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A preliminary study on the fire suppression efficacy of a prototype system on hydrocarbon-based diffusion flames

This is the Published version of the following publication

Original Research Article

A preliminary study on the fire suppression efficacy of a prototype system on hydrocarbon-based diffusion flames

Paul Joseph⬤, Malavika Arun and Khalid Moinuddin

Abstract
We have investigated the use of a novel dual-stage firefighting strategy, where an inert gas is deployed as a carrier agent to discharge foamed water, obtained by mixing environmentally friendly surface-active agents. Here we also report specifically on some in-house built practical strategies. With a view to gauging the relative fire suppression efficacies of the selected agents, each one was discharged as a fine spray onto fires involving hexane, and also optionally where a typical Li-ion battery electrolyte acted as the fuel. In summary, it can be inferred that the air- or nitrogen-detergent formulations showed enhanced fire suppression attributes, in small-scale experiments, as compared with the aqueous medium alone. Furthermore, in almost all cases, the fire extinction property can be attributed mainly to the physical phenomena, produced by the flow of the inert gas, or air and enhanced wettability of the medium. Given that the fire tests were done at a relatively small scale, no definite conclusions can be drawn than those provided above; however, this study warrants further investigation, especially, at a larger scale.

Keywords
Foamed-aqueous phase, surface-active agents, flow characteristics, diffusion flame, fire suppression efficiency

Institute for Sustainable Industries & Liveable Cities, Victoria University, Melbourne, VIC, Australia

Corresponding author:
Paul Joseph, Institute for Sustainable Industries & Liveable Cities, Victoria University, P.O. Box 14428, Melbourne, VIC 8001, Australia.
Email: Paul.Joseph@vu.edu.au

Introduction

Engine room fires, owing to flammable hydrocarbon-based fuel systems, can pose a serious hazard, especially, in moving marine platforms and ships. Furthermore, batteries, when they are used as main energy storage elements (say, in submarines), for auxiliary, or backup, purposes (for uninterruptible power supply), or as an energy source for portable provisions (for various equipment in a ship), can also initiate ignition and fire growth in maritime environments. Given that lithium-ion (Li-ion) batteries have well-known desirable attributes, such as greater energy density resulting in longer operation between charges and lower self-discharge rates, submarine manufacturers are increasingly considering them as alternate main power sources, by replacing traditional lead-acid battery systems.[1] Here again, the biggest disadvantage of Li-ion batteries is the fire risk from the combustion of the flammable electrolyte, and there is a need to cool post-fire to stop the spread of thermal runaway to neighboring batteries.[2]

Traditionally, halon-based gaseous agents are deployed to extinguish such fires, provided an appropriate concentration of such agents is maintained for a sufficiently long time.[3] However, owing to the known detrimental effects of such agents on the environment, the usage of halon-based agents is either being phased out or completely banned. An alternative firefighting agent for fires involving batteries is water, which offers cooling as well as extinguishment to reduce the risk of thermal runaway in adjoining cells in Li-ion battery systems. However, the noticeable electrical conductivity of water must be taken into account in gauging the overall efficiency of such systems. Historically, water is considered the most common firefighting agent in cases of fires caused by a variety of fuel loads.[4] However, despite its well-recognized and desirable attributes, water cannot be effectively used against some fires, where the burning of hydrocarbon-based fuels, water-sensitive chemicals, and live electrical equipment are involved. Such a problem can be circumvented, albeit to a limited degree, by using a suitable foaming agent which often drastically reduces its surface tension and concomitantly makes it more compatible in scenarios where predominantly hydrophobic environments prevail.[5]

Furthermore, it is also highly desirable to enhance the "wettability" of water by reducing its surface tension by employing some sort of surface-active reagent(s), thus making water a more suitable and compatible firefighting agent where there are fires that involve non-polar, hydrocarbon-based fuel loads. While aqueous film-forming agents based on per-fluorinated hydrocarbons (commonly known as AFFF agents) are very efficient in fighting fires involving hydrocarbon-based fuels, they have been progressively banned, and most of them are being completely phased out now, owing to their toxicity and adverse environmental implications.[6] Given the detrimental effects of traditional per-fluorinated hydrocarbons, several attempts were also carried out to synthesize more environmentally benign counterparts and also to enhance their effectiveness through co-reagents, such as dissolved salts.[7–12] Hence, it is highly prudent to devise novel and more efficient means of fire suppression in scenarios where hydrocarbon-based components form the primary fuel load. Hence, through this work, we have endeavored to design some prototype novel fire suppression systems that are endowed with several desirable attributes, as given below.

Through this study, we employed a novel dual-stage approach for extinguishing fires involving hydrocarbon-based fuel and Li-ion battery electrolytes. Here, we have also designed some in-house fire suppression proprietary rigs that were not previously described elsewhere. This setup essentially consisted of an initial discharge of water-based firefighting

foam, based on a fluorine-free and commercially available surfactant, driven by a carrier gas (either nitrogen or air), that was released primarily through the Venturi effect created by the high-pressure gas stream. Here, we also formulated different ingredients for the production of the foam, with a view to identifying optimally performing formulations. Here it is highly relevant to note that the surface-active agents were all constituted of non-toxic, environmentally benign, and non-ionic compounds. For the purpose of comparison, we have also included a commercially available and fluorine-free foaming agent, under the trade name of Solberg.

Furthermore, given that the ultimate aim of the study was to identify a suppression system for fires involving marine platforms/ships, we have also included sea water as the aqueous medium. In practice, especially in a real-fire scenario, it is envisaged that the initial nitrogen injection into the battery module enclosure would reduce the oxygen concentration below the threshold concentration in the surrounding air. The foam that will be subsequently released would in turn enhance the fire-extinguishing capacity of water, while the non-ionic surfactant is expected to decrease its surface tension. Alternatively, the foam can be discharged by employing a stream of inert gas, like nitrogen, where it is envisaged that the effect of oxygen depletion brought about by the inert gas stream will enhance the efficacy of the foaming agent.

Thus, the underpinning principle of this work was to identify a novel, environment-friendly, and efficient firefighting system based on water as a true alternative to the Halon-based gaseous fire extinguishing means. To the best of our knowledge, scientific studies of systems with all these desirable attributes are not reported elsewhere in the literature, apart from claims from some commercial suppliers. Also, our methodology consisted of two stages (i.e. initial discharge of an inert gas like nitrogen) followed by foamed water to work in tandem. Furthermore, both the inert gas and foaming agent were also deployed simultaneously, the former re-enforcing the latter, and thus possibly leading to synergistic effects. Therefore, the overall requirement of the constituents, in both stages, could be kept to a minimum thus eliminating the need for elaborate delivery provisions.

Experimentation

Materials

A wide variety of surfactant compounds belonging to different chemical classes were chosen for the study and were primarily sourced locally. As expected, the exact chemical natures and compositions of these were not known with any certainty owing to the commercial confidentiality associated with them. Seawater was sourced locally and was used as the aqueous medium instead of de-ionized water (milli-Q water). The main rationale here was to identify the chemical enhancements, if any, owing to the dissolved salts in the seawater.[12] All the chemicals, reagents, and solvents used in this study, including their sources, are listed in Table 1 (see also Figure 1 for the chemical structures of the ingredients of the fuel systems).

