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Experimental study on thermal stability and burn-back performance of aqueous film forming foam agent(AFFF) with short-chain fluorocarbon surfactant or flame retardant

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ABSTRACT

Long-chain fluorocarbon surfactant is widely used in aqueous film-forming AFFF due to its excellent interfacial property. It can effectively improve the extinguishing efficiency of foam by improving the stability of foam. However, due to its severity environmental damage, some studies in recent years have focused on using short-chain fluorocarbon surfactants or flame retardants to replace long-chain fluorocarbon surfactants. However, the stability mechanism of foam after adding new additives and its performance in high-temperature thermal radiation environment are still unclear and require further clarification. Therefore, in this work, the effect of different additives on the interfacial properties of foam solution, foaming ability and foam stability, thermal stability and burn-back performance under the heat radiation environment are discussed. The results indicate that the thermal stability and burn-back performance of AFFF mixed with long-chain fluorocarbon surfactant (FS-30) or flame retardant (APP and MCA) was not significantly improved. However, the foam mixed with FS-50 exhibits excellent thermal stability and burn-back performance, it could be a proper substitute for long-chain fluorocarbon surfactants to be used in the AFFF mixed system. Through exploring the adsorption behavior of surfactant molecules on the liquid-air interface of the foam, FS-50 molecules and hydrocarbon surfactant molecules have a strong synergistic effect, which making it more difficult for water molecules to enter the surface of the mixed system. and the stability of foam will be enhanced. Besides, the proper mass concentration will also affect the interfacial properties of foam solution, foaming ability and foam stability, thermal stability and burn-back performance of the foam in fire environment, the mass concentration of additive in the foam solution should be remained at 0.3 wt%.

1. Introduction

Compared to other fire disasters, flammable liquid fires have a higher combustion heat and faster spreading rate [1]. In addition, a large amount of toxic and harmful substances are generated during the combustion process, making it difficult to wipe out and posing a serious threat to human life and property safety [2]. Numerous cases have shown that foam agent is the most effective technical means for extinguishing flammable liquid fires. Among them, aqueous film forming foam agent(AFFF) is the most widely used around world [3–5]. Fluorocarbon surfactant is the core component for AFFF. It can greatly reduce the surface tension of aqueous liquid and ensure that the solution has higher surface activity. Water film can be formed on the surface of combustible liquid fuels. Foam layer and water film together can isolate combustibles and oxygen, achieving the coordinated cooling effect, which is conducive to rapid control and extinguishing of fires [6]. However, some reports has proved that perfluorooctane carboxylates and perfluorooctanesulfonates contained in fluorocarbon surfactants has extremely environmental hazard [7,8]. These substances are extremely stable in the environment, unhydrolyzable, and non-biodegradable, and they can be active in the food chain and subsequently accumulate and migrate. It is difficult to degrade for a long time, thus causing environmental pollution and posing a serious threat to the survival of animals and plants [9,10]. Therefore, in order to

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Table 1
The components of the AFFF agent.

Item	Components	Concentration
Water-soluble ionic surfactant	Lauryl sodium sulfate Perfluoroalkyl betain Coconut oil amide propyl betaine	6.5%
Cosolvent	Ethylene glycol	10%
Pour point depressant	Urea	5%
Complexing agent	Tripropylene glycol	1%
Foam stabilizer	Xanthan gum	2.5%
Solvent	Deionized Water	75%

reduce the impact of residual pollutants after the fire extinguishing process on the ecological environment, it is the focus of current research to find alternatives to long-chain fluorocarbon without reducing the fire extinguishing efficiency.

At present, the research on solving the environmental pollution problem of traditional AFFF mainly focuses on two fields. The first strategy is to use new hydrocarbon surfactants or flame retardant to replace traditional fluorocarbon surfactants completely. According to the fire extinguishing agent sealing test method (DEF (AUST) 5706) in the Australian Defense Forces specification. Schaefer et al. [11] explored the sealing ability of fluorine-free surfactant foam and AFFF on flammable liquid fuel vapors. The results showed that under laboratory conditions, the fluorine-free foam layer thickness (RF6) reached 1 or 2 cm deep can make better sealing performance, The other two fluorine-free foam fire extinguishing agents have almost no sealing performance against fuel vapor. On this basis, Williams et al. [12] found that the fire-extinguishing and fire-resistant performance of RF6 fluorine-free foam is weaker than that of AFFF in liquid fires with higher combustion heat values such as gasoline and heptane fires. Hinnant et al. [13] [–] [15] investigated and compared the fire extinguishing efficiency of the commercial fluorine-free formula AFFF with that of the long-chain fluorocarbon surfactant formula, and found that the fire extinguishing performance of most fluorine-free foam products is generally worse than that of AFFF. In addition, some scholars have also explored the combination mode between the flame retardant and AFFF. Li et al. [16] studied the influence of APP with different polymerization degrees on dynamic interfacial properties and foaming ability of the two oppositely charged surfactants. The results showed that the stability of anionic surfactant foam could be reduced by adding APP to foam solution. On the other hand, the foaming ability of the mixed system containing cationic surfactants will also be weakened. Vinogradov et al. [17] reported that the fire extinguishing agents using large-scale ultrafast gelated foams possess new properties and unique characteristics, which can make agents obtain the extremely high fire prevention efficiency and complete biodegradation. The research results of fluorine-free foam mostly show that there are major defects in its foaming ability and stability. Some formulations can only meet the technical standards in one aspect, but the comprehensive spreading performance and fire extinguishing efficiency are far lower than traditional AFFF. Another efficient way to improve the biodegradability and ease the toxicity of long-chain fluorocarbon surfactants is to reduce the number of carbon atoms in a perfluorinated radical from C8–C10 to C4–C6 [18]. Some of the short-chain fluorocarbon surfactants have been

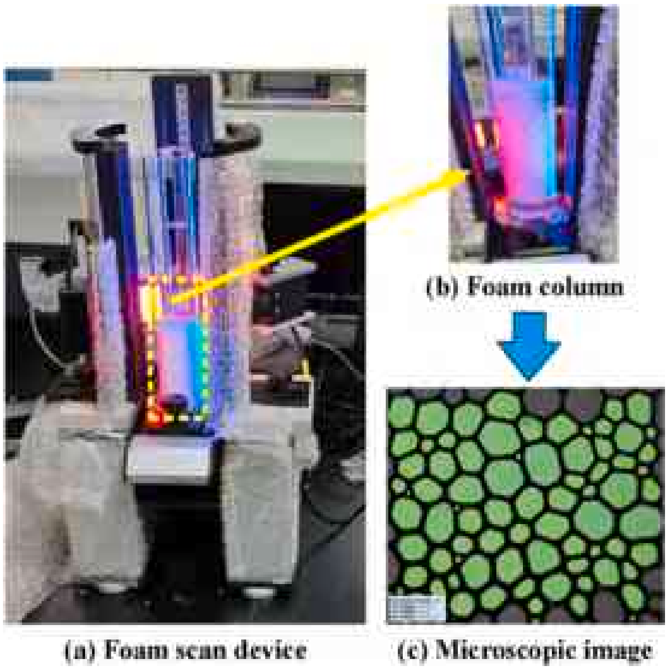


Fig. 2. The schematic diagram of Foam scan device.

Table 2
The parameters of additives.

Category	Title	Molecular formula
Long-chain fluorocarbon surfactants	FS-30	$CF_3(CF_2)_5(CH_2)_2(OCH_2CH_2)_{10}OH$
Short-chain fluorocarbon surfactants	FS-50	$CF_3(CF_2)_5CH(NCOO)CH_3$
Flame retardant	APP	$(NH_4)_{n+2}P_nO_{3n+1}$ (n = 10)
	MCA	$C_6H_9N_9O_3$

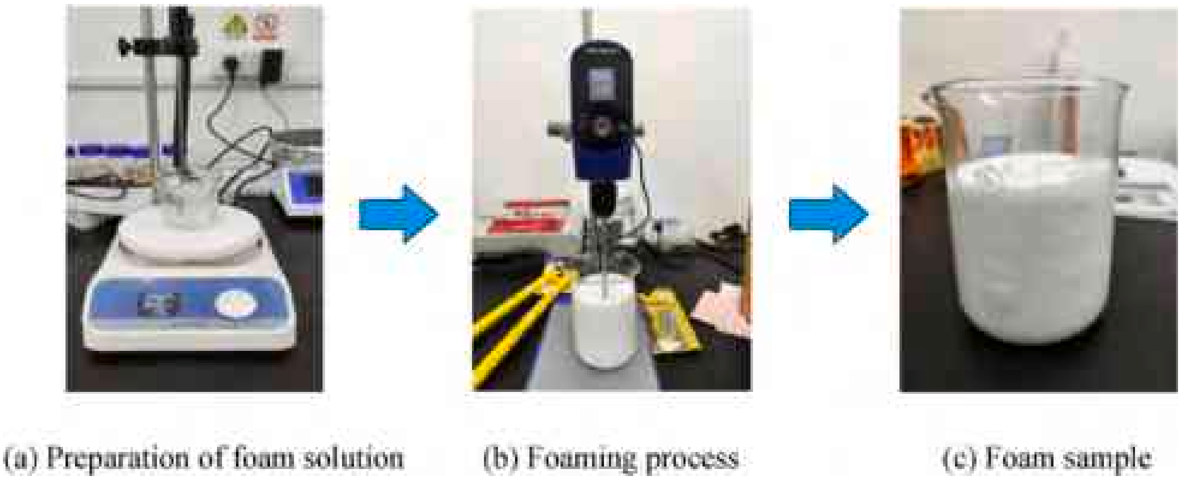


Fig. 1. Preparation of foam solution and foaming process.

