Improving the performance of fluoroprotein foam in extinguishing gasoline pool fires with addition of bromofluoropropene

Mei Zhao, Xiaomin Ni*,†, Shaogang Zhang, Wei Cao, Yu Guan, Canjun Liang, Xishi Wang and Heping Zhang*,†

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230022, Anhui, PR China

SUMMARY

The fluoroprotein foam is one of the most widely used fire suppressants for its low cost, low toxicity and biodegradability. However, its fire extinguishing performance is limited. In this article, fluoroprotein foam was combined with a clean and degradable fire suppressant of 2-bromo-3,3,3-trifluoropropene (BTP) to improve its fire extinguishing efficiency. Laboratory scale suppression experiments on gasoline pool fires were conducted in a $27\,m^3$ confined space. An optimized volume flow ratio of air to foam solution was found out first to acquire fluoroprotein foam with best fire extinguishing efficiency; then varied amounts of BTP were added to the foam at the optimal flow ratio for performance examination. Results demonstrated: at the optimized volume flow ratio of air to foam solution of 9 and the volume flow ratio of BTP to foam solution of 3.75%, a superior fire extinguishing performance was achieved with the fire extinguishing time reduced by 43% in comparison to that without any BTP added. The fire suppression mechanism of the foam with BTP additive was discussed based on established fire suppression theories and experimental results. Copyright © 2014 John Wiley & Sons, Ltd.

1. INTRODUCTION

It has long been recognized that aqueous film-forming foam (AFFF) has undesirable environmental characteristics [1–3]. The fluorocarbon surfactant in the AFFF degrades to perfluorooctanesulfonate (PFOS), which has been identified by the Environmental Protection Agency (EPA) as environmentally persistent, bioaccumulative and toxic [4]. It is urgent to identify and develop an alternative firefighting foam, which has equal or superior fire extinguishing performance and is more environmentally safe [5].

Alsaati *et al.* [6] proposed the replacement of halons with nonfluorocarban such as protein foam to reduce the rate of ozone depletion. Especially after restriction on the use of PFOS by EPA, as an alternative option of PFOS foam, protein foam has been widely used due to its relatively low cost, low toxicity and biodegradability. Two kinds of protein foam are most often seen in the markets, protein-based foam and fluoroprotein foam (FP foam). The protein-based foam concentrate is prepared from hydrolyzed protein either from animal or vegetable source with suitable stabilizers and preservatives added. The FP foam is similar to protein-based foam but with fluorochemicals added, which make it more effective than protein-based foam [7]. The fluorochemicals are generally poly hexafluoropylene benzene sulfonic acid sodium (ODS) obtained by oliomerization, which has a nonlinear structure in the

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*Correspondence to: Xiaomin Ni and Heping Zhang, State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei 230022, Anhui, PR China.
†E-mail: nxmin@ustc.edu.cn; hpzhang@ustc.edu.cn

main chain and high fork degrees making it out of the ban of international environmental conventions on the Stockholm Convention on Persistent Organic Pollutants (POPS) [8]. Although FP foam is environmentally friendly, its extinguishing performance is indicated to be poorer than AFFF [9, 10]. It's meaningful to improve the performance of FP foam to replace AFFF fire-fighting agent.

FP foam extinguishes fires mainly through physical effects, including cooling effect by the evaporation of water draining out of foam, attenuation of thermal radiation and separation of fuel from air [11–13]. It is known that when a small amount of a very effective radical chain-stopping agent is added to a physical agent, an impressively improved fire extinguishing efficiency could be achieved [14]. For example, FP foam with heptafluoropropane (HFC-227ea) as a foaming agent can put out low boiling point liquid fires promptly and effectively; while the air foam without HFC-227ea could hardly control and restrain it [15–17]. Whereas, HFC-227ea has been listed as a controlled and unfavorable long-term substitute for halon1301, as has a relatively long atmospheric lifetime of 31–34 years and a global warming potential of 0.6 [18, 19]. Presently, it is still challenging to find more efficient and environmentally friendly clean agents as additive to FP foam.