We also chose two types of fuels that were purchased from Aldrich Chemical Company: hexane (98% pure—i.e. n-hexane for liquid chromatography: boiling point = 69° C; flash point = –22° C; auto-ignition temperature = 225° C at 760 mmHg) which resembles typical hydrocarbon fuels used in marine engines, and a typical electrolyte used in making Li-ion battery (it contained equal volumes of ethylene carbonate (EC) and diethyl carbonate (DEC), with the LiPF6; i.e. 1.0 molar LiPF6 in EC/DEC = 50/50 v/v).[13] The relevant

Table 1. List of chemicals, reagents, and associated materials

Sl. No.	Chemical name	Suppliers	Molecular formula
1	Hexane	Sigma-Aldrich	C_6H_{14}
2	Lithium-ion battery electrolyte	Sigma-Aldrich	$C_5H_{10}O_3/C_3H_4O_3/LiPF_6$
3	*Palmolive* commercial hand wash	Local supplier	N/A
4	*Ajax* multi-purpose domestic cleaner	Local supplier	N/A
5	*Chlorhexidine-based-surgical handwash*	Local supplier	N/A
6	*Solberg* commercial fire suppression agent	Solberg	N/A
7	Seawater	Locally sourced	See Table 7 for details
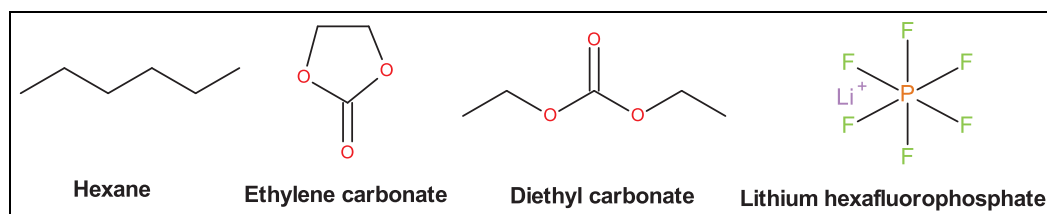
Figure 1. Chemical structure of the fuel system.

physical properties of the electrolyte, provided by the supplier, included boiling point 90° C and flash point 25° C. The chemical composition, structural features, thermal stability, and combustion characteristics of the Li-ion battery electrolyte were also characterized by employing a variety of analytical techniques, such as gas chromatography/mass spectrometry (GC/MS), Fourier-transform infrared (FT-IR) spectroscopy, solution-state nuclear magnetic resonance (NMR) spectroscopy (^{1}H, ^{31}P, and ^{19}F), thermogravimetric analysis (TGA), and pyrolysis combustion flow calorimetry (PCFC). Solid-state ^{31}P NMR spectrum was also recorded on the char residue collected upon the combustion of the electrolyte. The flammability profile of the electrolyte was also previously evaluated in our laboratories using a cone calorimeter, which was published elsewhere.[14]

Methods

Compositional and structural analyses of the materials

Gas chromatography/mass spectrometry. For the GC/MS runs, a GCMS-QP2010 instrument equipped with a capillary column with specifications as follows was used: ZB-5MS; length: 30 m; thickness: 0.5 μm; and diameter: 0.25 mm. The column oven temperature was set at 45°C, and the injection temperature was set at 250°C. The carrier gas pressure was maintained at 86.6 kPa, with a column flow rate of 1.5 mL min^{-1} where the total flow was set at 154.4 mL min^{-1}. The GC was coupled to the mass spectrometer which utilized electron impact ionization. The associated operating parameters of the MS were as follows: ion source temperature: 250°C, interface temperature: 300°C; solvent cut time: 3 min; and GC program time: 12.2 min.

FT-IR spectroscopy. In this study, a Perkin Elmer 1600 model instrument was used, in which the test sample was irradiated with infrared radiation in the range of 4000 to 600 cm^{-1} in the attenuated total reflectance (ATR) mode. In each case, a few milligrams were used as neat and were mounted onto the diamond crystal stage. The spectrum of absorbance versus wavenumber is generated for each of the samples, after appropriate baseline correction for each run (number of scans: 16; resolution: 4 cm^{-1}), aiding in identifying various functional groups present within their structure.

NMR spectroscopy. With a view to obtaining the chemical structure of the Li-ion battery electrolyte, the NMR spectra (^1H, ^{31}P, and ^{19}F) of the electrolyte were recorded using a Bruker 600 MHz instrument, in deuterated solvents (D_2O or d_6-DMSO) at ambient probe conditions. The solid-state NMR (^{31}P, in cross-polarization coupled to magic-angle spinning, CP/MAS, mode)[15] spectrum of the char residue obtained from the electrolyte upon combustion was obtained using a 500-MHz Bruker Avance III spectrometer working at ambient probe conditions. A 4-mm H/F-X double-resonance probe was used to record the spectrum, typically at 10 kHz rotor speed, and the signals were calibrated against phosphoric acid as the external calibrant. In both cases, the raw data were processed by using proprietary software from the manufacturer (TopSpin 4.1.1).

Thermal and calorimetric analysis

Thermogravimetric analysis. For the TGA analysis of the electrolyte, the test was carried out in a nitrogen atmosphere, at a heating rate of 10°C min^{-1}, from 30 to 800°C, using a Mettler-Toledo instrument with a gas flow rate of 50 mL min^{-1}.

Pyrolysis combustion flow calorimetry. This technique, also known as "microscale combustion calorimetry" (MCC), is a small-scale calorimetric testing method used to analyze the fire behavior of various solid materials when subjected to forced non-flaming combustion, under anaerobic, or aerobic, conditions (ASTM D7309). The seminal work behind this technique was carried out at the Federal Aviation Administration in the United States in the late 1990s, and is based on oxygen consumption calorimetry. This method is assumed to reproduce and decipher the condensed and gaseous parts of flaming combustion, in a non-flaming test regime, through rapid and controlled pyrolysis of the sample in an inert atmosphere (i.e. in nitrogen) followed by high-temperature oxidation (i.e. combustion) of the pyrolyzed components in the presence of oxygen.[16] The main advantage of using PCFC is that only a very small quantity (mg) of a sample is required, and the test method often provides information regarding useful combustion parameters of the test sample, such as peak heat release rate (pHHR), temperature to pHRR, total heat released (THR), heat release capacity (HRC), effective heat of combustion (EHC), and percentage of char yield. Although PCFC is able to provide some useful data regarding heat-related parameters on a smaller scale, the correlation of the available data with real-fire scenarios is still limited. In this work, PCFC runs were carried out in some chosen substrates (mainly step-growth polymers) at a heating rate of 1°C min^{-1}, using an FTT microscale calorimeter using method A—that is, in an atmosphere of nitrogen.[17]

*Evaluation of relevant physical properties of the surfactant solutions*

PH measurement. The pH measurements of water and other various sample surfactant solutions were measured using a pH meter, inoLab® pH 7110. Prior to the measurements of the pH of various solutions, the instrument was calibrated against two buffer solutions of known pH values, one in the acidic region (ca. 4.00) and the second one in the alkaline range (ca. 10.00).

Horiba water quality meter. This instrument is generally used to monitor the quality of potable water and for those used for various environmental and industrial purposes. A Horiba water quality meter typically provides both qualitative and quantitative information regarding the pH, resistivity, conductivity, salinity counts, oxidation–reduction potential (ORP) values, total dissolved solids (TDS) counts, and associated measurements related to dissolved oxygen concentration, dissolved organic matter contents, and so on of the test samples.