(a) tensiometer

(b) rotational viscometer

Fig. 3. The schematic diagram of device.

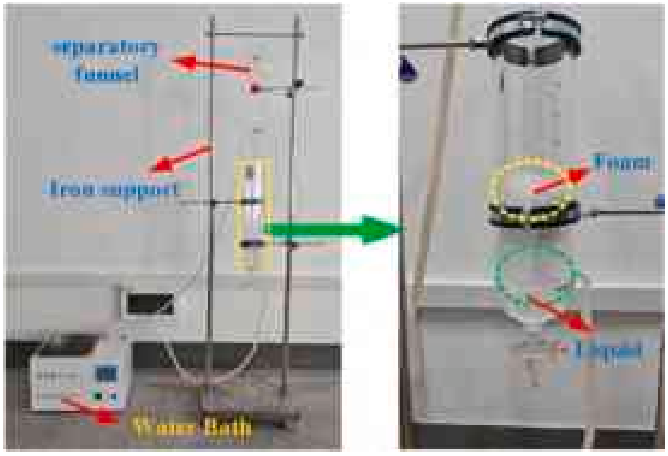


Fig. 4. The testing process with the Ross-Miles device.

developed and applied recently. Some scholars have studied the effect of short-chain fluorocarbon surfactants on the properties of the foam. Jiang et al. [19] explored that the synergistic interaction exists in the mixture of short-chain FS-50 and SDS. The results indicated that mixed system has good surface activity, foaming property and foam stability. It could be a proper substitute for long-chain ones to be used in the mixed system of fluorocarbon and hydrocarbon surfactants. Yu et al. [20] investigated the foaming behavior of short-chain fluorocarbon surfactant(FC-1157) used in fire-fighting. By compounding it with various hydrocarbon surfactants, the mixed system of fluorocarbon and hydrocarbon surfactant exhibit good foaming and foam stability. However, increasing the mass concentration of FC-1157 also increases the viscosity of the mixed system solution. Although these researchers have proved that the interfacial properties and foaming ability of the foam mixed with flame retardant or short-chain fluorocarbon surfactant could been improved, the current understanding for the causes of these phenomena is insufficient. The arrangement of surfactant molecules at the gas-liquid interface of foam shall be clarified, which requires further research from a new perspective. So far, the studies on the thermal stability and burn-back performance of the fire-fighting foam mixed with flame retardant or short-chain fluorocarbon were quite rare. Therefore, it is of great significance to develop systematic research for this issue.

In this work, the interfacial properties, foaming ability and foam stability of the AFFF mixed with different additives, including long-chain fluorocarbon surfactants, short-chain fluorocarbon surfactants, and flame retardants, were investigated. The differences of interfacial properties between foam solution mixed with fluorocarbon surfactant and foam solution mixed with flame retardant were shown by the variation of surface tension and viscosity. The adsorption behavior of surfactant molecules at the liquid-air interface were simulated by molecular dynamics software, which was used to explain the change of foaming ability and the foam stability. At last, the influence mechanism of high temperature environment and flame heat radiation on the attenuation behavior of foam was clarified by conducting tests on the thermal stability and burn-back performance of AFFF with different additives.

2. Experimental setup

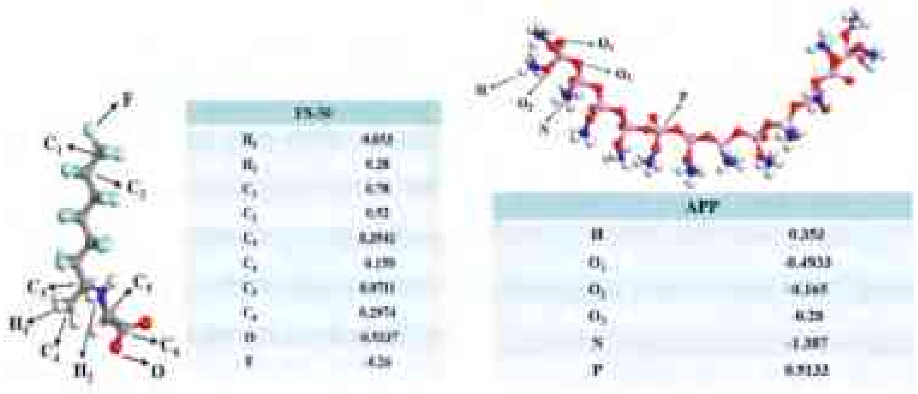
2.1. Materials

In this paper, the AFFF agent used in this study was prepared based on the formulation of the concentrate provided by Zhou et al. [21]. The components of the AFFF agent and concentration are listed in Table 1. Firstly, water-soluble ionic surfactant, ethylene glycol, and half content of deionized water were added into the beaker in sequence, and stir thoroughly for 30 min. Then mixing the xanthan gum and urea powder evenly on the weighing paper, slowly add them to the beaker and stir for 90 min. Lastly, put the remaining deionized water into the beaker and continue stirring for 30 min. After the stirring process is completed, fill the foam concentrate in a bottle for storage. Foam solution is composed of foam concentrate and deionized water in a volume ratio of 3:97.

The preparing process of foam solution is shown in Fig. 1. Foam concentrate are mixed with deionized water according to mixing ratio, and then the mixture solution is diluted into foam solution through a magnetic stirring machine. The high-speed stirring foaming method is used to obtain AFFF foam. It can be seen that the height of foam column does not change for a long time. Foam scan device(DFA-100) was used to show the shape of foam layer at micro scale after the foaming process completed, as shown in Fig. 2. It can be seen that the most of bubble's size are basically the same, and the shape of bubbles mostly appears as polygons, which can help the foam layer maintain stable structure. Based on the above analysis, the extinguishing agent prepared in this paper can obtain the foam with strong stability. The decay behavior of

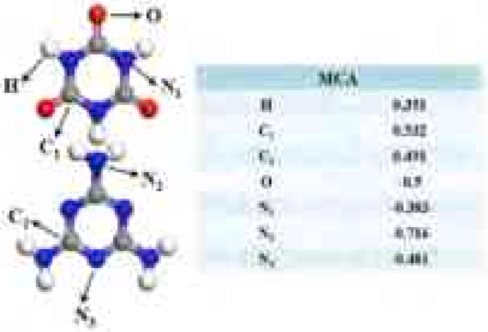
(a) SDS

(b) FS-30



(c) FS-50

(d) APP



(e) MCA

Fig. 5. Structure of molecular chain and the charges on the atoms.

the foam at heat radiation environment is tested by other experiments.

Different types of additives will be mixed with AFFF foam solution in a certain proportion. Three kinds of additives, namely, the long-chain fluorocarbon surfactant, the short-chain fluorocarbon surfactant and flame retardant were used in this study. The long-chain fluorocarbon surfactant is Capstone® FS-30, an non-ionic fluorocarbon surfactant with eight carbon atoms in its perfluorinated radical [22]. The short-chain fluorocarbon surfactant is Capstone® FS-50, an amphoteric fluorocarbon surfactant with six carbon atoms in its perfluorinated radical [23]. Water-soluble ammonium polyphosphate with a low polymerization degree(n = 10) was used as a comparison to observe the impact of different types of components added to foam solution on various properties. Besides, many researchers have proved that functional particles can be used as stabilizers to create more stable fire-extinguishing foam [21]. Some flame retardant particles with insoluble characteristics under high temperature can effectively dissipate heat and dilute oxygen concentration. These flame retardant particles may also have the same effect on improving thermal stability of the fire-fighting foam. To confirm this conjecture, non water-soluble melamine cyanuric acid (MCA) were also used in this study. The physical parameters of various additives are listed in Table 2.

2.2. *Surface tension and viscosity measurements*

Digital display rotational viscometer was selected to measure the viscosity of foam solution with components, as shown in Fig. 3(a). Based on the previous research, it can be seen that the viscosity of foam solution is generally less than 15 mPa s. Therefore, rotor #0 was equipped in test, and the speed is set at 60 RPM. To ensure the accuracy of the results, the test process was repeated three times, and the average value was used to analyze. The surface tension of the foam solution is measured with tensiometer, the test process is shown in Fig. 3(b).

