VAPOUR SUPPRESSION OF n-HEPTANE WITH FIRE FIGHTING FOAMS USING LABORATORY FLUX CHAMBER

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ABSTRACT

This paper presents the experimental measurements to compare the vapour-suppression performance of recently developed synthetic foam formulations (that do not use fluorosurfactants) with that of an aqueous film forming foam (AFFF). A laboratory-scale method involving a flux chamber was deployed to create an environment that imitates the conditions of field tests. The method utilises a gas chromatograph to determine the breakthrough points of AFFF and synthetic-based foams. The measurements indicate that an AFFF formulation affords the best overall performance for the vapour suppression, with the longest times for breakthrough. The synthetic foams with no xanthan gum are characterised by almost-immediate break through time, while those incorporating xanthan gum achieve strong breakthrough resistance, delaying the onset of flammability conditions above the 2-cm foam blanket for 130 min. This performance can be compared with 159 min achieved by 1-cm blanket of AFFF formulation. Clearly, xanthan gum plays an important role in enhancing a mixture of synthetic hydrocarbon surfactants to achieve improved vapour suppression of water immiscible fuels.

KEYWORDS: Fluorine-free foams, Fire-fighting foams, Xanthan gum, Suppression of Class B fires

INTRODUCTION

In 1991, Australia experienced its largest chemical fire, at Melbourne's Coode Island facility, where 27 tanks were damaged by fire. This was a reminder of the dangers that a petrochemical-reliant society can face. The cloud of volatile organic compounds released from this incident included benzene, acetone, acrylonitrile, and phenol, which caused irritations to the respiratory tract and eyes as well as other allergenic responses reported by individuals in the vicinity.[1]

Physical barriers can be successfully employed to limit or suppress the evolution of volatile organic compounds (VOC). The barrier may be a film, foam, or a gel, and would be applied to reduce the concentration of VOC in fire fighting, spills, and waste sites. Methods of vapour suppression can be evaluated in a laboratory setting. By using a closed chamber it is possible to create a microenvironment to examine the factors influencing the evolution of VOC and mechanisms for subsequent suppression of these compounds. Some of the more innovative and well cited papers written about the vapour suppression of VOC using fire fighting foams include those of Hardy and Purnell [2], Pignato [3], as well as the Masters Thesis of Hanauska [4].

The work of Hardy and Purnell [2] centred on the suppression of toluene diisocyanate using fire fighting foam. They examined the use of a 4% protein foam, 3% synthetic foam (made of hydrocarbon surfactants, but without fluorosurfactants), 6% fluorochemical foam (an AFFF, which is a synthetic foam containing fluorosurfactants), and 4% alcohol resistant foam solutions using a chamber to create a closed environment. Pignato [3] compared AFFF, including alcohol resistant AFFF (i.e., AFFF-ARF), to protein foam on a series of hydrocarbon and polar solvents. In both cases, the researchers used a chamber to create a closed and controllable environment. The vessel utilised an air flow over top of the foam to allow for a sample stream as well as to simulate the presence of a wind or breeze. The sample stream was tested using a grab bag technique, then analysed employing a gas chromatograph (GC) equipped with a flame ionisation detector (FID).

The papers reveal that over an initial period, AFFF technology is capable of keeping the VOC vapours of heptane at concentrations of below 1% of the lower flammability limit (LFL), as measured with a flame ionisation meter. Protein based technology could not do the same. When the blanket of the foam was disturbed at 5 min intervals, simulating a fire fighter walking through the hazard, it was found that the protein foam could not maintain vapour suppression under 20% of LFL after 10 min, or the second foam disturbance. In contrast, the AFFF maintained vapour suppression under 20% LFL for more than 45 min with regular foam disturbance.

Another important point covered in the work of Pignato [3], Hanauska [4] and Carruette et al. [5] is the vapour suppression of polar fuels. A total of eight polar fuels including acetic acid, pyridine, dioxane, isopropyl alcohol, ethanol, methanol, tetrahydrofuran (THF), and acetone are reported in these investigations. In the situation of a polar solvent, the alcohol resistant foam could only withstand one disturbance before it degraded, losing its integrity and allowing concentration of flammable vapours to exceed 20% LFL after 15 min, above the foam blanket.

Carruette et al. [5] used a flux chamber configuration very similar to that of Pignato [3] to compare xanthan based AFFF-ARF versus a new fluorinated polymer that could be used to decrease the level of xanthan gum. The authors claim a 50% reduction of xanthan gum with 0.02% active weight fluoropolymer could be achieved, resulting in a foam concentrate viscosity reduction of 60%.