2-Bromo-3,3,3-trifluoropropene (BTP) as a degradable clean gas fire suppressant is proposed as a potential candidate in replacement of Halon1301 [20], which has the best mix of fire suppression capability, environmental effect, toxicity and boiling point [21]. The ozone destroying potential (ODP) and the global warming potential (GWP) values of BTP are zero [22, 23]. Moreover, with a low boiling point of 34 °C, BTP is liquid at room temperature and can be delivered in a pipe system under normal pressure. As a result, BTP is regarded as a clean gas fire suppressant, very suitable to combine with others [24]. Previously, we experimentally verified that a small amount of BTP addition could improve the efficiency of water mist in extinguishing gasoline pool fires in terms of reduced fire extinguishing time and agent mass [25].

In this paper, we attempted to add BTP to commercially available 6% FP foam solution to improve its efficiency in suppressing gasoline pool fires. Tests were conducted in a 27 m³ room with natural ventilation using FP foam containing different amounts of BTP as suppressants. An optimized volume flow ratio of air to FP foam solution was found out first; then foams with different amounts of BTP added at this optimized flow ratio were tested to find the optimal ratio of BTP additive to compressed-air FP foam. Moreover, the suppressing mechanism was discussed based on the experimental observations.

2. EXPERIMENTAL SETUP AND PROCEDURES

Schematic illustration of the experimental setup was shown as Figure 1. All the tests were conducted in a confined space measured 3.0 m long, 3.0 m wide and 3.0 m high and enclosed by glass walls. The room was naturally ventilated through two vent openings about 2.5 m × 0.1 m at the bottom of the two symmetrical side walls. The test facility mainly consisted of compressed-air foam generators, fire sources and instruments for data collection.
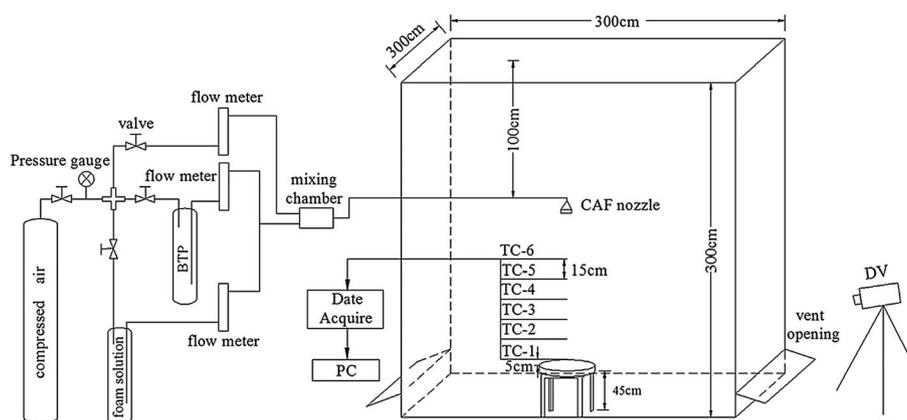
Figure 1. Schematic illustration of the experimental apparatus.

The compressed-air foam system was composed of compressed air, foam solution storage vessel, BTP storage vessel, flow meters, a coaxial mixing chamber for foam production and foam transportation pipelines, etc. The compressed air not only supplied the air for foam formation, but also provided the driving force for the delivery of foam solution and BTP. The discharge pressure was kept at 0.4 MPa for all tests. The flow rates of foam solution, BTP and air transported to the coaxial mixing chamber were controlled by glass type rotameters, respectively. The distance from the nozzle to the floor was kept as 2.0 m. The foam solution was commercially available 6% FP foam solution. BTP was synthesized by a solution method with the purity above 99.4%. Before the experiments, both the pressure and the flow rate were adjusted to preset values, worked for several minutes until the test system reached a stable condition. In the tests, the discharging medium (flow rate and pressure) was kept uniform by controlling the pressure valve and glass type rotameters at constant values. The flow rate of FP foam was rather uniform with relative standard deviation (RSD) lower than 1% (as seen in Table S5 and Figure S1).