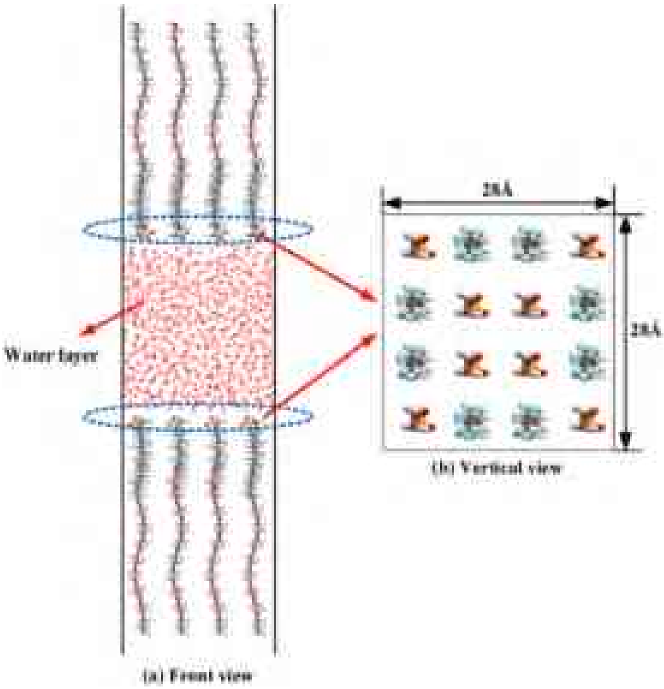


Fig. 6. Numerical model for characterizing gas-liquid interface of the foam.

Table 3
The loading capacity of additive molecules and water molecules in simulation.

Order	Number of Hydrocarbon surfactant molecules(N)	Number of Additive molecules(N)	Number of H_2O
#1	SDS(N = 8)	FS-30(N = 8)	1000
#2	SDS(N = 8)	FS-50(N = 8)	1000
#3	SDS(N = 8)	APP(N = 1)	1000
#4	SDS(N = 8)	MCA(N = 5)	1000

2.3. Foaming ability and foam stability assessment

The foaming ability and foam stability can be obtained by Rose-Miles device [20], as shown in Fig. 4. The upper part of the device is a 200 ml separatory funnel. Below the device is a jacket insulation cylinder. The inner diameter is 50 mm and the outer diameter is 70 mm. The water bath is used to maintain the temperature in the jacket insulation cylinder at 50 ± 5 °C. Open the diversion valve in the middle of the separatory funnel. The foam solution in the separatory funnel is converted into liquid drops through the metering pipe. When the liquid drops impacts the surface of the solution in the cylinder, it can carry some air into the solution surface, thus the foam will be produced. Until all the solution in the separatory funnel flows out, the initial height of foam h_0(ml) can be obtained by reading the scale value, which is used to define the foaming ability of the AFFF with different components. After waiting for 5min, observe the foam height again, which is recorded as h_5(ml). The remaining foam rate can be obtained by Eq (1), which is recorded as R_5(ml). This value can be used to evaluate the foam stability. The test process was repeated three times, and the average value was used to analyze.

$$R_5 = \left(\frac{h_5}{h_0}\right) \times 100\% \tag{1}$$

2.4. Model building and optimization by the Materials Studio molecular simulation

Materials Studio(MS) is a complete modeling and simulation environment designed to allow researchers to predict and understand the relationships of atomic and molecular structure with its properties and behavior [24,25]. In order to quantitatively explain the reasons for the difference in interfacial properties and foam stability performance of the fire-fighting foam mixed with different additives. MS(2020 version) was used to analyze the molecular arrangement at the gas-liquid interface of foam. The liquid-air interface models of the foam mixed with different additives and hydrocarbon surfactants were constructed by MS software. The molecular structure and the charges on the atoms can be obtained based on the molecular formula listed in Table 2, as is shown in Fig. 5.

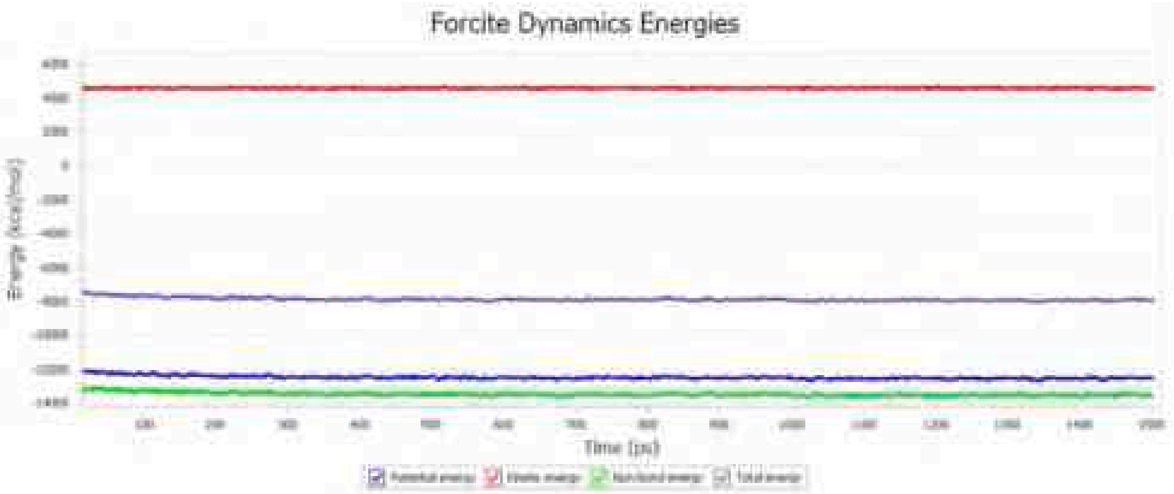
In this study, the liquid-air interface is constructed based on the sandwich model proposed by Gamba et al. [26], as is shown in Fig. 6. Two additive molecular layers are located at the top and bottom of the gas-liquid interface. The loading of surfactant molecules must be documented in a Table 3. The length of the established simulation region in the X or Y directions is set to 28 Å, which means that the surface concentration is 0.49 nm^2/molecule (each molecule occupies a surface area of 7 Å × 7 Å). The water layer located at the middle of the gas-liquid interface. The module named Amorphous Cell in MS software was used to mix the water molecules with ions in surfactant molecules. This process can create a water layer with a density of 1 g/cm^3. In order to assemble periodic structural cells of “additive-water-additive” by splicing various molecular layers. it is required that the water molecular layer and surfactant molecular layer have the same size in the X and Y directions (the Z direction can be set as needed). Therefore, the size of the water box in the X and Y directions is the same as that of the surfactant molecular layer, both of them are 28 Å. The Build Layers tool was used to splice two surfactant layers and water layers together. The molecules were oriented and arranged perpendicular to the upper and lower surfaces of the water layer, with hydrophilic groups facing the water layer and hydrophobic chains facing outward.

After the numerical model established, “Forcite+” module was used for simulation calculations. This model was geometrically optimized using the “Smart method”, with the accuracy selected as “Medium” and the force field could be selected as “PASS”. The optimized model was subjected to a 2ns dynamic equilibrium simulation under the NVT ensemble, and the ambient temperature was set to 298K. The electrostatic effect was summed using the “Ewald method”, while the vdW effect was summed using the “Atom based method”. The simulation time step was 1fs, and the simulation accuracy was chosen as “Coarse”. Finally, under the NVT ensemble, the same settings were used to continue the dynamic equilibrium simulation at 200ps. The trajectory information of the model was recorded every 10ps, and the simulation results for that time period were selected for analysis. As is shown in Fig. 7, The energy and temperature variation during the simulation process were used to determine whether the system had reached steady state. When the energy fluctuations within the system were not greater than 10% of the total energy and the temperature fluctuations were within 5%, it was determined that the system had reached a stable state.

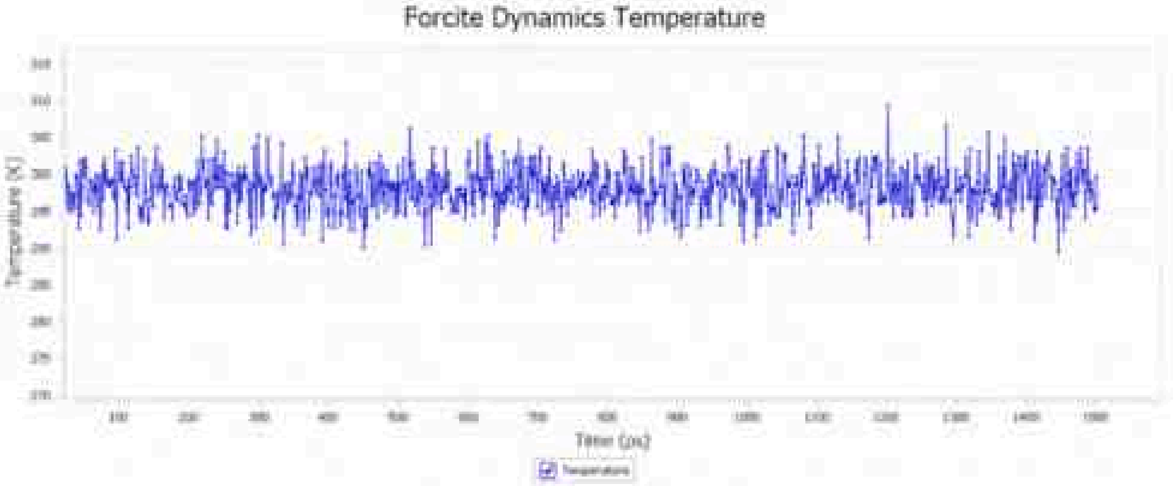
2.5. Test of thermal stability characteristics and burn-back performance

According to foam solution preparation process from the previous cases [27], small micelles will appear in the solution when the concentration of surfactant solution is lower than its CMC value, which mean a small number of molecules will pile up with each other. When the concentration exceeds 10 times of the CMC value, the aggregation structure of the micelles appears rod-shaped, as the rod-shaped arrangement can greatly reduce the contact area between the hydrocarbon chains of surfactant molecules and water, thereby improving the stability of the foam structure.