The objective of the present research is to add fluorine-free synthetic foams as another category of fire fighting foam to those covered in the studies by Hardy and Prunell, Pignato, Hanauska, and Carruette et al. The current paper also reports measurements for a fluorosurfactant formulation, as a baseline. Thus the paper examines the behaviour of four synthetic foams and their vapour suppression capabilities. The study is restricted to a single common fire test fuel, n-heptane, to simplify the analysis. The synthetic foam concentrates are grouped into two classes: (i) low viscosity synthetic concentrates; and (ii) non-Newtonian synthetic concentrates. The non-Newtonian synthetic concentrates contain xanthan gum, a complex sugar that modifies viscosity, and extends foam drain times. From a rheological perspective, the behaviour of the concentrates is described by pseudoplasticity (i.e., shear thinning) and the appearance of a small yield stress in the order of 5 Pa. This rheological behaviours is similar to that exhibited by a number of AFFF-ARF formulations.[6]

MATERIALS AND METHODS

The chamber described in this paper was larger than that used by Pignato [3] or Hardy and Purnell [2], yet smaller than the chamber used by Balfour et al. [7]. However, the 250 mm diameter flux chamber of this study was very similar to that designed by Hanauska [4], which was 248 mm in diameter. Therefore, the expectation was that there would be some similarities in the experimental results. However, Hanauska examined the use of stabilised AFFF foams on acetone and methylpentane. Stabilised AFFF foams have drain times that extend to days, using an isocyante to enhance the foam stability. The present investigation used aqueous foams, with the drain times measured in minutes, to mitigate the diffusion of n-heptane vapours.

The flux chambers used in experimentation by Hardy and Purnell [4], Pignato [3], Hanuaska [4], and Carruette et al. [5] were made of glass. Balfour et al. [7] and Alm et al. [8] made further refinement of the experimental flux chamber apparatus by employing a desiccator with a transparent lid and a high density polyethylene base. We included these design modifications in constructing a flux chamber employed in the present study. Refer to Fig. 1 for a detailed scale diagram of the assembled apparatus. The desiccator had a diameter of 250 mm, with the total volume of the desiccator calculated as 9.88 L.
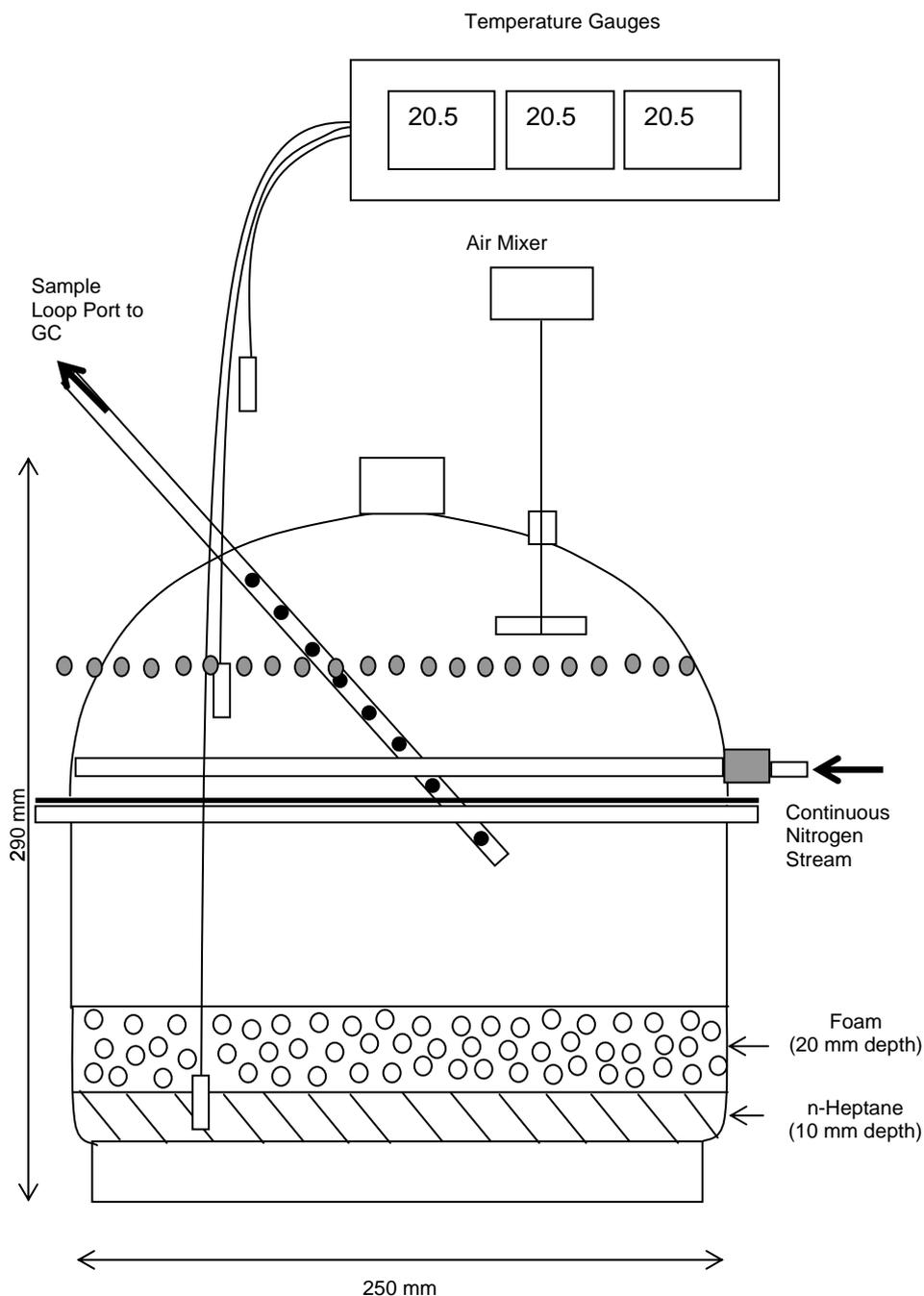
FIGURE 1. Schematic diagram of flux chamber