A thermocouple tree, containing six thermocouples with interval of 0.15 m and the lowest thermocouple 0.05 m above the fuel pan, was set up to measure the flame temperatures. The fire suppression process was recorded by a video camera. The vessels were weighed before and after the tests to determine the total mass of suppressants consumed. Each test was repeated at least three times to get an average value. In the tests with different α, the maximal RSD of T_{ext}, m_{fs}, T_{burn} and $T_{25\%}$ was calculated as 8.39%, 4.71%, 3.11% and 10.0%, indicating that the measurement errors were acceptable (as seen in Tables S1–S4 in the supplementary materials).

3. CHARACTERIZATION OF THE FOAM WITHOUT BTP ADDITION

For the foam agent, the ratio of air to foam solution (denoted as β) determines the expansion ratio, the stability and liquidity of foam, and further affects its fire extinguishing performance [26, 27].

3.1. Physical properties of compressed-air fluoroprotein foam

At a certain pressure, ER directly influenced the rheology and fluidity of compressed-air foams [28, 29]. Different ER values were obtained by adjusting the ratio of gas to foam solution (β); the relationship between ER and β at 0.4 MPa was shown in Figure 2. When β was smaller than 20, ER increased with the increase of β, while decreased as β exceeded 20. The gas promoted the foaming process; however, excessive gas would cause the foam to be dry, resulting in instability and lower ER [30]. Thus, β from 4 to 20 were selected for the following tests to find out the optimized volume flow ratio of compressed air to FP foam solution.

Liquid drainage as a function of time was used to characterize the stability of foam for its simplicity [29, 31]. Figure 3 showed the variation of time required for 25% of solution to drain out of foam ($T_{25\%}$)
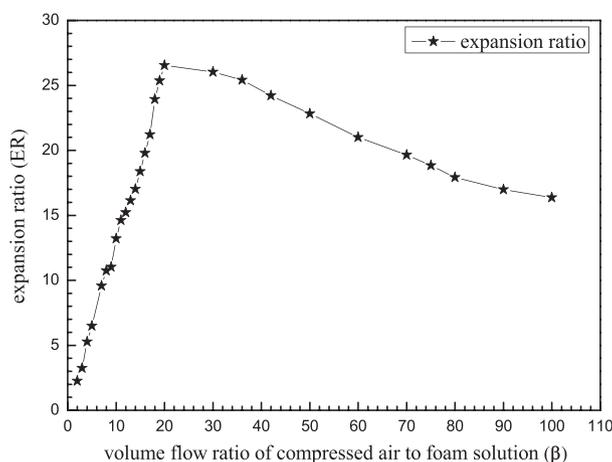
Figure 2. Variation of expansion ratio (ER) with β.
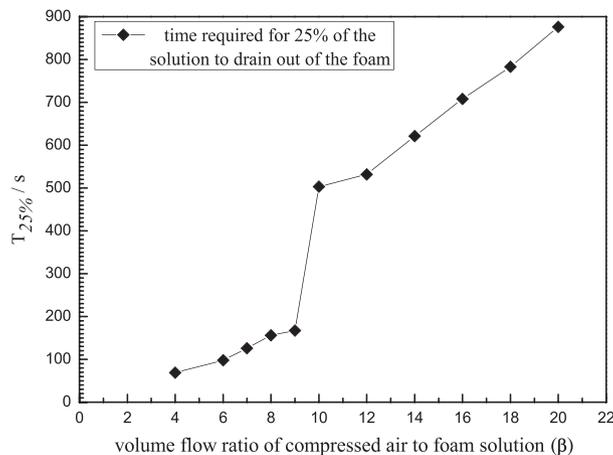
Figure 3. Variation of $T_{25\%}$ with β.

with β. It was seen that $T_{25\%}$ increased with β rising, indicating that the moisture content of bubbles decreased and foam became drier with β increasing [32]. Correspondingly, the viscosity of foam increased, and the spreading performance and liquidity became poor, especially when β exceeded 9 [33].