Based on the physical parameters provided by the product manual, the CMC micelle concentration of fluorocarbon surfactants selected in this paper is approximately stable at 0.01 wt%. The content of FS-30 is 25 wt % in commercial solution, the content of FS-50 is 27 wt % in commercial solution. The fluorocarbon surfactants were added to the



(a) The variation of energy



(b) The variation of temperature

Fig. 7. Energy and temperature changes in molecular dynamics simulations.

Table 4
Test conditions.

Category	Title	Radiation intensity (kW/m^2)	Mass concentration (wt.%)
Long-chain fluorocarbon surfactants	FS-30	25	0.1/0.2/0.3/0.4/0.5
Short-chain fluorocarbon surfactants	FS-50		
Flame retardant	APP MCA		

foam solution to improve interfacial property. The initial mass concentration is set at 0.1 wt%, as shown in Table 4, then gradually increase the mass concentration of additives in the foam solution. The influence of the mass concentration of different additives in foam solution on the thermal stability and burn-back performance of the foam can be explored.

A series of tests on the thermal stability characteristics of the foam were carried out with the cone, as shown in Fig. 8. Put the foam in the quartz beaker and applied it directly below the radiant cone. The quartz beaker can withstand a maximum temperature of 1000 °C. Based on the previous research results [21], the distance between the upper of the beaker and the radiant cone was maintained at 3 cm by adjusting the lifting support, so as to ensure that the foam in the beaker can receive all the heat radiation as much as possible. The thermal radiation value was adjusted to 25 kW/m^2. Make certain that the heat radiation received by the foam in the beaker can generally maintained at 18–20 kW/m^2, which is closer to the radiant heat value of the real fire environment. The test process was repeated three times, and the average value was used to analyze.

The burn-back performance of AFFF with different additives was evaluated according to the test requirements from Chinese standard GB15308-2006 Appendix-A [12,28]. Due to the combustion efficiency of n-heptane is relatively higher than others. The flame generated by this fuel has moderate brightness and less smoke production, which can help to observe the characteristics of flame shape. Therefore, n-heptane was selected as the fuel. A square steel pan (length:20 cm, depth:5 cm) was

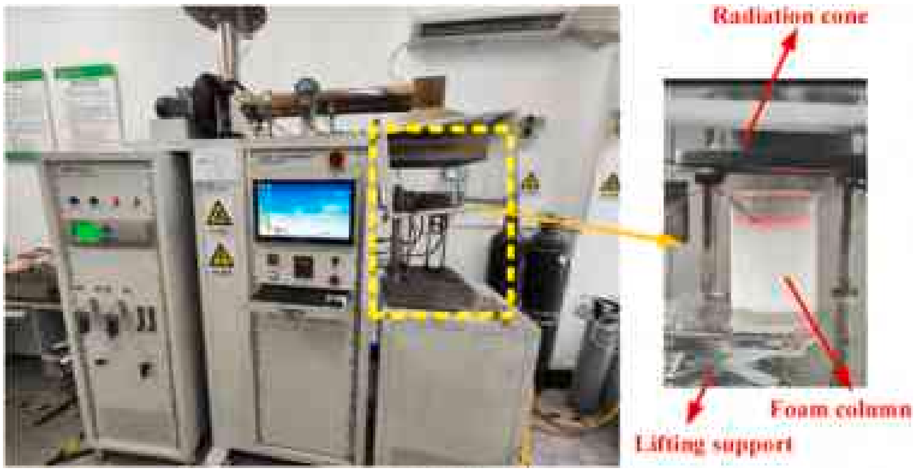


Fig. 8. The thermal stability characteristics test with cone.

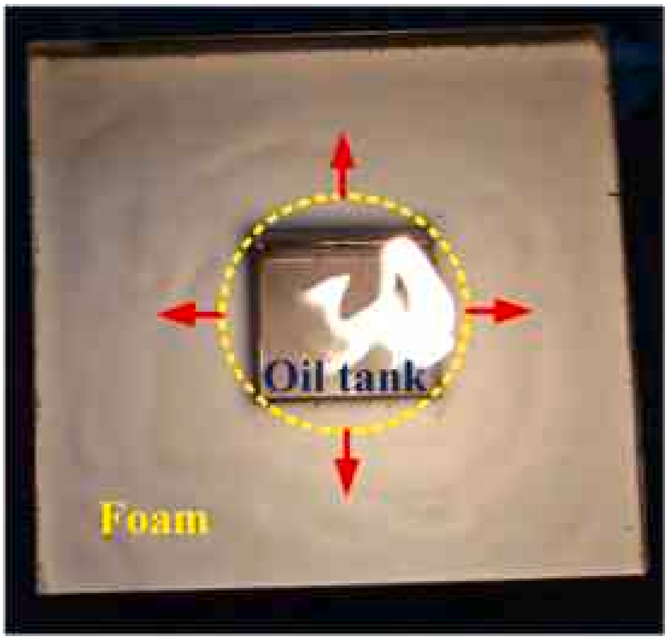


Fig. 9. The burn-back performance testing device.

used to hold the fuel and the AFFF foam. The burn-back pot (length:5 cm, depth:6 cm) was located at the center of the steel pan. Before carrying out the test, n-heptane with a thickness of 1 cm was covered with the bottom of the steel pan. The burn-back pot also needs to be filled with n-heptane. Then evenly cover 1000 ml AFFF foam in the steel pan. Ignite the tank filled with n-heptane fuel and the ignition time was recorded as 0 s. The diffusion form of the flame and the change of foam area in the steel pan could be observed in testing, as shown in Fig. 9. The foam layer gradually collapse under the effect of the heat radiation from the flame. The period when the foam in the steel pan completely disappears is defined as 100% burn-back time, which can be used to compare the burn-back performance of AFFF foam. The test process was repeated three times, and the average value was used to analyze.

3. Results and discussion

3.1. Effect of different components on the physical properties of foam solution

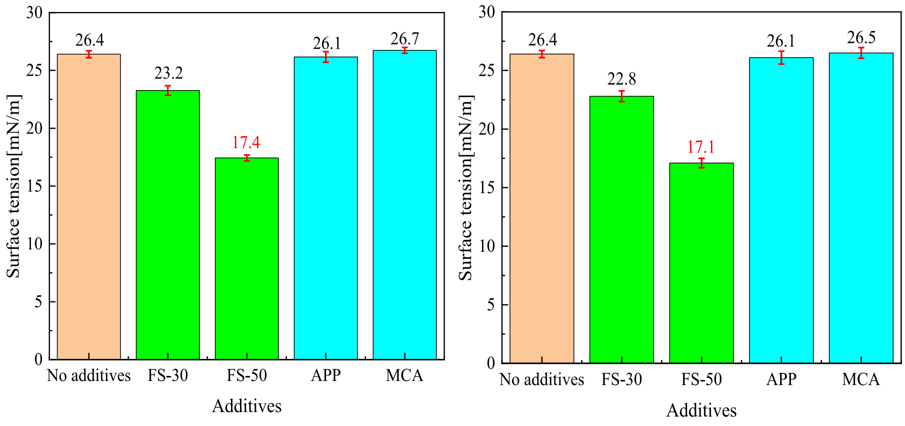
3.1.1. The variation of surface tension

Surface tension is one of the important parameters to evaluate the strength of foam structural stability. Generally, the Gibbs free energy required for the foam generated will be significantly reduced when the surface tension is lower, thus making the foaming behavior of the foam solution easier [29]. Fig. 10 shows the change of surface tension of AFFF after adding different components. This indicated that the surface tension of foam solution after adding fluorocarbon surfactant all show a downward trend when the additive concentration is fixed. The surface tension of foam solution mixed with FS-50 decreases the most. But for the mixture of flame retardant and foam solution, the surface tension has no obvious change. To sum up, these phenomena shows that compared with the foam solution with a single hydrocarbon surfactant, the surface activity of the foam can be effectively improved after adding fluorocarbon surfactant.

As shown in Fig. 11, for the foam solution with flame retardant added, increasing the mass concentration can not reduce the value of surface tension. However, as the mass concentration increased from 0.1 wt% to 0.3 wt%, the surface tension of AFFF solution with fluorocarbon surfactant decreases gradually. At this moment, the number of surfactant molecules on the gas-liquid interface of the foam also continue to increase, so the surface tension value of the solution continue to decrease. But when the mass concentration exceeds 0.3 wt%, the surface tension of the foam solution remains basically unchanged. The reason is that the mass concentration has reached the CMC value of mixture of foam solution and additives, and the number of surfactant molecules on the gas-liquid interface has been saturated. Even if the mass concentration continues to increase, it will not further reduce the surface tension again. To sum up, the above results show that when the mass concentration of fluorocarbon surfactant in foam solution reaches 0.3 wt %, the surface tension could reach the critical minimum value at this condition.