Contact angle measurement. In order to measure the "wettability" of the soap solutions, a contact angle measurement technique was used. For this purpose, the Kruss DSA25 drop analyzer was employed to measure the contact angle values for different soap solutions. Here, drops were allowed to form onto hydrophobic membranes, such as a Millipore Immobilon-P Transfer Membrane (a polyvinylidene fluoride: PVDF microporous membrane—surface 1, or onto a polypropylene surface (PP—surface 2)). Soap solution droplets were slowly allowed to fall onto the membrane that was fixed onto a glass plate, and the contact angle measurements were recorded immediately.

Rheometric measurements. Rheology is the study of the flow of fluids under the application of a force or stress.[18,19] The set of empirical data obtained through rheometric analysis is helpful in understanding the flow properties of fluids, like detergent solutions, especially when they are sprayed at a relatively high shear force, such as through various spray systems. In this study, a rotational rheometer, Physica MCR 301 from Anton Paar was used to analyze the soap solutions in an aqueous medium (i.e. in Milli-Q and seawater).

Testing the flammability attributes of the fuels. As the first step, the flammability attributes of the fuels, hexane, and Li-ion battery electrolyte solution were gauged in an ambient atmosphere (in an idle, i.e. where the air draft was absent, fume cupboard, i.e. without any convective currents). This was followed by two different bespoke tests, using different spray systems, which were carried out (see sections "Tests on hexane fires with a spray "gun" system" and "Medium-scale fire tests using an in-house built Venturi spray system"). The salient features of the experimental setup and the efficacies of the various extinguishing agents on diffusion flames of hexane,[20] and optionally on Li-ion electrolyte fires,[13] are given in the latter parts of the "Results and Discussion" section. It is relevant to note here that given the inherent variability in the time measurements associated with flaming combustion/extinction experiments, each test was repeated several times and the average over the three closest values are quoted, and the deviations are given as applicable.
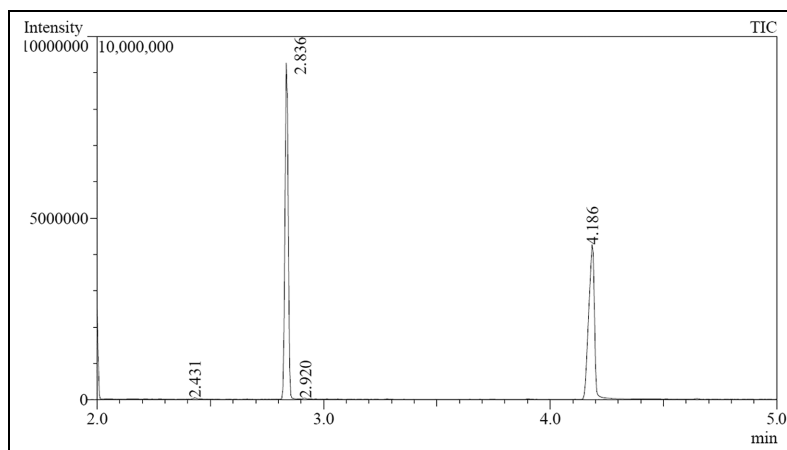
Figure 2. GC/MS data of Li-ion battery electrolyte.
The ordinate denotes the intensity in arbitrary units, and the abscissa represents the retention time in minutes.

Table 2. Parameters obtained from GC-MS runs of the Li-ion battery electrolyte

| Sl. No.	Peaks	Retention time (min)	Area (arbitrary units)	Area (%)
1	Peak 1 (DEC)	2.84	9125055	55.63
2	Peak 2 (EC)	4.19	7279234	44.37

DEC: diethyl carbonate; EC: ethylene carbonate.

Results and discussion

Composition and chemical constitution of the Li-ion battery electrolyte

As is evident from the gas chromatogram (Figure 2), the Li-ion battery electrolyte consisted of approximately 50/50 vol.% of EC and DEC. Furthermore, the MS spectrum of the individual components (see Table 2) denoted the chemical natures of the constituent carbonates (peak 1 = DEC; peak 2 = EC). Here the intensity of a signal (plotted as the ordinate in arbitrary units in Figure 2) is directly proportional to the quantity of the chemical constituent corresponding to the peak in question.

The FT-IR spectrum of the electrolyte (Figure 3) clearly showed carbonyl stretching vibrations of the "carbonate" carbonyls from both the constituents (centered around 1700 cm^{-1}), as well -C-H stretching vibrations from the alkyl part (around 2900 cm^{-1}), and the unique fingerprint region (from 1500 to 650 cm^{-1}) of both the constituents. Complementary information relating to the chemical nature of the constituents of the electrolyte was gathered through NMR spectroscopy, and the corresponding spectra are given in Figures 4 to 6. In these figures, the ordinate denotes signal intensities in arbitrary units, whereas the abscissa represents the chemical shift values in ppm. Here through appropriate assignments of the peaks, it can be inferred that all chemical constituents have an acceptable level of purity.
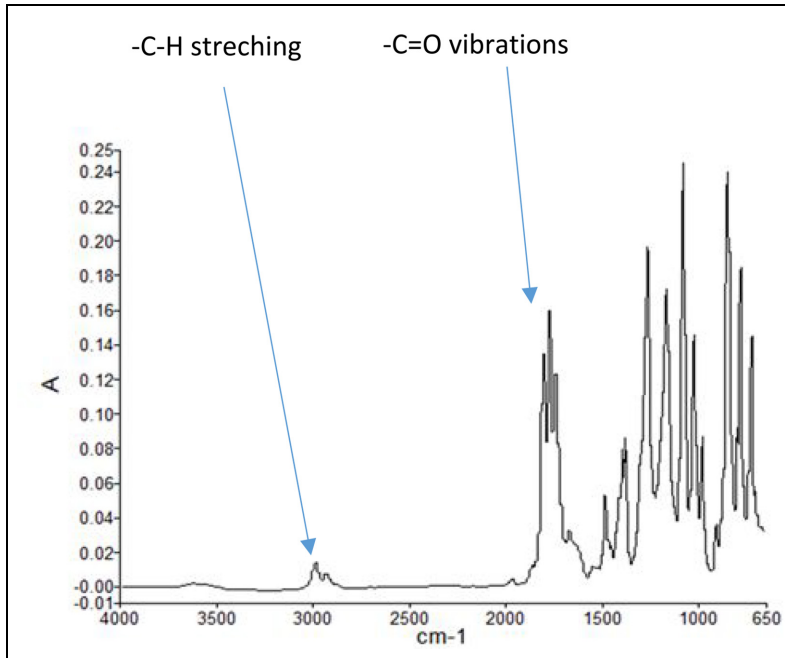
Figure 3. FT-IR spectra of Li-ion electrolyte.
ATR mode: attenuated total reflectance.

Thermal and combustion characteristics of the Li-ion battery electrolyte

As can be seen from the thermogram (weight loss % as the sample is heated) in Figure 7, the electrolyte (i.e. a mixture of the constituent carbonates: EC and DEC) degrades primarily through two steps, where the predominant step involves decarboxylation reactions. As expected, the lithium hexafluorophosphate part was only slightly viable to thermolysis, under the programmed heating regime in a TGA run, and appeared to be leftover as the residue toward the end of the run. This observation coincided with its behavior in the cone calorimetric experiments[14] where the residue that was collected in the sample holder was subjected to solid-state NMR analysis. The residue was found to be ~22.6% in the TGA run.