3.2. Fire extinguishing performance

Keeping the volume flow of foam solution constant at $40\,L\,h^{-1}$, fire suppression performance of FP foam with different β values was examined. Figure 4 gave the variation of extinguishing time with β increased from 4 to 20. It was shown that fire extinguishing time (T_{ext}) first sharply decreased and then slowly increased with β rising. The minimum value emerged at $\beta = 9$ with $T_{ext} = 28\,s$. Therefore, $\beta = 9$ was selected as the constantvolume flow ratio of air to FP foam solution in the following tests with BTP additive.

4. PERFORMANCE OF FOAM WITH DIFFERENT AMOUNTS OF BTP ADDITIVE

With constant application rates of foam solution of $40\,L\,h^{-1}$ and air of $360\,L\,h^{-1}$, the volume flow of BTP was changed to get different volume ratios of BTP to foam solution (α). Tests with α of 1.875%, 3.75%, 5.625%, 7.50% and 15.0% were carried out. Test with $\alpha = 0$ was taken as the blank test.
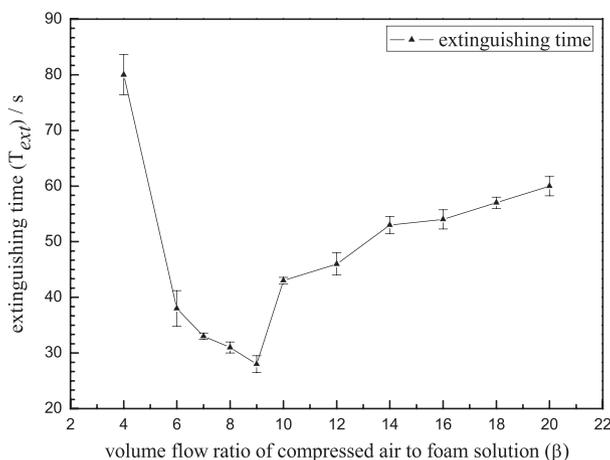
Figure 4. Variation of extinguishing time with β.

4.1. Fire suppression performance

Figure 5 showed the relationship between fire extinguishing time (T_{ext}) and α. It showed that the extinguishing time first decreased, and then increased with the increase of α. The critical value was α = 3.75% with T_{ext} = 16 s, which was reduced nearly by 43% in comparison to the test with α = 0 (T_{ext} = 28 s). Figure 5 also presented the profile of the mass of foam solution (m_{fs}) consumed for fire extinguishment with α, which showed similar varying trend to that of T_{ext} for the constant discharging rate of foam solution.

4.2. Burn-back performance

Figure 6 gave the burn-back time of above tests. It was apparently seen that FP foam with BTP exhibited a much longer burn-back time than that without BTP. When α was larger than 3.75%, the increase of burn-back time become less significant.