The flux chamber was plumbed to a nitrogen cylinder with nylon tubing. The nitrogen flow was continuously sweeping heptane vapour to the sampling loop. The nitrogen flow was controlled by a flow meter at a rate of 3.7 L min^{-1}. This flow rate was verified with a bubble flow meter and stopwatch as a cross-check. An air-driven impeller stirrer was incorporated to evenly disperse the vapour within the chamber and to prevent zones of varying concentration that could impact the gas sample analysis.

Nylon tubing was utilised inside the flux chamber to disperse the nitrogen sweep more evenly within the chamber. A nylon tube, with dispersion holes, was positioned around the equatorial circumference of the chamber. The holes were pointed inward to direct the nitrogen over the fuel surface, and direct the vapour to the sample point. The sample point consisted of a straight nylon tube with 10 induction

holes to draw sample to the sample loop stream. The nitrogen sweep created a positive pressure in the flux chamber, requiring four spring clamps holding the top and bottom sections of the chamber together. A rubber seal prevented the contents from escaping and a detergent solution was used to detect leaks.

The exiting nitrogen purge gas flowed to the sample loop and then was vented to the atmosphere. A grab sample was taken from the exit gas stream utilising an air pressure activated sample loop. The sample automatically injected into a Hewlett-Packard 5890 gas chromatograph (GC) equipped with a Hewlett Packard P-5 capillary column, and a flame ionisation detector (FID) was used to quantify the concentration of n-heptane in the exhaust gas. The procedure was to take a sample every 7 min, with the experiments continuing until the foam collapsed. The experimental runs lasted up to 6 h, including the initial start up and chamber stabilisation. By sampling every 7 min, the heptane was cleared from the GC column and no residual peaks would appear on the chromotographs to contaminate the data. The GC oven was set for 80°C. The GC signal was directed to a personal computer, which used software to integrate the signal from the FID and control the sample timing. Calibration involved measuring the response of the instrument to the pre-set injection volumes of heptane. The results of the experiments were expressed in terms of fluxes; i.e., as mass of n-heptane diffusing through a foam layer per unit cross-sectional area per unit time.

During the experiments, the room temperature was controlled at 20.5°C. All samples and solvent were conditioned in the room for 24 h to ensure that their temperature attained 20.5°C. In the experiments, foam was applied once at an expansion ratio of 5:1 at a foam depth of 1 cm. This expansion ratio is representative of the expected foam quality from either a sprinkler head or a non-aspirating foam nozzle. The foam was generated using a food blender similar to a seven-speed Waring blender. The lowest blender speed was used to generate the foam. The foam solution was weighed before being placed in the blender flask, for better precision. The foam depth of 1 cm at expansion of 5:1 corresponds to a thin cover of foam achieved with a foam solution density of 2 L m^{-2}. If one of the non-fluorosurfactant based foams had performance that was considered significant, then the foam was applied at a depth of 2 cm, which represented a doubling of solution density to 4 L m^{-2} at the same foam expansion factor. For comparison with practical applications, Pignato[3] suggests a 15-cm thickness of AFFF foam to protect and keep n-heptane below the LFL for 60 min.

Fig. 2 provides a schematic diagram of the equipment set up for the flux chamber experiments. After the application of the foam to the surface of the n-heptane, the chamber was purged of vapours for 30 s using a nitrogen stream, and the chamber lid was re-attached. Upon securing the lid, the sampling sequence was initiated.

The samples of foam concentrates (Formulations A and B; RF6; and AFFF (FC-206CF), described in Table 1) were sourced locally and mixed with water at the manufacturers' recommended concentration. All foams were recommended for use on non-water miscible hydrocarbon fuels, such as n-heptane, which was used in the present study. RF6 was chosen as a potential AFFF alternative, as it was evaluated by the US Navy and short-listed for further assessment. [9]

The initial experiments verified the expected profile of performance from the AFFF foam, with results very similar to those of Pignato [3]. Typically, the AFFF gave good vapour suppression initially, and then the performance declined, slowly at first, then the foam collapsed and vapours rose to unsuppressed level. It was noted that a flux of 1.96×10^{-5} kg m^{-2} s^{-1} (corresponding to 0.0037 mole fraction of C_7H_{16} in the outlet gases) was the unsuppressed heptane flux for the experimental apparatus. For comparison, Hanauska [4] reported a mass flux of 1.0×10^{-3} kg m^{-2} s^{-1} for methylpentane and 8.0×10^{-4} kg m^{-2} s^{-1} for acetone. The higher flux of 2-methylpentane is a reflection of its greater vapour pressure of 0.2248 atm as compared to 0.0445 atm for n-heptane. [10] This comparison suggests that the experimental conditions reached only one tenth of the saturation concentration for n-heptane, as a consequence of high nitrogen flow through the chamber. Leakage from the chamber was not expected to be the cause of the lower concentrations of n-heptane, as measures were made to seal and monitor any escaping sample through the use of detergent solution on the chamber lid.

