapour phase mechanisms of action for phosphorus compounds [11].

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 [12]. 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.

The FID signal was noted to decrease (evidence for some extinguishing activity occurring), when the phosphorus containing agent reached the flame zone. The signal briefly stabilised, then dropped rapidly to zero as the flame extinguished. This phenomenon is thought to be due to the two different mechanisms of activity of the phosphorus, and could also account in the delay in extinguishing times measured, relative to the non-phosphorus containing agents.

The first mechanism is that of vapour phase phosphorus initiated hydrogen radical recombination and oxygen scavenging, which inhibits the rate controlling, branching stage of combustion. This occurs almost immediately when the phosphorus enters the flame zone, is likely to be responsible for the first reduction in FID signal observed. However, if both the vapour and condensed phase mechanisms working in concert are required to achieve flame extinction, the second stage of activity indicated by the FID signal, could be due to a slight delay before the condensed phase mechanism became efficient enough to significantly influence the flame chemistry. The occurrence of char formation is supported by experimental observation of a deposit forming on the jet nozzle of the FID, in the region that the methane fuel is introduced into the flame zone. This potentially indicates phosphorus acid initiated dehydration of the methane fuel, and subsequent deposit of carbonised material, providing the early stages of char formation.

This dual mechanism for phosphorus compounds contrasts with the bromine containing compounds, where vapour phase, catalytic hydrogen radical recombination is the predominant method of extinguishing activity [2].

CONCLUSIONS

A brief study into the solubility of phosphorus agents in CO_2 and R134a as supercritical fluids indicated that supercritical conditions were not required for the agents to show good solubility. This study is now being supplemented with small-scale experimental investigations into the efficiency of the novel phosphorus agents when combined with carrier compounds, to support an informed selection of compounds and their proportions for future studies of fire extinguisher delivery systems. To date a method for this investigation has been designed, trialled, and preliminary results obtained. Even in the combination of the lowest agent and carrier medium concentrations, the phosphorus compounds extinguished the flame, albeit after a significantly prolonged time, whereas Halon 1011 and 2-bromo-3,3,3-trifluoropropene, at these low combination levels, failed to extinguishing within the 5 minute test duration.

A tentative trend was observed, of a slight delay in flame extinction time with the phosphorus agent. This is thought to be due to the dual vapour phase and condensed phase mechanisms of the phosphorus compounds, which together generate the very efficient flame extinguishing results previously observed, compared with the predominant catalytic, vapour phase mechanism inherent to the bromine containing agents.

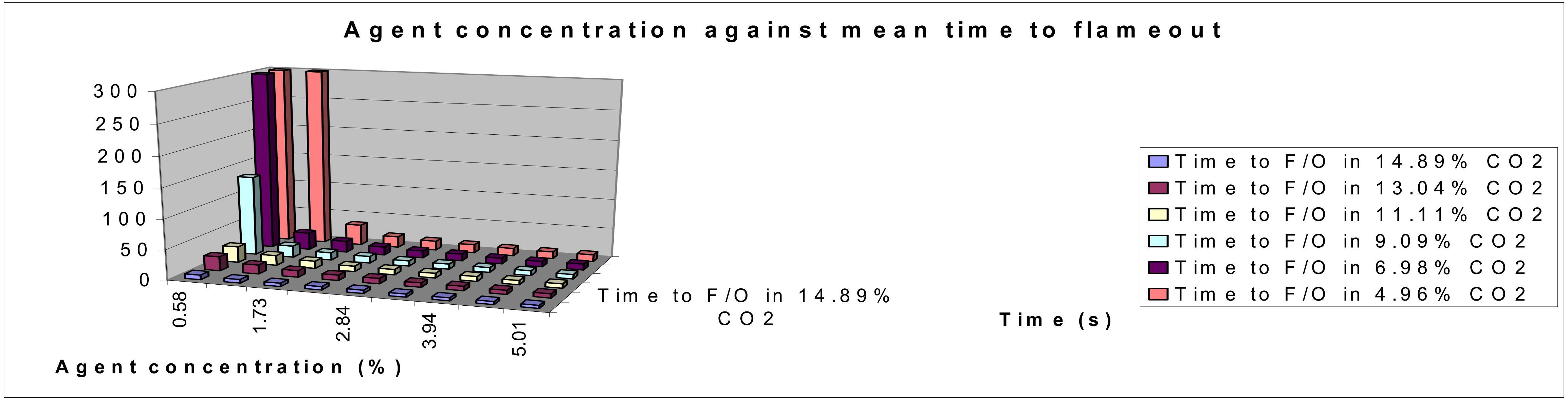

Figure 1. Mean time to flameout for Halon 1011 in carbon dioxide

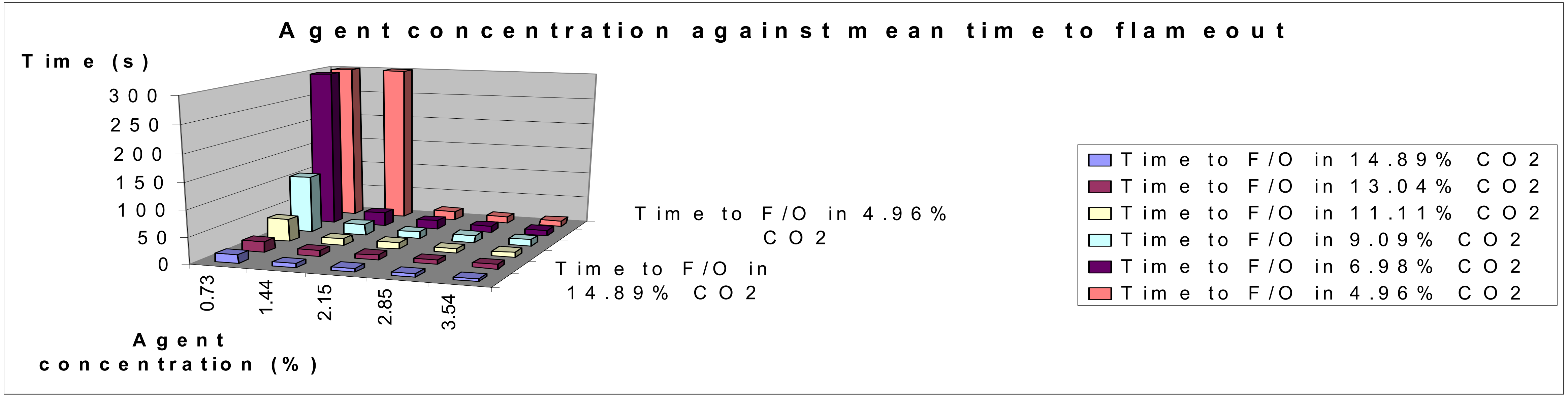

Figure 2. Mean time to flameout for 2-bromo-3,3,3-trifluoropropene in carbon dioxide

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