Figure 7 showed the typical images of foams containing different amounts of BTP before and after burn-back tests. Before burn-back tests, it was observed that foam layer on the fuel surface became thinner with the increase of α after fire extinguishment. Meanwhile, the phenomenon of 'accumulation' disappeared gradually, and the bubbles near the pan edge became sparser. After burn-back tests, the foam layer of FP foam with BTP additive became thicker than before, as shown
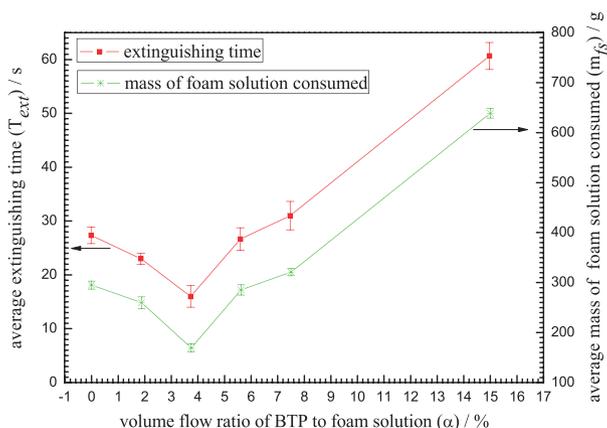
Figure 5. Effects of different α values on fire extinguishing time (T_{ext}) and mass of FP foam solution consumed (m_{fs}) at β = 9.
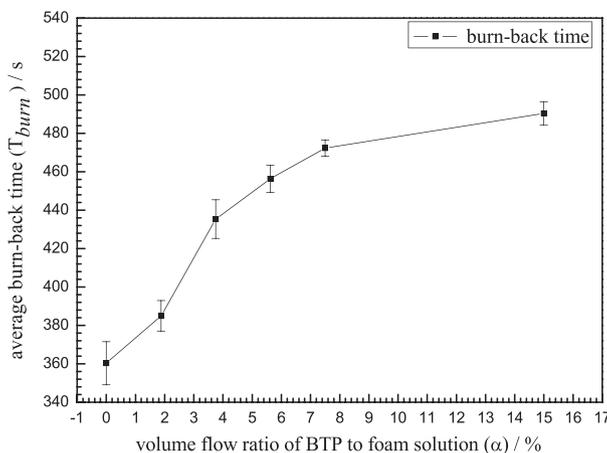
Figure 6. Effects of different α on burn-back time (β = 9).
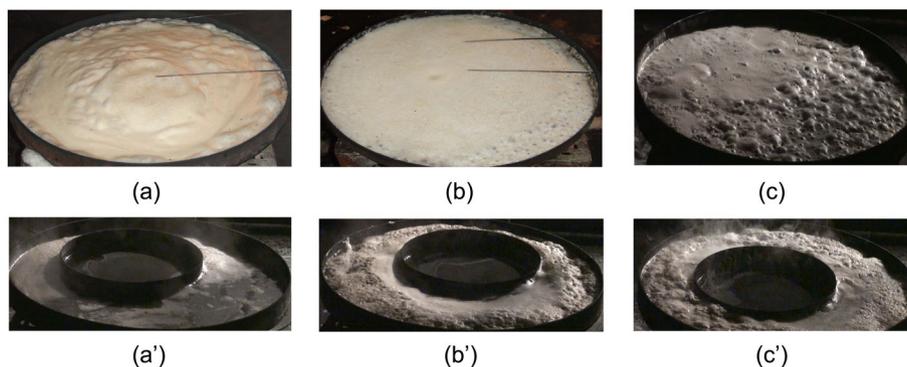
Figure 7. Images of the foam with different α before and after burn-back test: (a) α = 0 before burn-back test; (a′) α = 0 after burn-back test; (b) α = 3.75% before burn-back test; (b′) α = 3.75% after burn-back test; (c) α = 15.0% before burn-back test; (c′) α = 15.0% after burn-back test.

in Figure 7(b′) and (c′); however, there was little foam layer left in the fuel pan for the test without BTP (Figure 7(a′)).

Here, it was considered that the BTP additive played an important role for the extended burn-back time. In the burn-back tests, heat release from the starter pan fire eroded the foam and ignited fuel vapors which penetrated the foam layer, resulting in the fire outside the starter pan and its further spreading across the main burn pan. For the foam layer with BTP additive, when heated by thermal radiation of the starter pan fire, BTP with lower boiling point were easily evaporated from the foam and transformed into gas. The BTP gas would dilute the mixture of gasoline vapor and air, which acted as an 'inert' agent and extended the burn-back time. On the other hand, it was possibly that the foaming of FP foam solution resumed as the evaporation of BTP, as observed that the foam layer became thicker after burn-back tests. The resumed foaming ability after BTP evaporation also helped to resist the eroding of the heat radiation from the starter pan fire and thus contributed to a longer burn-back time. Therefore, for the tests with α varying from 0 to 15.0%, the increased FP foam and BTP agents improved the burn back resistance, resulting in continuously increased burn-back time. For the foam without BTP additive, it was just the foam layer itself that hampered the penetration of gasoline vapor and reaching its lowest combustion limit to re-ignite. Thus, a much shorter burn-back time was shown.