The heat release rate versus temperature curve from the PCFC run is presented in Figure 8. The average values of the relevant parameters, over triplicate runs, are as follows:

$$\text{Peak Heat Release Rate} = 167.4 \text{ Wg}^{-1}$$

$$\text{Total Heat Released} = 8.6 \text{ kJg}^{-1}$$

$$\text{Heat Release Capacity} = 205.5 \text{ Jg}^{-1}\text{K}^{-1}$$

$$\text{Residue(inpercentage)} = 5.36$$

$$\text{Effective Heats of Combustion} = 8.55 \text{ kJg}^{-1}$$

The relevant parameters from the PCFC run clearly showed that the Li-ion battery electrolyte is relatively combustible, and, as expected, the hydrocarbon moieties emanating from
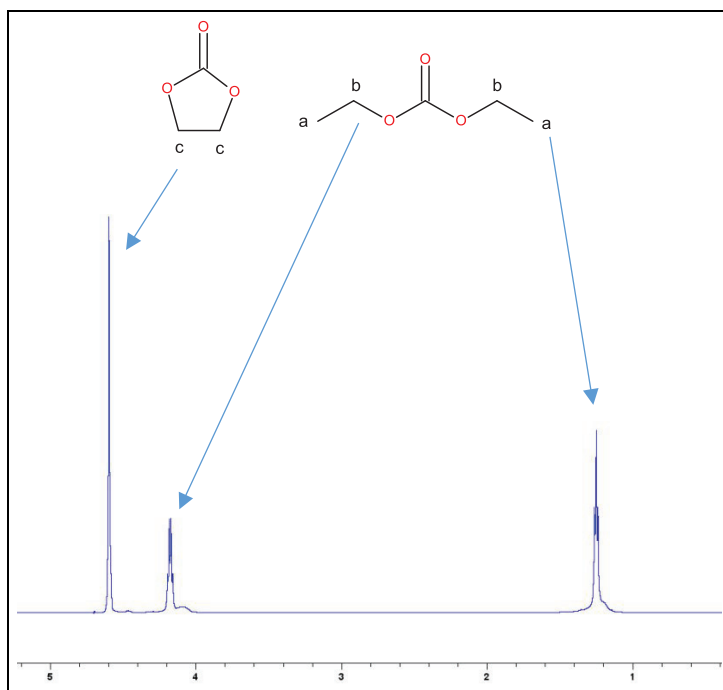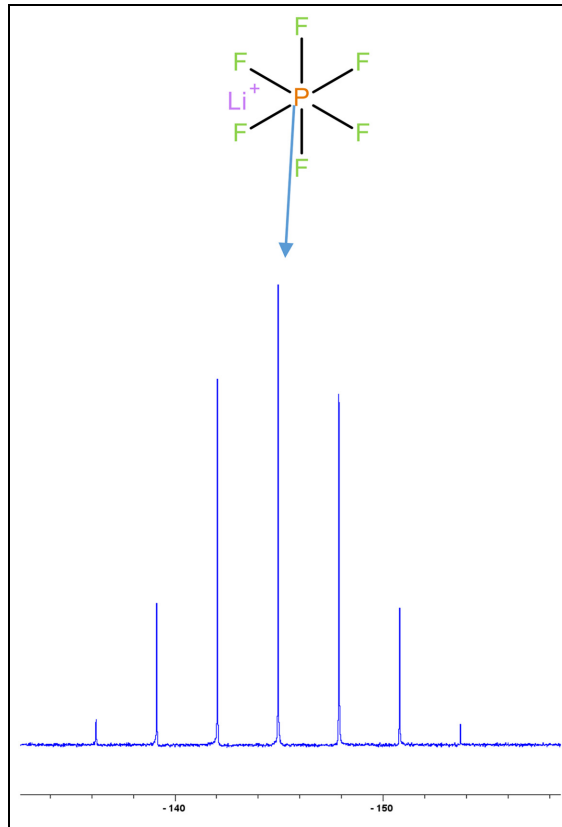
Figure 4. ^{1}H solution-state NMR spectra of the Li-ion electrolyte in D_2O (600 MHz at ambient probe conditions—here the residual proton signals from H_2O were "suppressed" during the acquisition).

initial decarboxylation reactions of the carbonates constituted the primary fuel. Here again, it is to be assumed that the char residue mainly consisted of the lithium hexafluorophosphate part of the electrolyte, which remained predominantly intact and appeared to be resistant to degradation/combustion. The corroborative evidence of this type of behavior was obtained through the ^{31}P solid-state NMR spectrum of the char residue (Figure 9: the signal intensities in arbitrary units are plotted against the chemical shift values in ppm). Here it is interesting to note that the splitting of the phosphorus signal by the ^{19}F centers was retained in the char residue, thus closely resembling the splitting pattern for the signal from the phosphorus nucleus in the corresponding solution-state NMR spectrum of the electrolyte. This indicates that during the combustion of the electrolyte, $LiPF_6$ did not seem to undergo any substantial degree of degradation, and therefore the chemical environment of the P-atom is retained as in the virgin electrolyte.

Fire extinguishing efficacy tests

Flammability characteristics of the fuels. The fuels were first taken in a porcelain crucible with a capacity of 20 mL (inner diameter = 3.4 cm) and ignited using a butane torch (luminous flame of ca. 2 cm in length). The tests were then repeated at least three times in both cases and with varying volumes of the fuels, where metallic containers of appropriate dimensions were also used (2.5, 5.0, and 10.0 mL). Subsequently, the time to extinguish in each case was recorded. The details are given in Table 3.

Figure 5. ^{31}P solution-state NMR spectra of the Li-ion electrolyte in D_2O (600 MHz at ambient probe conditions—with coupling to the ^{19}F centers).

From Table 3, it can be noticed that in the case of Li-ion electrolyte fuel, some amount of residue was left in all three cases whereas hexane, as expected, underwent complete combustion. Furthermore, in the case of 10 mL volume, both hexane and the electrolyte exhibited similar burning times. However, as the volumes were reduced to 5 and 2.5 mL, the Li electrolyte seemed to undergo extinction relatively faster than hexane. Following on from the inferences obtained through these preliminary experiments, it was decided to continue the active suppression experiment using hexane only, and that about 1 min was taken as the threshold period, in all tests, for the flame to equilibrate. It is relevant to note here that, upon heat treatment, the electrolyte will undergo decomposition (except the $LiPF_6$ fraction) yielding lower aliphatic hydrocarbons—thus, in a way the flame characteristics closely resemble that of laminar diffusion flame of liquid hydrocarbon fuels.[13,20] Therefore, apart from some optional tests, hexane was chosen as the main fuel for further investigations.