The repeatability of the flux chamber experiments was verified with a replicate of the RF6 experiment having a foam expansion factor of 5.0 and a foam depth of 1.0 cm. In Fig. 3, a 10% error bar was applied to the data sets to assist in illustration of the good data fit between experiments. The expected primary causes of the observed variation are the sampling frequency and the variations in rate of foam collapse.
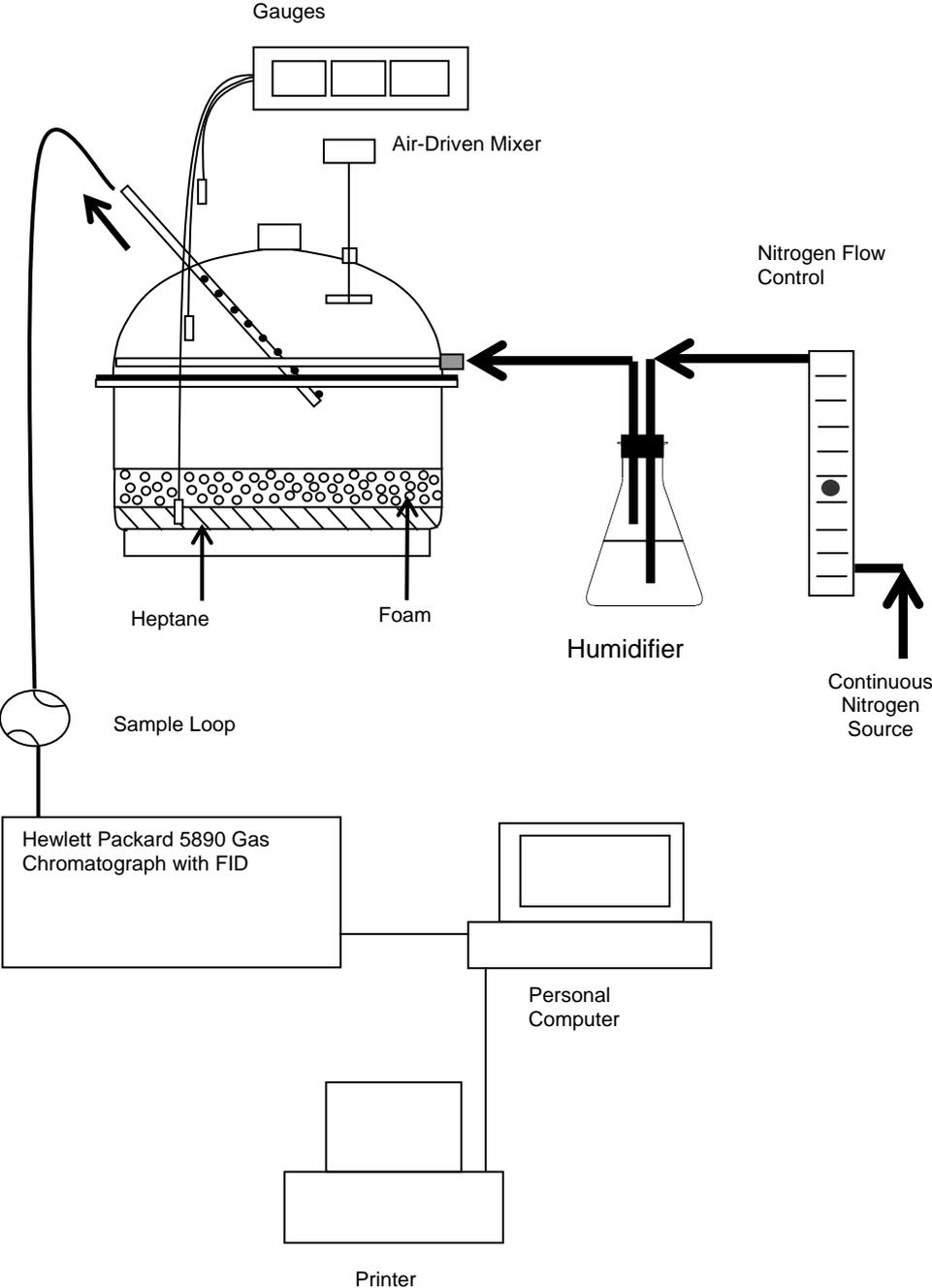
FIGURE 2. Flux chamber and peripherals

TABLE 1. List of fire-fighting foams used in experimentation including some physical characteristics of the concentrates