4.3. Fire suppression process

To investigate the fire suppression process in detail, typical variations of flame temperatures, flame shapes and comparisons of the temperature gradient of TC-2 with distance to pan surface of 20 cm in the tests with α = 0, α = 3.75% and α = 15.0% were illustrated in Figures 8–14.

In test with β = 9 and α = 0, the fire cannot be quickly restrained by compressed-air FP foam. It took a relatively long time of foam injection to noticeably reduce the flame temperature as shown in Figure 8. The corresponding flame shape evolution was illustrated in Figure 9. It was shown that most area of the pan was covered by the foam layer after 20 s of injection, but the small fire near the pan edge still persisted, as seen in Figure 9 (d). A further foam application of 8 s was consumed for extinguishing the small fire near the pan edge, implying the limited spreading performance of the foam.

Different to that of FP foam, FP foam with the BTP additive (β = 9 and α = 3.75%) could fast extinguish gasoline fire in a short time of 16 s. The fire extinguishing time was reduced by 43% in comparison to that of test with β = 9 and α = 0. As seen in Figure 10, with the agent discharged into the flame zone, the temperatures of thermocouples declined quickly. The flame was controlled within 10 s after the suppressant injection as observed in Figure 11 (d).

As to the test with β = 9 and α = 15.0%, the temperature of thermocouples decreased slowly as shown in Figure 12. Combined with the suppressing process recorded in Figure 13, the flame was controlled after 20 s of injection, but it still took over most area of the fuel pan (Figure 13(d)). The fire extinguishing time was 50 s, even longer than that of test with β = 9 and α = 0.
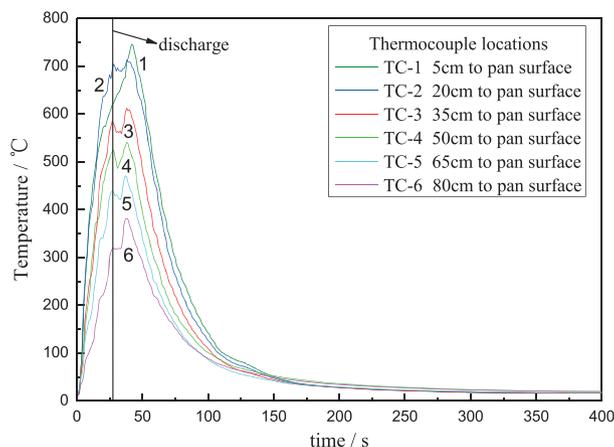
Figure 8. Variations of the flame temperature in test with β = 9, α = 0.
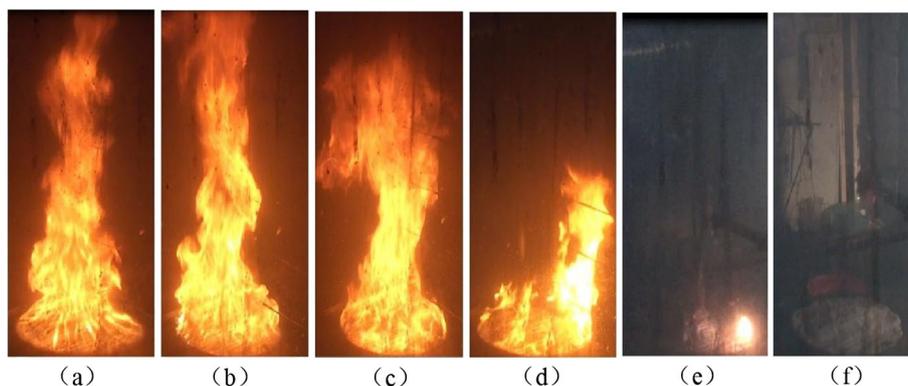
Figure 9. Variations of the flame shapes in the test with β = 9, α = 0: (a) 30 s after ignition; (b) the instant of injection; (c) 5 s after injection; (d) 20 s after injection; (e) 27 s after injection; (f) 28 s after injection.
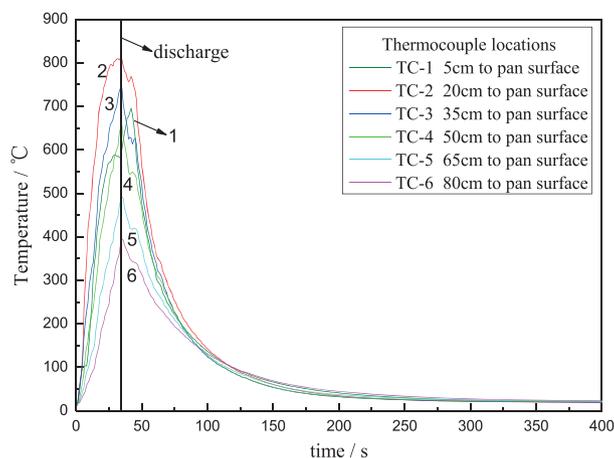
Figure 10. Variations of the flame temperature in test with β = 9, α = 3.75%.