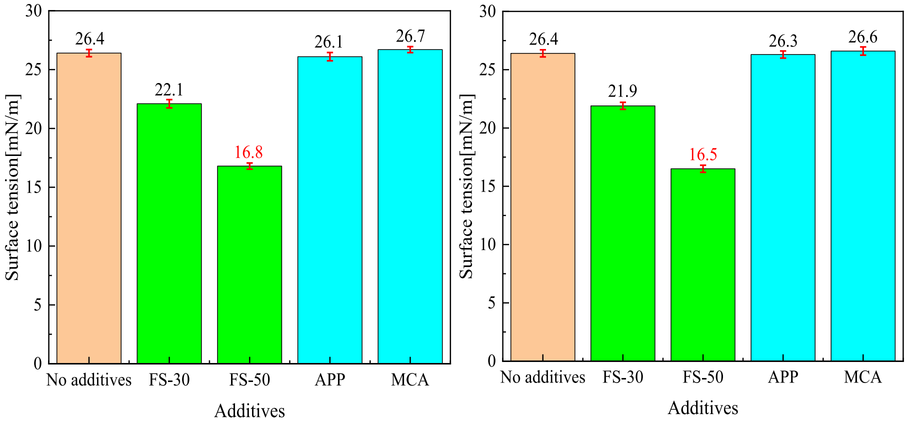
3.1.2. The variation of viscosity

Previous studies have shown that for AFFF with higher viscosity, the molecular arrangement adsorbed on the surface of foam liquid membrane will be more concentrated, the relative gas permeability will be weakened, and the stability of foam will be enhanced to a certain extent [30,31]. However, excessively high solution viscosity can have a certain impact on the spreading ability of the foam, which can not conducive to quickly covering the fire source and thus reducing fire extinguishing



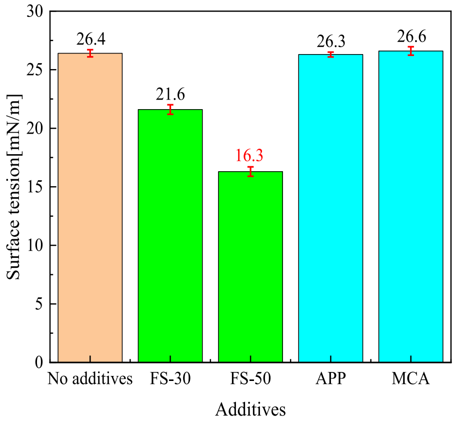
(a) 0.1wt.%

(b) 0.2wt.%



(c) 0.3wt.%

(d) 0.4wt.%



(e) 0.5wt.%

Fig. 10. Comparison of surface tension for the mixture of foam solution and additives.

efficiency. Therefore, the viscosity of foam solution should fluctuate within a reasonable range, both sealing and spreading rates can be considered simultaneously. The viscosity distribution for AFFF after added different additives are shown in Fig. 12. It can be seen that the viscosity of solution can be improved by adding fluorocarbon surfactants or flame retardants to AFFF. When the mass concentration is fixed, the viscosity of foam solution added APP is significantly higher. The reason is that APP can easily soluble in water, and a large number of APP will produce colloidal substances after being dissolved in liquid, which will greatly increase the viscosity of foam. In addition, the viscosity of foam solution after adding fluorocarbon surfactant also changed. When its mass concentration increases from 0.1 wt% to 0.3 wt%, a large number of surfactant molecules adsorb on the surface of the liquid membrane, which not only improves the stability of the liquid membrane but also increases the viscosity of the liquid. However, the solution viscosity will also decrease when the mass concentration of components in AFFF exceeds 0.3 wt%. Except for the foam solution with short-chain fluorocarbon surfactants(FS-50), its viscosity value will drop slightly. And also

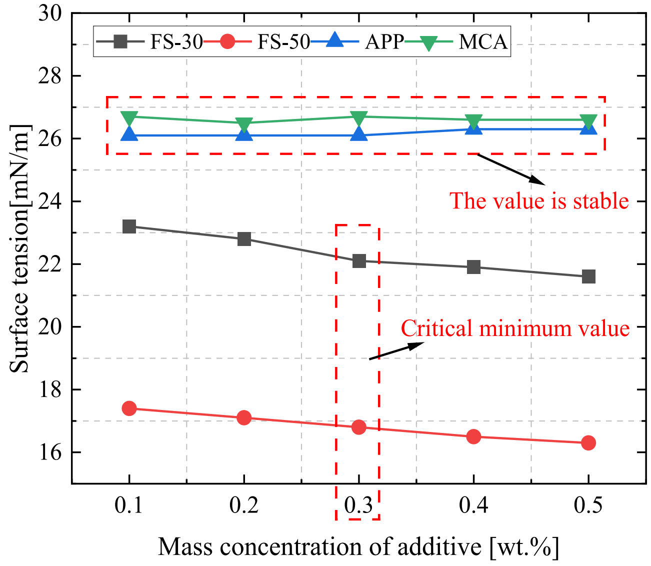


Fig. 11. The effect of mass concentration of additive on surface tension.

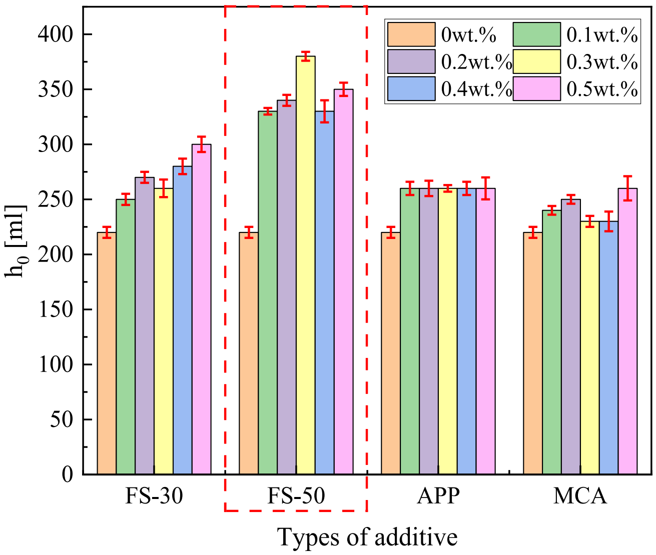


Fig. 13. The comparison of foaming ability for AFFF with different additives.

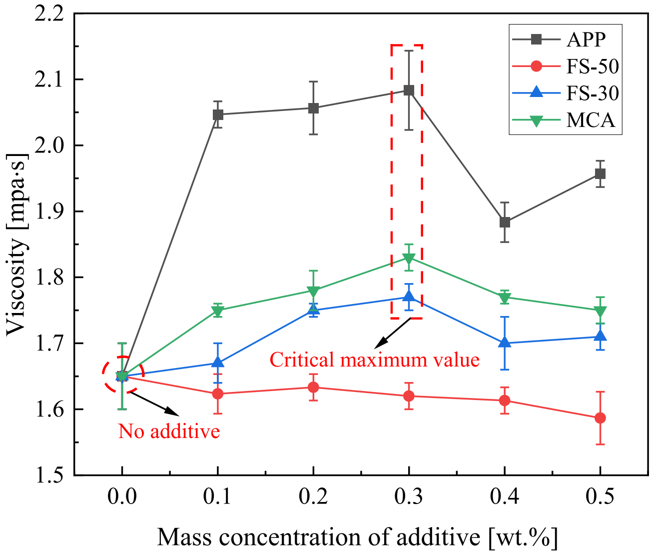


Fig. 12. The viscosity distribution for the mixture of foam solution and different additives.

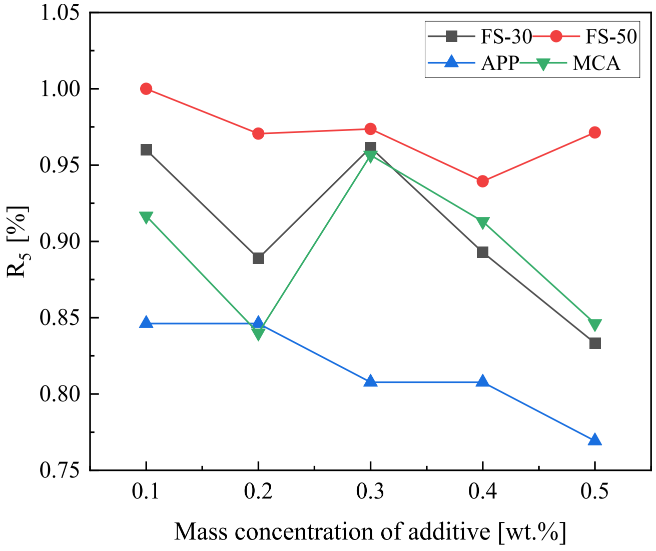


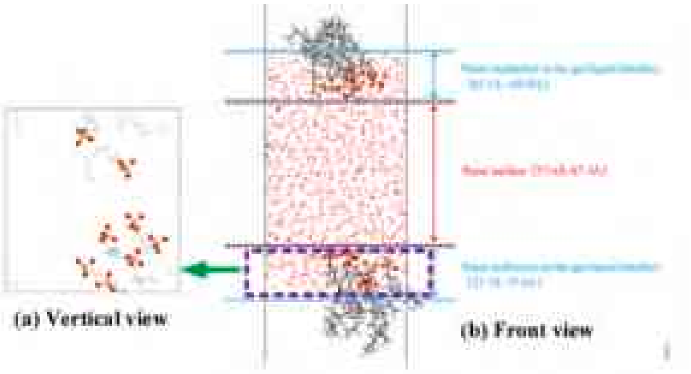
Fig. 14. The comparison of foam stability for the foam with different additives.

increasing the mass concentration has little effect on its viscosity value. For MCA, due to its physical and chemical properties that are almost insoluble in water. A large number of solid powders will adhere to the liquid film area of foam, and the particle size of MCA solid powder is approximately 4 μm. These solid powders can not affect the viscosity of the solution, and improve the stability of the foam structure to a certain extent. To sum up, the above results show that when the mass concentration of fluorocarbon surfactant or flame retardants in foam solution reaches 0.3 wt%, the viscosity of foam reaches the critical maximum value at this condition.