Property	FC-206CF [3M 1999]	RF6 [3M 2005]	Formulation A	Formulation B
Use concentration	6%	6%	0.4%	1-3%
Technology base	AFFF	Synthetic	Synthetic	Synthetic/ bacteria
Surfactants system	Hydrocarbon/ fluorocarbon	Hydrocarbon	Hydrocarbon	Hydrocarbon and selected non-toxic/non- pathogenic microbes
Concentrate type	Newtonian, low viscosity liquid	Non-Newtonian, pseudoplastic	Newtonian, low viscosity liquid	Newtonian, low viscosity liquid
Viscosity @25°C (Pa s)	3×10^{-3}	1.5*	9.5×10^{-3}	9.4×10^{-3}
Static surface tension (mN m^{-1})	16.2 (6% solution)	26.4 (6% solution)	24.0 (0.4% solution)	27.0 (2% solution)
Static interfacial tension with cyclohexane (mN m^{-1})	4.7 (6% solution)	2.4 (6% solution)	0.6 (0.4% solution)	0.8 (2% solution)
Spreading coefficient on cyclohexane	3.1	-4.8	-0.6	-3.8

* Note: At Brookfield LVF spindle #4 at 30 rpm.
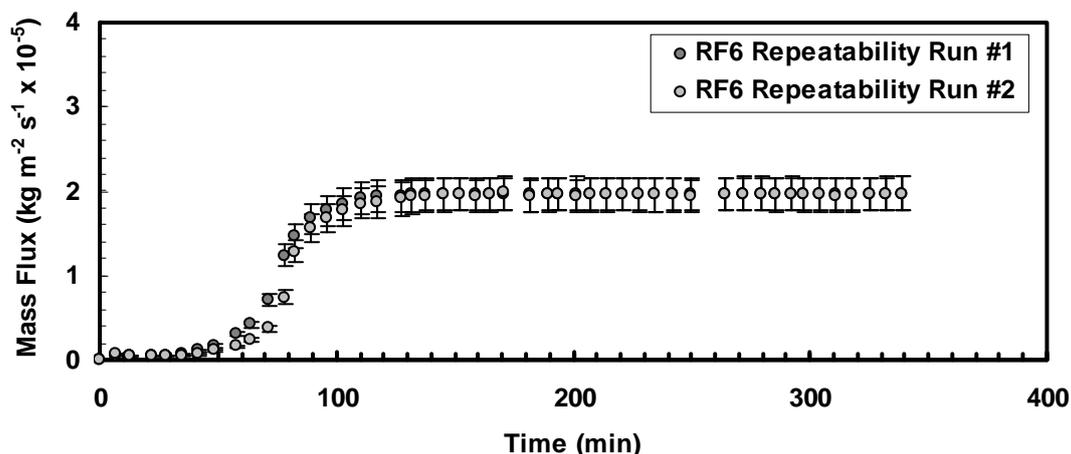
FIGURE 3. Repeated mass flux experiments of RF6 with 10% error bars attached to all data points

RESULTS AND DISCUSSION

Fig. 4 illustrates the vapour suppression capabilities of the studied foams, involving foam blankets 1 cm in thickness, with foams generated from potable water. The AFFF kept the n-heptane vapour suppressed for approximately 140 min before the point of vapour break-through, while the RF6 foam, under the same conditions, held for approximately 60 min. Formulations A and B could only temporarily suppress the n-heptane vapours. Formulations A and B gave limited vapour suppression through the first 7 min, becoming ineffective beyond that time. It should be noted that Formulation B recommends its product for vapour suppression of water immiscible hydrocarbon fuels.

A major factor influencing the vapour suppression performance of RF6 is the inclusion of the viscosity modifier xanthan resin, which results in significantly longer vapour suppression performance of RF6 foam over Formulations A and B, which are low viscosity and contain no resin component. The xanthan resin gave the RF6 a longer foam drain time, which improved the ability of the foam structure to hold back VOC vapour.

The better performance by the AFFF formulation is a consequence of the surfactant layers present at the air-surfactant solution interfaces that constitute barriers to diffusion of organic compounds through the foams. It is also possible, though this was not verified in this study, that fluorosurfactants decrease the solubility of organic compounds in the aqueous phase further suppressing the flux of n-heptane across foam layers.

As a single foam application, the RF6 foam significantly suppressed the vapours with its performance attributed to a longer drain time than that of AFFF. When the thickness of RF6 foam layer was increased to a foam depth of 2 cm, the effective vapour suppression time increased to 131 min. This performance was comparable to that of a 1 cm layer of AFFF.

Fig. 5 uses logarithmic plots of mass flux to illustrate the points of vapour break-through for the foams. In Fig. 5a, the vapour break-through point of RF6 foam at 1 cm depth is identified as 'A', while the vapour break-through points for RF6 foam at 2 cm depth and AFFF at 1 cm depth are shown as 'B'. Using a logarithmic scale accentuates the breakthrough point on the plot, making this event easier to identify. Although, Fig. 4b shows some suppression of vapour by the Formulation A, the logarithmic plot (Fig. 5b) disclosed that the break-through was immediate and no prolonged suppression has occurred.