For easy comparison, the temperature curves of TC-2 with the distance of 20 cm to fuel surface in tests with α = 0, α = 3.75 and α = 15.0% was selected and shown simultaneously in Figure 14. The temperature gradient provided clearer information at the initial stage right after applying the fire suppression agents. When dT/dt < 0, the fire was inhabited. If dT/dt decreased, the fire was more
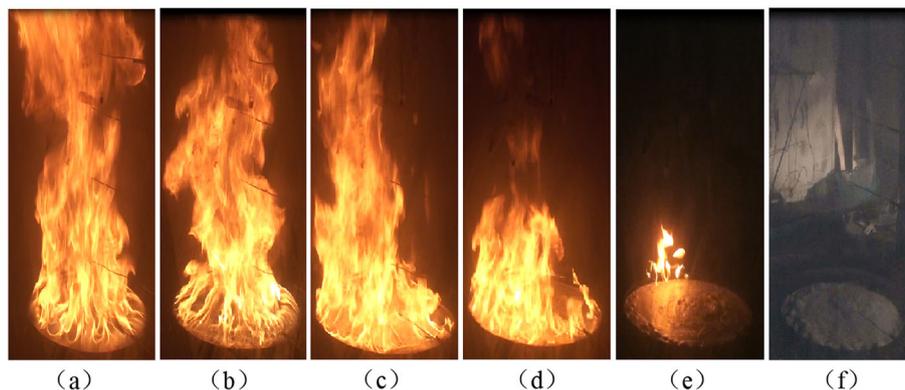
Figure 11. Variations of the flame shapes in test with β = 9, α = 3.75%: (a) 30 s after ignition; (b) the instant of injection; (c) 5 s after injection; (d) 10 s after injection; (e) 15 s after injection; (f) 16 s after injection.
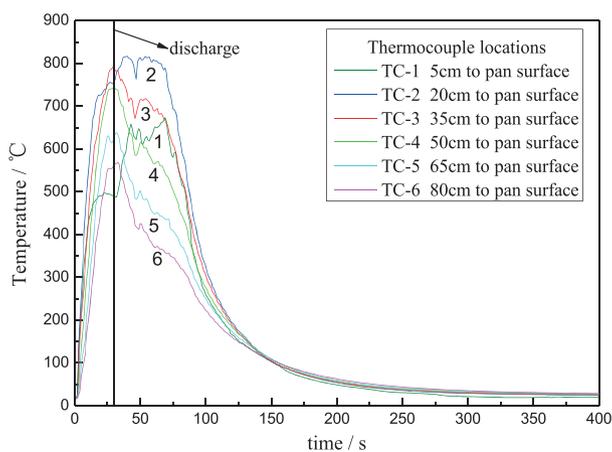
Figure 12. Variations of the flame temperature in test with β = 9, α = 15.0%.
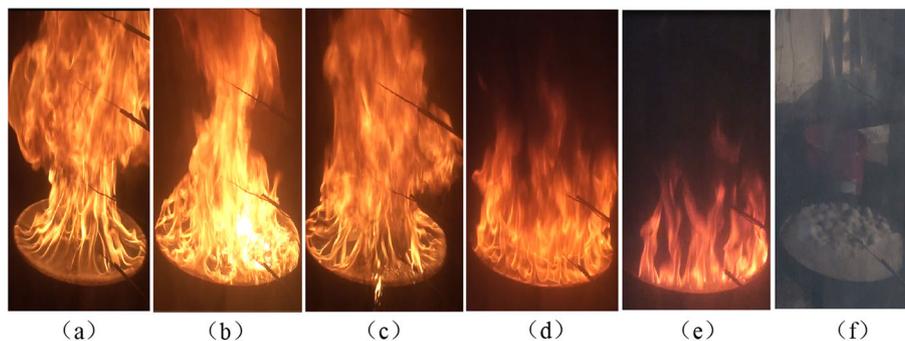
Figure 13. Variations of the flame shapes in test with β = 9, α = 15.0%: (a) 30 s after ignition; (b) the instant of injection; (c) 5 s after injection; (d) 20 s after injection; (e) 50 s after injection; (f) 56 s after injection.