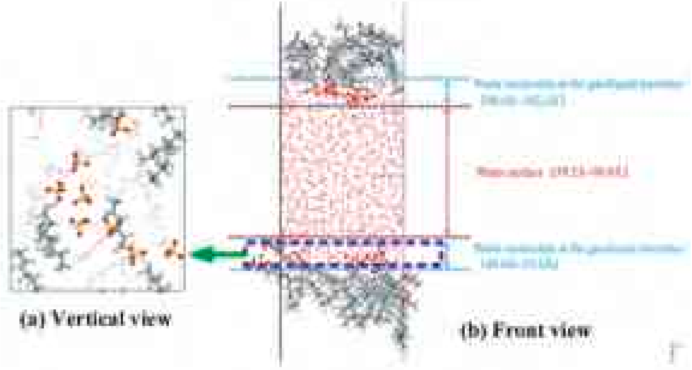
3.2. *Effect of different components on the foam performance*

3.2.1. *Foaming ability*

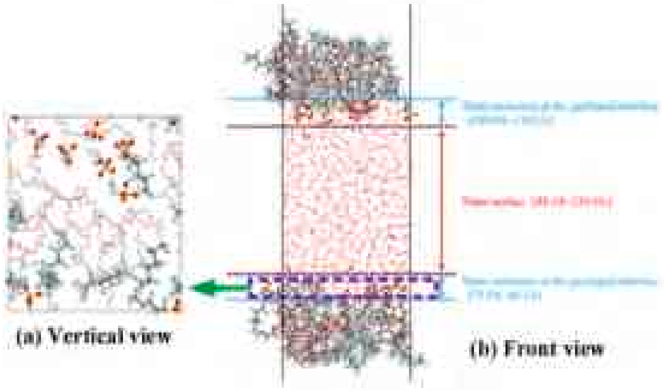
The foaming ability of AFFF plays an important role in isolating combustibles and oxygen. Through Rose-Miles device, compare the foaming ability of foam solutions after added fluorocarbon surfactants or flame retardants under the same condition. Previous literature shows that the initial foaming height(h_0) is related to the mass concentration of surfactant in solution and the dynamic adsorption of surfactant molecules [32,33]. When the mass concentration of surfactant reaches above its CMC value, its foam liquid film usually has good interfacial viscoelasticity, which can effectively inhibit the rupture of the film during foaming. The comparison of foaming ability of foam samples with different components is shown in Fig. 13. It can be seen that the foaming ability of foam solution with APP or MCA is basically same and weaker than others. The initial foaming height(h_0) of both have only increased by 24%. Even if the mass concentration of additive in the solution is increased, the foaming ability of the solution has no obvious change yet. On the contrary, after adding fluorocarbon surfactant, the foaming ability of foam solution will significantly improve. The foaming performance of the foam solution with the addition of short-chain fluorocarbon surfactants(FS-50) is the strongest. Its initial foaming height(h_0) increases by 71% at most. For other surfactants, regardless of the length of the carbon chain, the increase in foaming height is basically within the range of 40%–50%. As a result, adding short-chain fluorocarbon



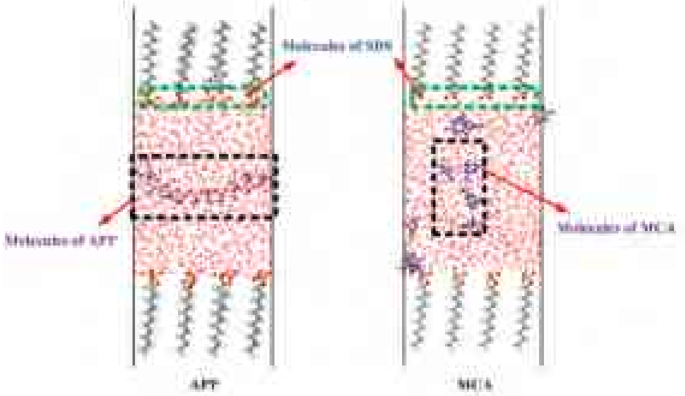
(a) without fluorocarbon surfactants



(b) mixed system of SDS and FS-50

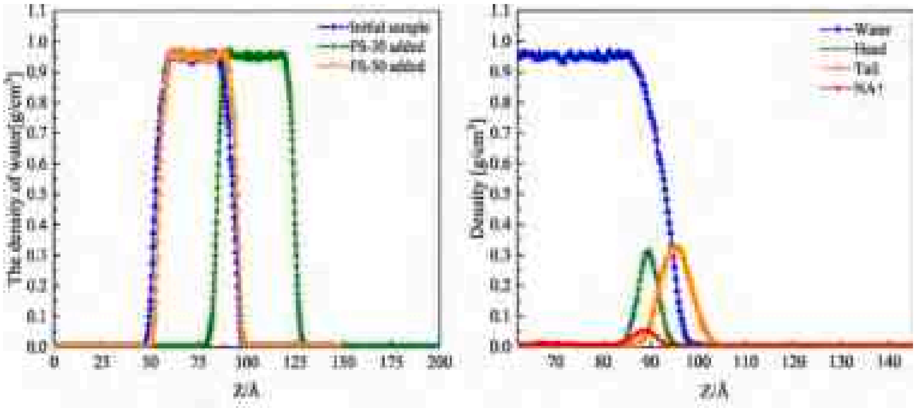


(c) mixed system of SDS and FS-30

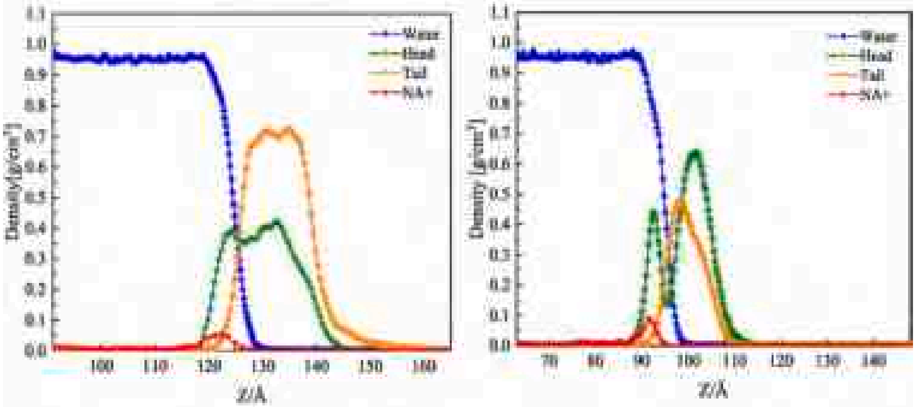


(d) mixed system of SDS and flame retardant

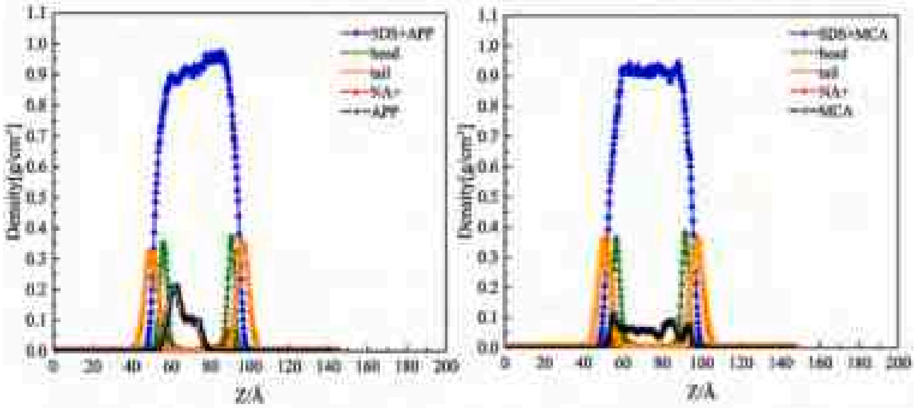
Fig. 15. The arrangement of molecules at the liquid-air interface.



(a) The Comparison of water density (b) AFFF without fluorocarbon surfactants



(c) The mixed system of SDS and FS-30 (d) The mixed system of SDS and FS-50



(e) The mixed system of SDS and APP (f) The mixed system of SDS and MCA

Fig. 16. Density distribution of different components along Z-axis.

Table 5
The physical parameters of liquid-air interface in the foam.

Additives	SDS	SDS/ FS-30	SDS/ FS-50	SDS/ APP	SDS/ MCA
Thickness of water layer(Å)	29.7	32.8	31.6	31.6	32.0
Number of water molecules	257	190	201	390	262
Proportion of water molecules at the liquid-air interface	25.7%	19%	20.1%	39%	26.2%

surfactants to the foam solution can effectively improve foaming performance.