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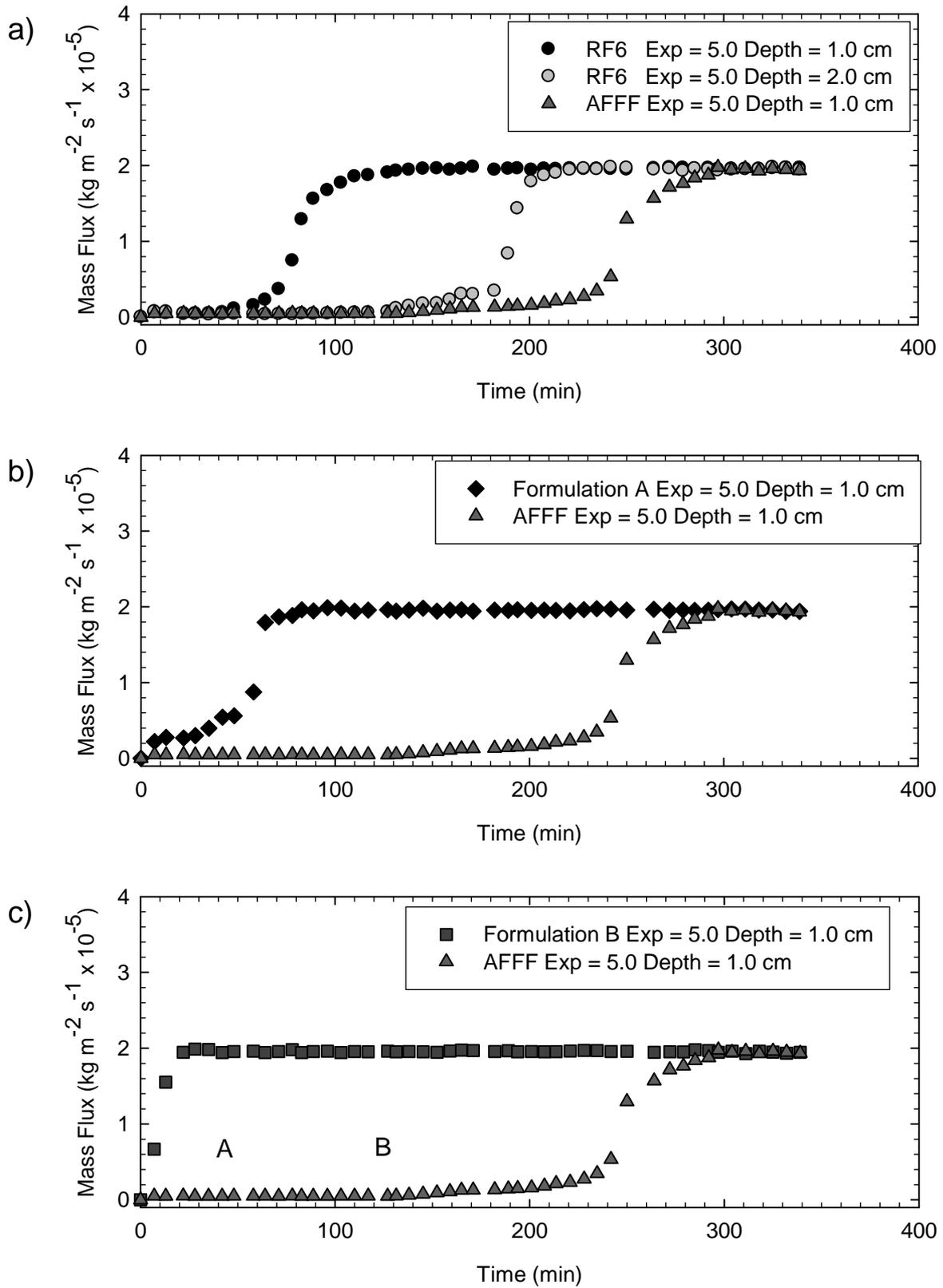
FIGURE 4. Comparison of mass flux of n-heptane across 1 cm foam depth of AFFF with: a) RF6 (1 and 2 cm foam depth), b) Formulation A, and c) Formulation B
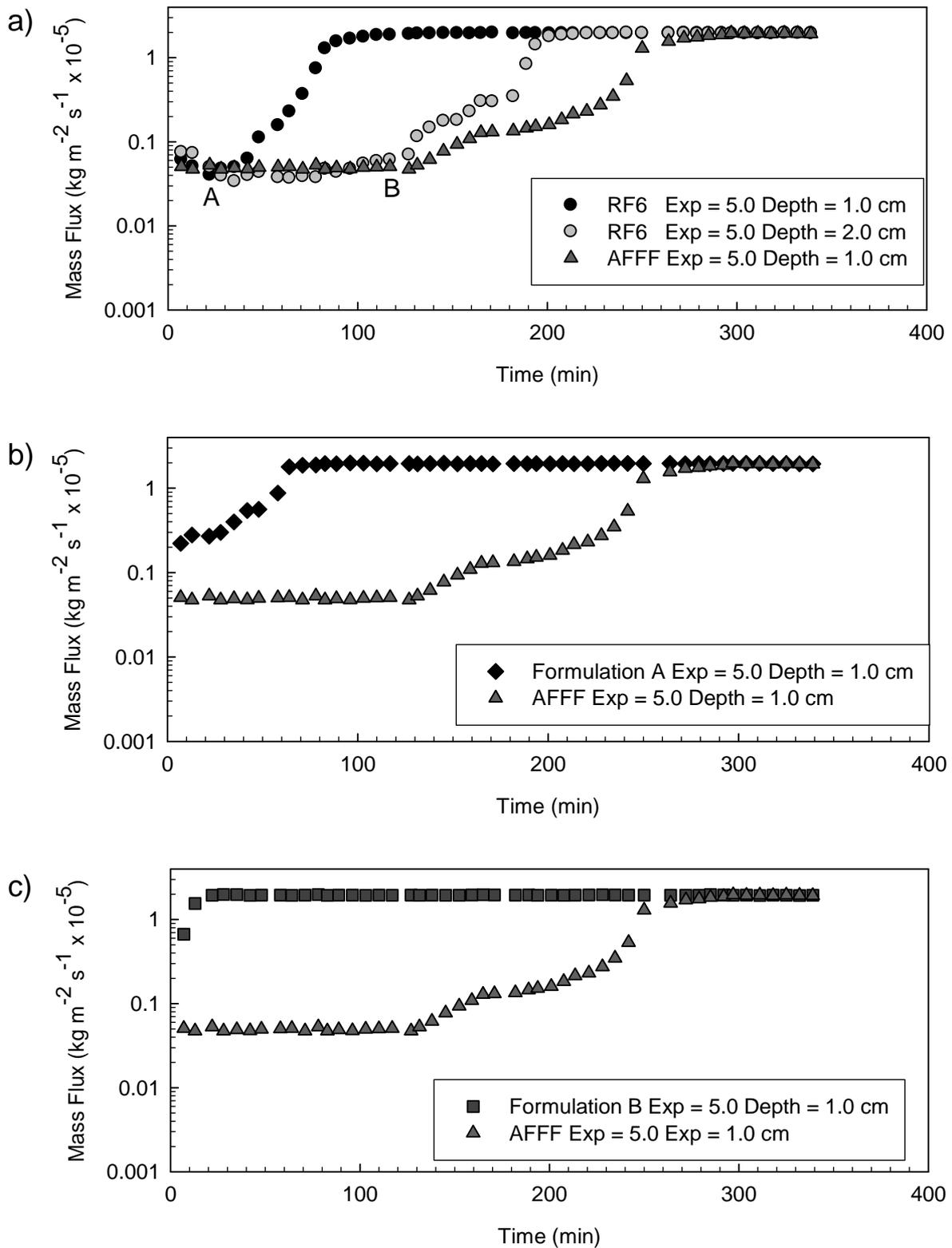
FIGURE 5. Comparison of the logarithmic plot of n-heptane mass flux across 1 cm foam depth of AFFF with: a) RF6 (1 and 2 cm foam depth), b) Formulation A, and c) Formulation B. The logarithmic plot accentuates the break-through point of the vapour.