As the next step, some readily available surfactants in our laboratories (in the form of powders/coarse particles) were selected and dissolved in milli-Q water with a view to improving the flame-inhibitory effect of the latter. For this purpose, 6 wt.% of the compounds were added to ca. 245 mL of milli-Q water and stirred, at room temperature, until a uniform
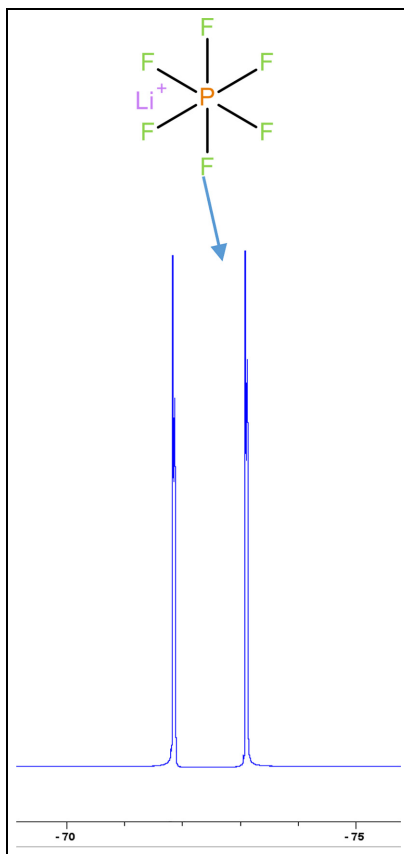
Figure 6. ^{19}F solution-state NMR spectra of the Li-ion electrolyte in D_2O (600 MHz at ambient probe conditions—with coupling to the phosphorus atom).

consistency was observed. These solutions were then filled in the same squirt bottles to carry out the simulated sprinkler tests. The acidity/alkalinity of the prepared soap solutions was measured using a laboratory-scale pH meter. The instrument was calibrated using both acidic and basic buffer solutions with known pH values prior to the measurements. The values are tabulated in Table 4.

As can be seen from Table 4, the soaps tend to make all of the solutions more acidic compared with pure milli-Q or tap water.

Tests on hexane fires with a spray "gun" system. For this purpose, a spray-gun apparatus that is normally used for commercial spray painting was employed. The equipment is fitted with a liquid reservoir (ca. 500 mL capacity) mounted onto the top of the spray "gun," which can be adjusted to obtain liquid with varying discharge characteristics (shown in Figure 10). Here the orientation of the nozzle, the rate of drainage of the liquid from a reservoir, and the rate of flow of the gas through the gun were initially adjusted, through trial and error, to reach optimal operating conditions (the spray gun was found to have a liquid discharge rate
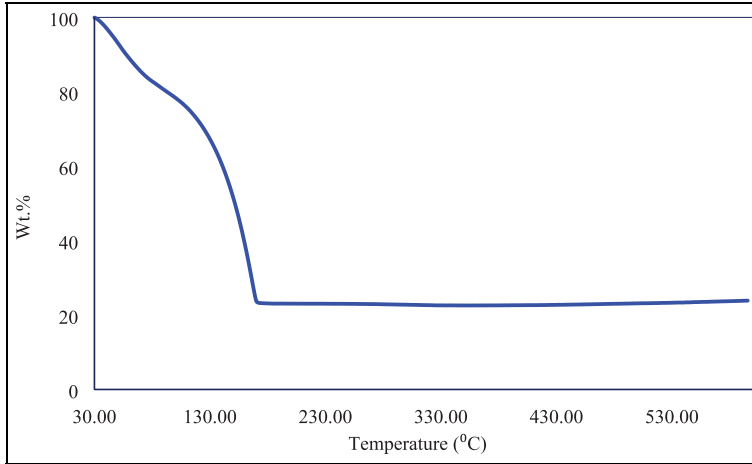
Figure 7. TGA curve of the Li-ion electrolyte, at 10°C min^{-1}, in a nitrogen atmosphere.
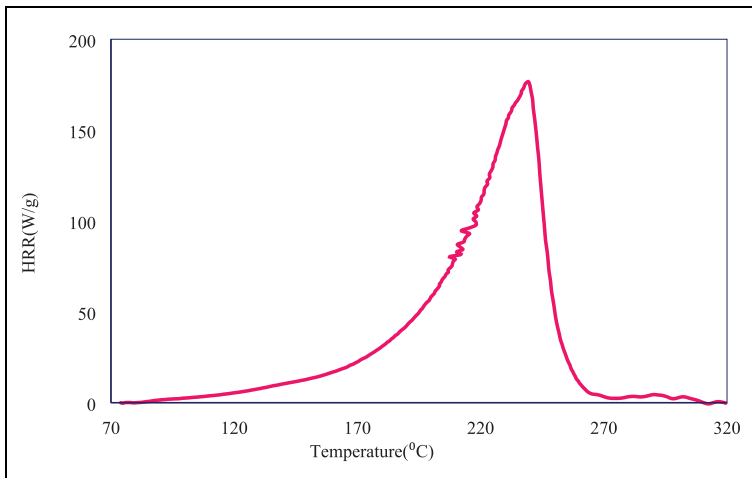
Figure 8. A sample heat release rate (HRR) curve of the Li-ion electrolyte obtained from the PCFC runs.

of around 120 mL per 30 s, as measured over several runs). The gas inlet was connected to the stem of the gun. For each test, ca. 250 mL solution was taken inside the reservoir. A wide-mouthed crucible of 25 mL volume and 4.5 cm diameter was used to hold the fuel (hexane). In this case, the crucible was fixed at a height of around 9 cm from the ground, primarily, with a view optimal for exposure of the flame to the gas–liquid mist that was sprayed from the nozzle of the "gun." The horizontal distance of the gun to the crucible was set to 39 cm, and this was kept constant throughout the experiments. All tests were repeated at least three times, and the average values of the time to extinction are reported in Table 5.
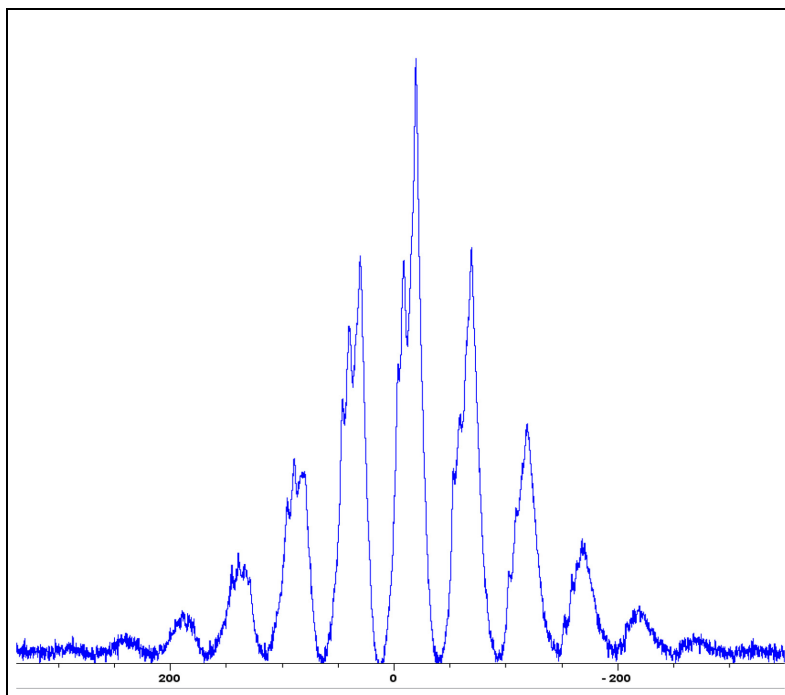
Figure 9. ^{31}P solid-state NMR spectra (CP/MAS mode) of the residue Li-ion electrolyte taken from a cone calorimetric run.