3.2.2. Foam stability

The residual foam rate(R_5) was used to evaluate the foam stability, as shown in Fig. 14. This indicated that the R_5 of foam solution mixed with FS-50 is generally higher than others, and with the increase of mass concentration, the R_5 is always stable around 95%. For other conditions, the R_5 of foam solution mixed with FS-30 or MCA is basically the same. Although the foaming ability of mixture of foam solution and MCA is not ideal, due to the solid powder is insoluble in water, a large amount of solid powder can be adsorbed in the liquid-air interface, which can slow

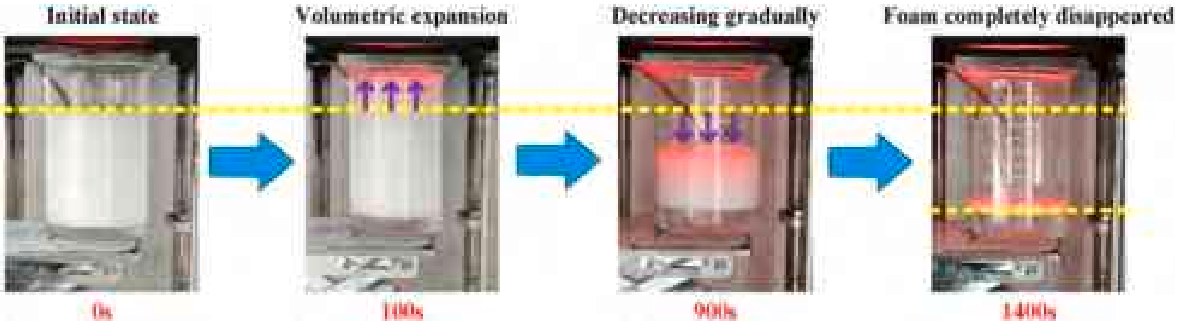


Fig. 17. Volume change of foam mixed with FS-50 at heat radiation environment(mass concentration = 0.3 wt%).

down the liquid discharge rate of foam to a certain extent. Therefore, high stability can be maintained in this situation. In addition, The excessive mass concentration can significantly weaken the foam stability, the R_5 is the highest when the mass concentration keep 0.3 wt%. The foam stability of foam solution mixed with APP is the worst in all test conditions, the R_5 basically remains in the range of 80%–85%. In conclusion, It can be concluded that adding short-chain fluorocarbon surfactants can effectively change the foaming ability of the AFFF agent, while improving stability of foam by reducing the decay rate.

3.2.3. The effect of surfactant molecular distribution on foam performance

The arrangement of molecules at the liquid-air interface after simulation finished is shown in Fig. 15. This indicated that the surface of liquid-air interface in the foam without additives can not completely covered by surfactant molecules, there are surfactant cavities and the water layer is thinner than others. However, after adding FS-50 or FS-30 in the foam, the thickness of the surfactant molecular layers significantly increases. In the mixture of hydrocarbon surfactants and fluorocarbon surfactants, the foam surface is covered with surfactant molecules, forming a thick and uniform surface, which is conducive to the stability of foam. Furthermore, after adding APP or MCA to AFFF, the thickness of the molecular layers is relatively thinner. At the gas-liquid interface, a large number of APP molecules are mixed with the water, and MCA solid particles are insoluble in water, resulting in their dispersion in the liquid. As a result, the surface of the molecular layer cannot be completely covered by the flame retardant. There are still large cavities at the gas-liquid interface, which is easy to cause a large amount of water leakage. This is the main reason for the weak structural stability of the foam mixed with flame retardant.

The density distribution of water molecule, surfactant head, tail and sodium ion (NA^+) along the Z-axis in the mixture of the foam and additives are shown in Fig. 16. The proportion of water in foam solution is 97%, and the density of water layer originally established in the mixed system is 1 g/cm^3. Making 90% proportion of the water layer as the dividing point, so the region with water density greater than 0.9 g/cm^3 in this curve can be regarded as the water layer. Based on this criterion, the density distribution curve of the water molecule can be used to obtain the thickness of the water layer and the number of water molecules at the liquid-air interface. The results are shown in Table 5.

As is shown in Table 5, the SDS has fewer molecular chains, resulting in more voids formed by surfactants on the surface of the water layer, making it the thinnest. On the surface formed by SDS molecules, water molecules are easier to enter and the water blocking effect is not ideal. It can be seen that after adding FS-30 and FS-50 in SDS, the thickness of the water layer in the mixed system increases, and the number of water molecules at the liquid-air interface significantly decreases yet. This indicated that the surface formed by adding FS-30 and FS-50 molecules can improve water blocking effect, which means the water molecules are more difficult to enter the surface formed by the mixed system of fluorocarbon and hydrocarbon surfactants. The molecular chains of FS-30 are arranged more evenly at the liquid-air interface, and the position of the head group relative to the water molecules in the model is relatively outer, which can create the thickest water layer. The molecular chains of FS-50 are arranged irregularly at the liquid-air interface, and the hydrophilic head groups are scattered on the surface of the liquid film and make water layer thinner, which has a certain impact on the stability of the liquid film. However, the number of water molecules passing through the surfactant layer in the mixed system of SDS and FS-50 is less than that in the FS-30. The reason for this phenomenon is that FS-50 molecules and SDS molecules have a strong synergistic effect. The combination of two components can form spherical or wormlike associations, increasing the interaction between molecular chains, making it more difficult for water molecules to enter the surface of the mixed system, resulting in better water retention performance.

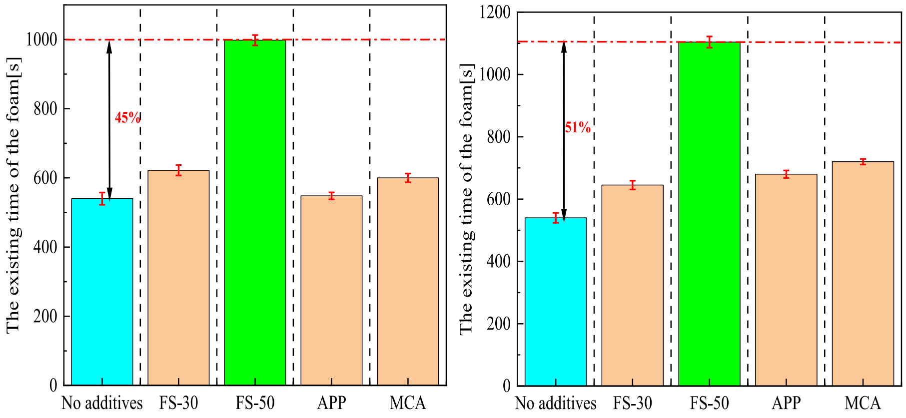
After adding APP and MCA, the water molecules entering the surfactant layer increase, the water blocking effect decreases, and the density of foam liquid film decreases. In the mixed system of SDS and APP, the alkyl chain ($C_{12}H_{25}$) of SDS will interact with the $PO3^{3-}$ ion from APP, reducing the dispersion of APP in the foam solution. Therefore, the long-chain molecules from the APP can not fill the holes in the surfactant molecular layer, resulting in more water molecules entering the surfactant molecular layer. In the mixed system of SDS and MCA, the amino group of MCA reacts with the NA^+ from SDS to produce a water-soluble melamine salt, which has good dispersibility on the surface of the liquid film and better water blocking effect compared to APP.

3.3. Thermal stability and burn-back performance of AFFF with different additives

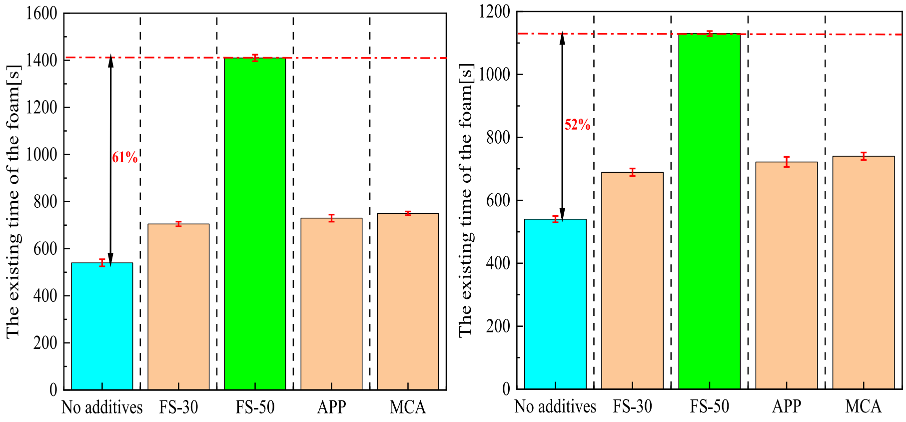
3.3.1. Thermal stability

Under the effect of the heat radiation, the height of the foam column in the quartz beaker first slightly increased and then gradually decreased, as is shown in Fig. 17. In this work, the existing time of foam in heat radiation environment was used to characterize the thermal stability of AFFF with different additives.