The common practice of vapour suppression from cold spills and from post-fire evaporation of fuel using fire fighting foam includes the reapplication of foam at 15 to 25 min intervals to maintain the foam blanket. The foam application density is normally in the range of 4.1 to 6.5 L m^{-2} min^{-1} [11], which is at least 10 times higher than that utilised in this study. Normally 7 cm of foam would be recommended to suppress n-heptane for approximately 20 min.[3] This initial laboratory scale investigation suggests that it is possible to suppress hydrocarbon vapours of spills involving low flash point fuels, such as petrol, with RF6 foam. The present results indicate a time penalty due to the lack of fluorosurfactants in the foam solution. Therefore, for successful vapour suppression operations with RF6 foam, greater foam application is required to achieve performance equivalent to that of AFFF.

We applied three criteria to rank the foams. The first was the vapour break-through, which was identified as the sampling time when the mass flux exceeded 1 x 10^{-6} kg m^{-2} s^{-1}. This second measure corresponded to the maximum rate of flux, i.e., a point of inflection in Fig. 6. The inflection point usually occurs at the mass of around 9.5 x 10^{-6} kg m^{-2} s^{-1}, which is approximately half of the unsuppressed flux for the conditions of study. The final criterion was the time to attain the unsuppressed flux of heptane.

Table 2 summarises the rankings, showing RF6 second to AFFF and the remaining foams a distant third and fourth place to AFFF. This result may be due to the fluorosurfactant technology allowing an aqueous film to persist longer at the fuel-air interface than the expected life of the bubbles. When the other non-fluorosurfactant foams are broken, their functionality fails quite dramatically. The measurements show a gradual increase in flammable vapour concentration with time for AFFF that is not as dramatic as for the other foams.