Table 3. Time to extinguishment measurements (average over at least triplicate runs)

Sl. No.	Fuels	Volume (mL)	Burning time (min)	Residue (mL)
1	Hexane	10	19	0.0
2	Li-ion battery electrolyte	10	20	3.0
3	Hexane	5.0	13	0.0
4	Li-ion electrolyte	5.0	9.0	2.5
5	Hexane	2.5	8.0	0.0
6	Li-ion electrolyte	2.5	3.0	2.0

Table 4. pH measurements on different soap formulations

Sl. No.	Sample	pH (range)
1	*Milli-Q* water	6.9 (near neutral)
2	Tap water	6.9 (near neutral)
3	*Palmolive* solution	4.9 (acidic)
4	*Ajax* solution	3.2 (acidic)
5	*Chlorhexidine* solution	5.4 (acidic)
6	*Solberg* solution	5.6 (acidic)

Figure 10. Experimental setup for spray "gun."

Table 5. Extinction experiments using nitrogen and air

N$_2$			Air[*]		
Sl. No.	Test runs N$_2$ gas + solutions	Time to extinction (s ± 1)	Sl. No.	Test runs air + solutions	Time to extinction (s ± 1)
N1	N$_2$ alone	36.7	—	—	—
N2	+ *Milli-Q*	9.33	A2	+ *Milli-Q*	7.0
N3	+ *Palmolive*	9.00	A3	+ *Palmolive*	7.5
N4	+ *Ajax cleaner*	8.60	A4	+ *Ajax cleaner*	7.0
N5	+ *Chlorhexidine*	11.3	A5	+ *Chlorhexidine*	8.6
N6	+ *Solberg*	6.00	A6	+ *Solberg*	5.3

[*] Blowing compressed air alone did not extinguish the flame; therefore, the experiments were not repeated with air alone.

Nitrogen gas was dispensed from a pressurized bottle (ca. total head pressure of 4000 kPa). The gas pressure at the outlet was maintained at 200 kPa throughout the whole set of experiments. The results obtained are given in Table 5.

In order to compare the efficacies of using nitrogen gas and air, when used as the carrier gases extinguishing a hydrocarbon flame, a set of compressed air tests employing the same spray-gun apparatus and agents were conducted under the same set of conditions. Compressed air was obtained through a bench-line valve, and here again, the outlet pressure was adjusted to 200 kPa, using a diaphragm dial. The results obtained are given in Table 5. Generally, the compressed air-mediated sprays seemed to have a slightly improved performance than those with nitrogen. This can be attributed to the differences in the delivery of the gaseous agents, such as the variation in the orientation of the agent relative to the flame.

The next stages in the investigation involved the use of seawater (locally sourced), as the aqueous medium with a view to checking the chemical enhancements, if any, due to the

Table 6. Different parameters relating to the aqueous media

Sample	Temp (°C)	pH	ORP (mV)	Conductivity (mS cm^{-1})	Turbidity (NTU)	TDS (g L^{-1})	Salinity (ppt)	Density (σ t)	Depth (m)
Milli-Q	20.34	8.85	−60	0.010	0.6	0.007	0.00	0.00	0.10
Seawater	18.00	9.21	−70	34.40	0.0	21.00	21.5	15.1	0.10
[a]Tap water	19.25	8.85	−15	0.131	1.0	0.085	0.10	0.00	0.10

The pH values of the tested samples were found to be alkaline range. The seawater, as expected, showed relatively higher values for conductivity, solid content, and salinity, owing to the presence of the various dissolved salts.
ORP: oxidation–reduction potential; NTU: nephelometric turbidity unit; TDS: total dissolved solids; ppt: salinity (parts per thousand); σt: density (kg L^{-1}).
[a]For the purpose of comparison only.

Table 7. The pH values of the various surfactants in seawater

Sl. No.	Samples	pH (range)
1	+ *Palmolive*	4.3 (acidic)
2	+ *Ajax*	4.1 (acidic)
3	+ *Chlorhexidine*	5.8 (acidic)
4	+ *Solberg*	6.0 (acidic)

dissolved salts. Here, the various physical attributes of the seawater were also measured using a Horiba Water Quality Meter. This was followed by contact angle measurements, using the Kruss drop analyzer, for determining the "wettability" of aqueous solutions on certain hydrophobic surfaces. Finally, one-off experiments including using the alternative fuel, that is, Li-ion battery electrolyte, were conducted.

An overview of the relevant parameters of the extinguishing media

The relevant physical parameters of the selected aqueous media were measured using a proprietary kit (Horiba Water Quality Meter). The probe was immersed in the medium in question and allowed to equilibrate for ca. 5 min, and then the readings were taken (Table 6).

This phase of the study included soap solutions that were prepared in both milli-Q water and seawater for the medium-scale tests. Here, the same detergents used in the previous small-scale study were again selected as they were found to be effective in extinguishing the flames. For this purpose, ca. 6 wt.% of the detergents were added to 460 mL of Milli-Q/sea water and stirred at room temperature, until a uniform consistency was obtained. These solutions were then filled in a beaker that was then connected to a Venturi spray system (see section "Medium-scale fire tests using an in-house built Venturi spray system"). Prior to the tests, the pH values of the soap solution in seawater were also measured (see Table 7) and found to be very similar to those obtained in the case of soap solutions in milli-Q water (see Table 4 and section "Flammability characteristics of the fuels").

It can be observed that the detergents tend to make the solutions more acidic as compared with plain seawater which was found to be in the alkaline range (see Table 6).

Table 8. Contact angle data for soap solutions

| Sl. No.	Samples	Contact angle (°) on surface 1	Contact angle (°) on surface 2
1	*Milli-Q*	123	134
2	*+ Ajax*	96.1	63.5
3	*+ Chlorhexidine*	62.9	87.3
4	*+ Palmolive*	99.5	115
5	*+ Solberg*	90.8	72.0
6	Seawater	128	125
7	*+ Ajax*	117	68.0
8	*+ Chlorhexidine*	54.1	45.3
9	*+ Palmolive*	66.1	62.0
10	*+ Solberg*	58.1	60.1
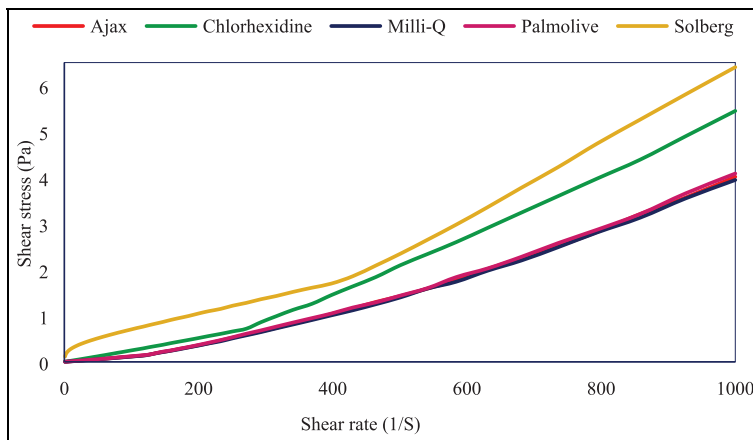
Figure 11. Plots of shear stress versus shear rate of soap solutions in mill-Q water.

For contact angle determinations, an average of three values were measured in each case, and are given in Table 8.

The contact angle data from Table 8 show a reduction in the angle measurements for detergent solutions compared with milli-Q and seawater. Thus, as expected, the addition of surfactants was found to enhance the wettability of water, thereby improving its compatibility and flame-extinguishing characteristics in cases of fires that involve hydrocarbon-based fuels.[7–12]

The flow behavior of various detergent solutions, under the application of a shear force, was studied using the Physica MCR 301 Rheometer. The data (shear stress, or viscosity, vs. shear rate) obtained were plotted for each set of samples and are given in Figures 11 and 12.