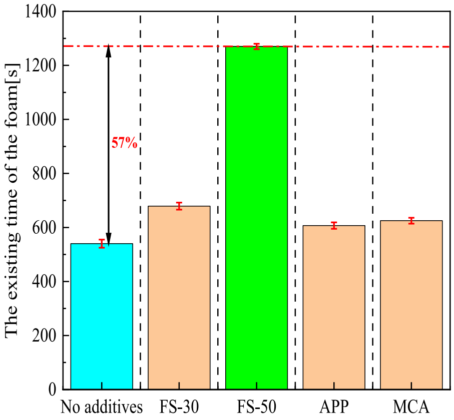
The change of thermal stability of AFFF after adding different additives is shown in Fig. 18. It can be seen that when the mass concentration is fixed, the existing time of the foam after adding FS-50 under high temperature thermal radiation is increased by 53% nearly, which is significantly higher than others. The thermal stability of the foam with FS-30 was not significantly improved. In addition, the existence time of the foam with flame retardant APP or MCA is close to that of the foam with FS-30. The mass concentration of additives will also affect the thermal stability of the foam, as is shown in Fig. 19. It can be seen that the thermal stability of the foam is enhanced with the increase of mass concentration of additives. When the mass concentration increases to 0.3 wt%, the duration of the foam with various additives under the thermal radiation environment is at the highest condition. The survival time of the foam gradually decreases when the mass concentration exceeds 0.3 wt%. This result shows that the thermal stability of the foam can be significantly improved by maintaining 0.3 wt% mass concentration of additives.



(a) 0.1wt.%		(b) 0.2wt.%



(c) 0.3wt.%		(d) 0.4wt.%



(e) 0.5wt.%

Fig. 18. Thermal stability of the foam with different additives.

3.3.2. Burn-back performance

The whole test process is shown in Fig. 20. When the burn-back pot filled with n-heptane in the center of the steel pan is ignited and continuously burned for 3min, the flame height and its shape inside the burn-back pot basically can not change. This phenomenon indicated that flame has entered a stable combustion stage. However, under the influence of the heat radiation released by the flame and the heat conduction generated by the side wall of the burn-back pot, the stability of the foam close to the burn-back pot gradually collapses. When the foam above the fuel completely disappear, the fuel is completely exposed and quickly ignited. At this time, the initial collapse time of foam is marked as t_0, which indicates that the burn-back performance of the foam begins to decrease. Under the continuous influence of high temperature and flame heat radiation, the sealing of the foam layer is also gradually weakened. A large amount of fuel vapor generated by high temperature diffuses and will be ignited, thus accelerating the flame spread rate from

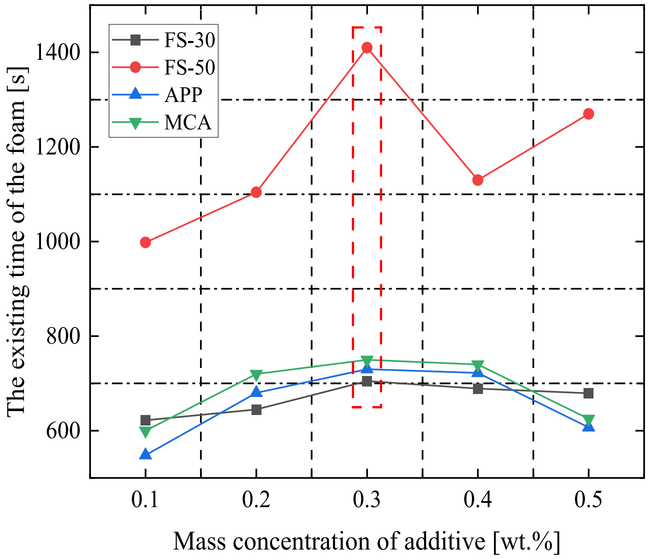


Fig. 19. The effect of mass concentration on thermal stability of the foam.

the side wall of the burn-back pot to the outside area, resulting in the combustion area continues to expand until the foam above the fuel disappear completely. At this time, all the fuel in the steel pan is ignited, the burn-back duration of the foam is marked as t_c. This indicated that the burn-back performance of the foam has been completely lost.

As shown in Fig. 21(a), adding fluorocarbon surfactants can significantly improve the burn-back performance of the AFFF foam. The burn-back duration of the foam mixed with FS-50 is the longest. As shown in Fig. 21(b), by comparing the time interval from the beginning of foam layer leak to the complete disappearance of foam layer, it can be seen that the foam with short-chain fluorocarbon surfactant FS-50 is significantly stronger than others. In the static combustion condition, the flow ability of foam on the fuel surface has a great influence on the burn-back performance. As shown in Fig. 22, according to the change of combustion area, since the surface tension of the solution can be significantly reduced by adding FS-50 to AFFF, it helps foam maintain higher spread rate on the fuel surface. Therefore, the foam can quickly make up for the gap burned by the flame.

In addition, increasing the mass concentration will also improve the burn-back performance of foam, especially for AFFF added with short-chain fluorocarbon surfactant FS-50. However, adding a single flame retardant foam has the smallest improvement. It show that the flame retardant could not effectively isolate the thermal radiation at the same concentration state of components, so the collapse rate of the foam would be greatly accelerated. To sum up, with the increase of mass concentration, the burn-back duration of the foam added with flame retardant and long-chain surfactant has no obvious change, while the burn-back duration of short-chain fluorocarbon surfactant FS-50 will increase significantly.

4. Conclusion

In this works, the physical properties of AFFF with different components and its performance under heat radiation environment were discussed. The adsorption behavior of surfactant molecules on liquid-air interface of the foam was characterized to illustrate the effect of surfactant molecular distribution on foam stability. Based on these studies, the following conclusions can be obtained.

(1) The tests of interfacial properties for foam solution indicate that interfacial properties of the foam can be effectively improved

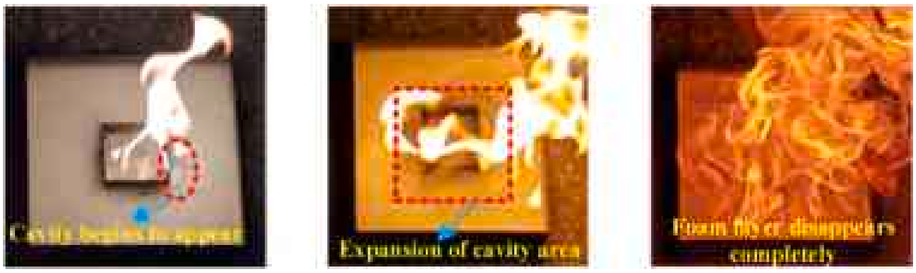
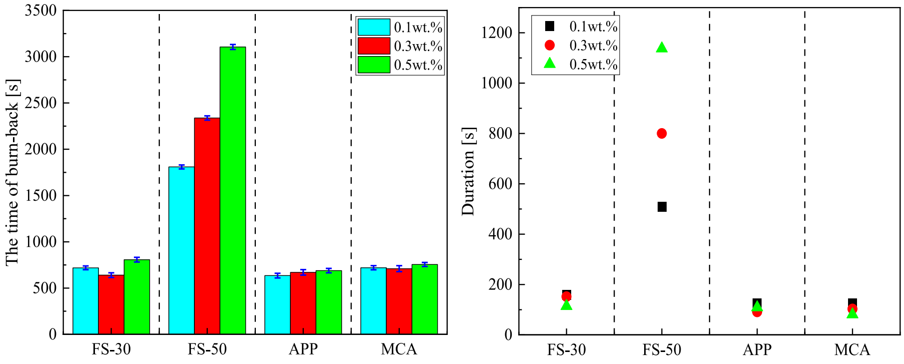


Fig. 20. The shape of the foam layer at different stages.



(a) comparison of burn-back performance

(b) burn-back duration

Fig. 21. The burn-back performance of AFFF with different components.

Fig. 22. Spreading process of the foam on oil surface.

after adding fluorocarbon surfactant. Especially for FS-50, the surface tension and viscosity of foam solution containing this short-chain fluorocarbon surfactant are at the lowest level. But for AFFF added with flame retardant, the surface tension has no obvious change, and for AFFF with water-soluble flame retardants added, its viscosity significantly increased due to the production of a large number of colloidal substances after flame retardants being dissolved in liquid.

(2) Based on excellent interfacial properties of foam solution, the foaming ability and foam stability of AFFF mixed with FS-50 is the strongest. The results from the molecular dynamics simulation indicate that FS-50 molecules and hydrocarbon surfactant have a strong synergistic effect. The combination of these two substances can increase the interaction between molecular chains, making it more difficult for water molecules to enter the surface of the mixed system, which enhances the stability of foam liquid film. It can be concluded that adding short-chain fluorocarbon surfactants can effectively change the foaming ability of the original AFFF foam, while improving stability of foam by reducing the decay rate. The foaming ability of foam solution with APP or MCA is basically same and weaker than others.

(3) The results reveal that foam mixed with FS-50 exhibits excellent thermal stability and burn-back performance. Thus it could be a proper substitute for long-chain fluorocarbon surfactants to be used in the AFFF mixed system. This mixed system can help the foam maintain higher spread rate on the fuel surface. Therefore, the foam can quickly make up for the gap burned by the flame. Maintaining proper mass concentration will also affect the key properties of the foam in fire environment, The mass concentration of additive in the foam solution should be kept at 0.3 wt%.

CRediT authorship contribution statement

Zhengyang Wang: Formal analysis, Methodology, Writing – original draft, Writing – review & editing. **Xuepeng Jiang:** Project administration, Supervision. **Chaojun Yang:** Data curation, Validation. **Biao Zhou:** Conceptualization, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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