TABLE 2. Ranking of foams in flux chamber experiments using fresh water

Foam Product	Water Type	Break-through Point (min)	Inflection Point (min)	Unsuppressed Flux (min)	Ranking
FC-206CF AFFF	Fresh	159	242	300	1
RF6 (1 cm depth)	Fresh	48	78	140	2
RF6 (2 cm depth)	Fresh	131	189	220	2
Formulation A (1 cm depth)	Fresh	0	58	80	3
Formulation B (1 cm depth)	Fresh	0	7	20	4

The studied foams could produce between one and three levels of steady state of heptane mass flux, including the unsuppressed level. In the fresh water experiments, most of the foams exhibited a period of a steady state before reaching the point of inflection, as illustrated in the logarithmic plots of Fig. 5. Formulation B foam was an exception, as no steady-state period was observed for this foam, prior to

the point of break-through. The AFFF achieved a steady state of 5×10^{-7} kg m^{-2} s^{-1} for the first 120 min into the experiment. In addition, the AFFF achieved a second steady state plateau before increasing to a level of 1.0×10^{-6} kgm^{-2}s^{-1} for approximately 40 min, then progressing to the unsuppressed mass flux of 1.96×10^{-5} kgm^{-2}s^{-1}.

The RF6 foam achieved a steady state below the break-through point of 48 min with a 1 cm layer of foam, and 131 min with a 2 cm layer. While Formulation A did achieve a steady state just after vapour break-through, Formulation B did not reach a steady state below the unsuppressed flux value. Table 3 summarises the experimental results for the steady-state suppression fluxes prior to the inflection point.
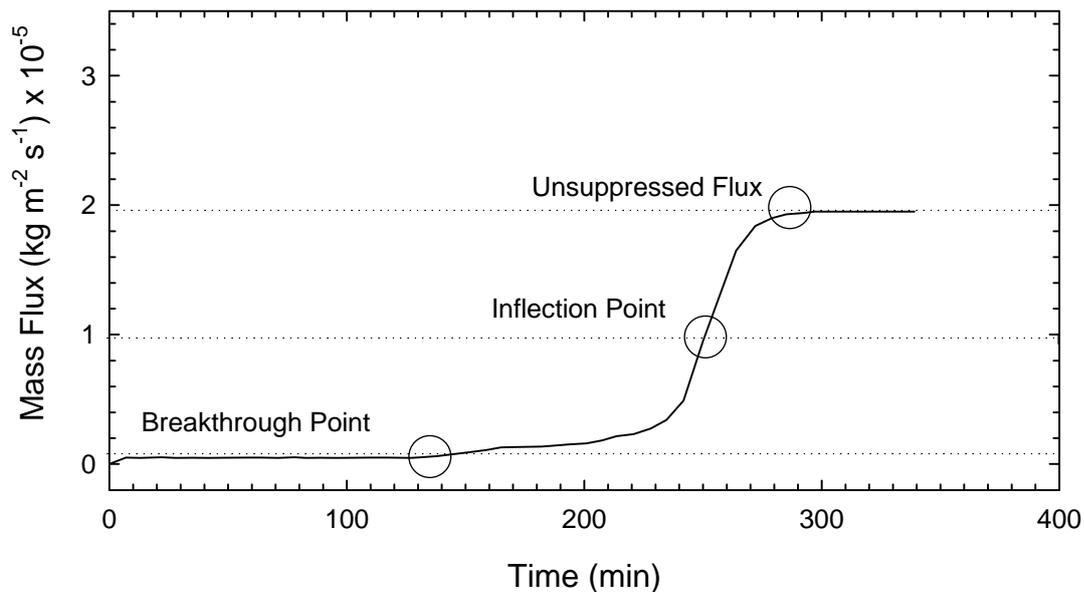
FIGURE 6. Illustration of measures used in ranking foams

TABLE 3. Summary of steady state suppression fluxes for fresh water experiments

Foam	Suppression Flux (kg m^{-2} s^{-1})	Duration (min)
AFFF	5×10^{-7}	120
RF6 (1 cm)	5×10^{-7}	40
RF6 (2 cm)	5×10^{-7}	80
Formulation A	3×10^{-6}	30
Formulation B	No steady state	-

CONCLUSIONS

The fire fighting foams selected for this study included the foams classified as synthetic by the fire fighting industry. AFFF was incorporated in the study to provide a base-case performance. The other

synthetic foams selected were not AFFF products and did not contain fluorosurfactants. The three synthetic formulations incorporated in the present investigation included two low-viscosity foam concentrates (Formulations A and B), and one non-Newtonian, pseudoplastic foam concentrate RF6.

The measurements have shown that the AFFF foam technology is the most capable of the suppression of vapours of n-heptane. AFFF forms aqueous films suppressing VOC as previously identified by Pignato.[3] The low viscosity synthetic foams (Formulations A and B) exhibited marginal vapour suppressing capabilities. They appeared to drain quickly under the stress of the vapour pressure of the VOC and offered limited resistance to mass flux. Formulations A and B offered less than 5% of the performance of the AFFF.

The current study compared the suppression of AFFF to RF6 at two levels of application density. The experiments showed the existence of two characteristic points the vapour suppression curve; i.e., the breakthrough and inflection points. The breakthrough points for 2-cm RF6 and 1-cm AFFF foam blankets were very similar. Doubling the foam layer of RF6 from 1 cm to 2 cm increases the time to vapour break-through by more than twice; i.e., from 48 to 131 min. This indicates that, the fluorine-free foam RF6 can be successfully used in place of AFFF for mitigating spills of flammable vapours. However, the application frequency of RF6 needs to be increased by two-three times in comparison to the application frequency of AFFF.

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