Generally, all the soap solutions tend to follow Newtonian characteristics as they show a near-linear trend of shear stress with respect to shear rate (Figure 11). However, it can be clearly noted that the Solberg solution exhibited shear thinning with shear rate, as indicated by a large drop in its viscosity (Figure 12), whereas, for the other formulations, the corresponding values remained more or less unchanged. Solberg, a commercially available
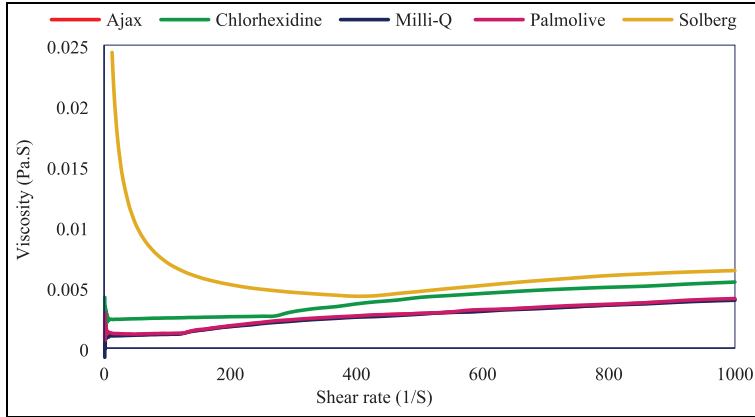
Figure 12. Plots of viscosity versus shear rate of soap solutions in mill-Q water.
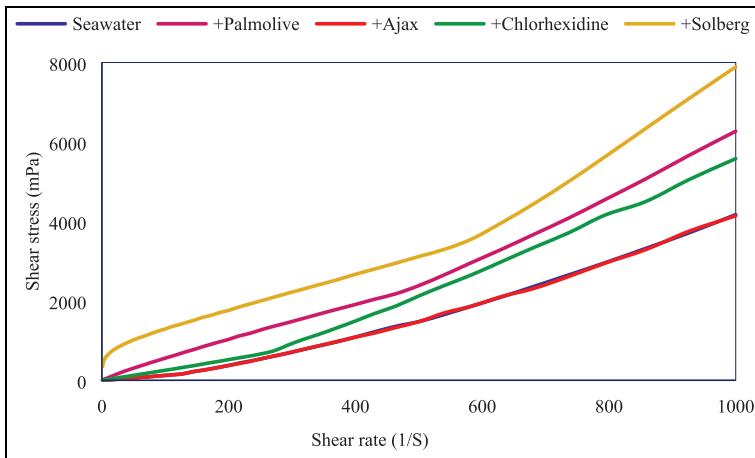

Figure 13. Plots of shear stress versus shear rate of soap solutions in seawater.

fluorine-free formulation, is a proprietary foaming agent that is widely used as a fire-fighting agent (generally used as a 3% concentrate) in hydrophobic environments. This is usually available as a thick concentrate (i.e. highly viscous in nature) and is expected to show shear thinning behavior at relatively higher shear rates for effective deployment during firefighting.

Figures 13 and 14 depict the variations in shear stress and viscosity with the shear rate for the soap solutions in seawater.

Here also, similar results were obtained as observed in the previous set of samples where milli-Q water was used as the aqueous medium. Thus, it can be assumed that the presence of dissolved ionic salts in the seawater has no discernible effects on the flow characteristics of the surfactant formulations.
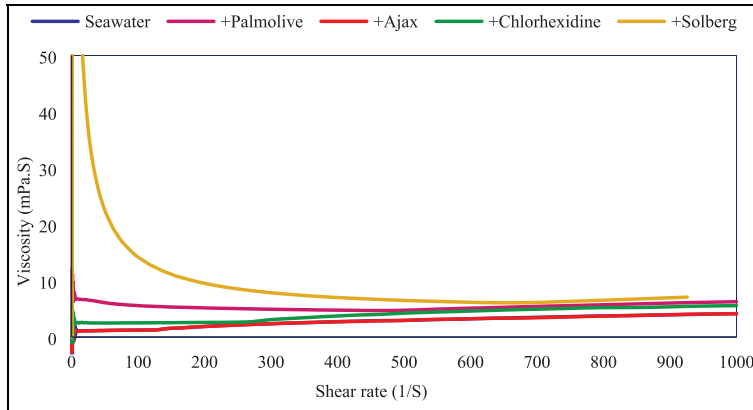
Figure 14. Plots of viscosity versus shear rate of soap solutions in seawater.
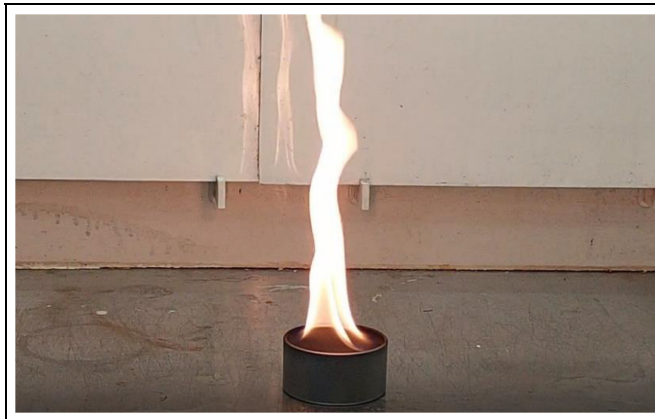
Figure 15. Medium-scale hexane pool fire.

Medium-scale fire tests using an in-house built Venturi spray system

For this purpose, a proprietary made Venturi spray apparatus was employed, which was assembled in our laboratories. This equipment can be connected directly to a gas supply and to a liquid reservoir through suitable nylon tubes. Trial-and-error runs were initially conducted, primarily by adjusting the rate of the gas through the apparatus, and optimal operating conditions were identified (i.e. a liquid discharge rate of around 217 mL per 30 s, as measured and averaged over several runs, at a gas head pressure of 200 kPa).

For each test, ca. 500 mL solution was taken in the beaker. A wide-mouthed crucible of 25 mm in height and 70 mm in diameter was used to hold the fuel(s) (Figure 15). In this case, the crucible was fixed at a height of around 130 mm from the ground, primarily, with a view optimal for exposure of the flame to the gas-liquid mist that was sprayed from the nozzle of the Venturi apparatus. The nozzle of the spray apparatus was also fixed at a

Figure 16. The proprietary Venturi spray system used for the medium-scale tests.

Table 9. Test results of different surfactant formulations discharged using the Venturi system onto hexane flame

Sl. No.	Test runs	Time to extinction for air (s)	Time to extinction for N_2 (s)
1	*Milli-Q water*	—*	—*
2	*+ Palmolive*	1.00	1.00
3	*+ Ajax cleaner*	5.67	1.67
4	*+ Chlorhexidine*	7.33	1.33
5	*+ Solberg*	6.33	1.33
6	*Seawater*	12.0	14.0
7	*+ Palmolive*	1.00	1.00
8	*+ Ajax cleaner*	1.00	1.00
9	*+ Chlorhexidine*	1.00	2.00
10	*+ Solberg*	1.50	1.50

*
Owing to the hazardous nature of putting out hydrocarbon fires with water alone, these trials were not attempted.

perpendicular distance of 430 mm from the ground, and the distance of the apparatus to the crucible was set to 240 mm, and this was kept constant throughout the experiments (Figure 16). All tests were repeated at least three times, and the average values of the time to extinction are reported in Table 9.

Similar to the small-scale experiments, a comparison between the effects of compressed air and nitrogen gas, in assisting the soap solutions to extinguish the flames, was also performed on a medium scale.

Compressed air was obtained through a pressurized cylinder fitted with a diaphragm valve, and the outlet pressure was adjusted to 200 kPa, using the dial. Here, the tests were conducted using soap solutions prepared in milli-Q water and seawater, deployed by compressed gases (i.e. air, or nitrogen, as the case may be), employing the in-built Venturi spray system. The results are given in Table 9.

Here again, the procedures were found to be effective in extinguishing the flame. In the case of the first set of samples (with milli-Q water, and with air, or nitrogen), Ajax, chlorhexidine, and Solberg solutions produced similar results by extinguishing the flame within 5–

Table 10. Test results of air/nitrogen Solberg discharged using the Venturi system on Li-ion electrolyte flame

Sl. No.	Test runs (in milli-Q)	Time to extinction (s)
1	Air + *Solberg*	1.00
2	N_2 + *Solberg*	6.00

7 s, whereas Palmolive solution showed an instantaneous extinguishment of the flame (~1 s). In the case of the second set (i.e. seawater, air, or nitrogen), all the tests showed effective fire extinction, probably due to the influence of the salts that are naturally present in the seawater. Generally, mixing 6 wt.% of various detergents in the seawater significantly enhanced the effects, leading to an instantaneous extinction of the flames, as can be seen in Table 9.

In the second step, the same tests were also performed using nitrogen as the carrier gas instead of compressed air. Nitrogen was dispensed from a pressurized bottle, and the gas pressure at the outlet was maintained at 200 kPa throughout the whole set of experiments. As can be seen from the table, nitrogen was also found to have an enhanced effect in extinguishing the flame for both sets of samples, resulting in instantaneous extinction. Here also, the results for seawater remained more or less the same as those observed in the previous case.

Following on from the completion of the set of tests on hydrocarbon fires, one-off experiments were performed using the lithium-ion electrolyte as the fuel. Here, the commercial fire suppressant Solberg was chosen as the detergent. A 6 wt.% of the agent was mixed in milli-Q water at ambient conditions and stirred until fully dispersed. As before, a wide-mouthed crucible of 25 mm in height and 70 mm in diameter was used to hold the fuel. Tests were performed in the same manner, employing both air and nitrogen as carrier gases. The results obtained are given in Table 10.

Instantaneous extinction of the flame was observed in both cases. So, it can be concluded that the combination of a non-ionic detergent solution in water and a carrier gas, sprayed at a relatively high shear rate (i.e. up to 100 s^{-1} as shown in Figure 13) is effective in extinguishing fires involving the Li-ion battery electrolyte. As indicated earlier (results from Table 5), there may be also variations associated with the delivery of the gaseous agents.

Conclusion

In summary, it can be inferred that the air/nitrogen-detergent formulations showed enhanced fire suppression attributes in small-scale experiments when compared with aqueous medium alone. Some key points obtained from the study are given below:

- The fuels (i.e. hexane and Li-ion battery electrolyte) showed typical characteristics of diffusion flames involving lower aliphatic hydrocarbons. In the latter case, the initial decarboxylation of the carbonates can be assumed to result in the production of combustible volatiles, whereas the lithium hexafluorophosphate remained intact and apparently did not exert any discernible effect(s) on the combustion of the fuel.
- Some of the commercially available and common detergents (Ajax, Palmolive, and chlorhexidine) were found to have very similar fire-extinguishing efficacies as

compared with the widely used proprietary firefighting agent (Solberg). However, it is relevant to note here that such an inference was primarily deducted through experiments at different scales and using various testing regimes. Furthermore, it is to be noted that the inferences are only based on some initial results and that we are currently continuing on with investigations on a larger scale. The outcomes from the latter study will be published separately.

- It can be assumed that, in almost all cases, the fire extinction property can be attributed mainly to the physical phenomena, such as the effect produced by the gas/air, enhanced wettability owing to the reduction in surface tension of water brought about by the foaming agent, or a combination of the two. However, such a straightforward assumption may not be valid in a higher-scale experiment, where surfactant might play a larger role in creating separation between the fuel and air, or by possibly creating an emulsion that is less flammable. Here it may be relevant to note that, apart from an apparent effect due to dissolved salts in the case of the seawater, no noticeable influence(s) of the chemical constituents of the surfactant formulations were evident.

- In general, the addition of surfactants was found to lower the pH of water/seawater, shifting the values in the acidic range. However, the shift in the pH values/ranges did not appear to be reflected in the fire suppression efficiencies of the different formulations.

- Contact angle data of the soap solutions generally showed significant improvements in the wettability attribute of the aqueous media. Evidently, this turned out to be quite beneficial in extinguishing the fires involving both the fuel systems. Such an effect could be attributed to the enhanced wettability of the extinguishing medium.

- The flow properties, as gauged by the rheometric analysis of all the test formulations, except the Solberg solution, conformed to a Newtonian behavior and closely resembled the aqueous media. Given that Solberg was presented as a very viscous and rather immobile state, shear thinning is assumed, especially, at the working concentration of 3 wt.% and at relatively high shear rates that are encountered when such formulations are deployed through bespoke spray nozzles.

- All tests that were based on seawater (with air, or nitrogen, as the carrier gas) showed instantaneous fire extinction as compared with those runs where milli-Q water was employed.

- The in-built Venturi system that was used for the medium-scale tests was found to be quite facile for studying the efficacies of the test solutions at a medium scale. Therefore, such a system warrants further investigations using novel detergents that can be derived from bio-sourced precursors.

- One-off fire suppression experiments using the Li-ion battery electrolyte as the fuel and Solberg as the suppressant produced similar effects that were observed in the case of hexane tests. This suggests that the Venturi technique that uses Solberg as the forming agent is efficient in mitigating the hazards involving Li-ion battery fires. It is also relevant to note here that, in an actual fire scenario involving battery fire, it is often difficult for the extinguishing agent to effectively reach the fire plume owing to physical constraints.

Given that the fire suppression tests conducted in the present are definitely at a relatively smaller scale, the observations and inferences from this work can be only treated as preliminary results. Hence, we have embarked on larger-scale tests, using heptane as the fuel in an

ISO Room setup, where relevant empirical parameters and a better combustion profile of the fuel are being collated. These tests also involve fire suppression using an in-house built water mist system. The results from these tests will be communicated in due course.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

ORCID iD

Paul Joseph iD https://orcid.org/0000-0002-5503-9979

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Author biographies

Paul Joseph is a chemist specializing in polymer science and combustion chemistry. His current research interests include: polymer syntheses and characterization, organophosphorus chemistry, bio-sourced fire retardants, combustion chemistry and toxicity.

Malavika Arun is polymer technologist, working predominantly in the field of polymer degradation and combustion. Her recent research activities are centred on chemically modifying styrenic and acrylic thermoplastics with a view to increasing their flame retardance.

Khalid Moinuddin is a Professor in Fire Modelling at Victoria University, Australia. His fundamental research work includes, simulation of gasification of solid fuels and combustion, fire dynamics, physics-based modelling using numerical tools, active fire suppression and bush fire modelling.