significantly suppressed; when dT/dt > 0, the fire flared up. If dT/dt increased, the fire was more enhanced. At the nadir point, the fire was extinguished. Thus, the time interval from agent discharge to the nadir point was the extinguishing time. The slope of dT/dt vs. time curve in the suppressing process reflected the extinguishing speed. In Figure 14, dT/dt of the test with α = 3.75% showed the greatest slop and minimum time interval to reach the nadir point, indicating its fastest fire suppressing rate and shortest fire extinguishing time. While dT/dt of the test with α = 15.0% gave the minimum slop and maximum time interval, demonstrating its slowest fire suppressing rate and
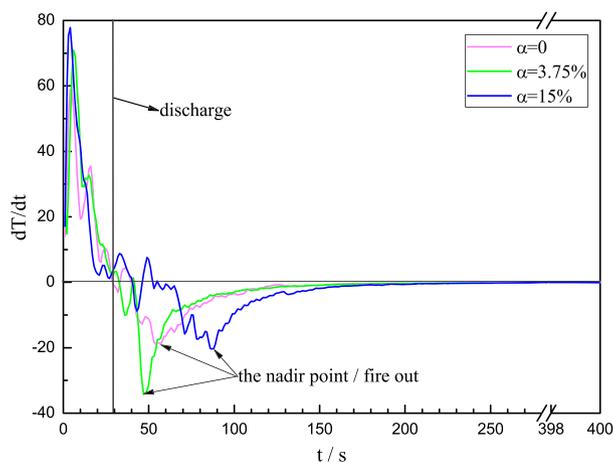
Figure 14. Comparisons of the temperature gradient of TC-2 with the distance of 20 cm to pan surface in tests with $\alpha = 0\%$, $\alpha = 3.75\%$ and $\alpha = 15.0\%$.

longest fire extinguishing time. These results from Figure 14 were in agreement with the video observations, validating the information from the curve of dT/dt vs. time.

Similar to the parameters of T_{ext}, m_{fs}, T_{burn} and $T_{25\%}$, here, the temperature curves of the parallel tests were similar with converged results shown. Figures 8, 10 and 12 were from the tests with the extinguishing time most close to related average value.

5. DISCUSSION ON THE EXTINGUISHING MECHANISM OF FP FOAM WITH BTP

FP foam is believed to extinguish fires mainly through physical effects including oxygen starvation, attenuation of thermal radiation, reduction of fuel evaporation by forming a blanket on the fuel surface and cooling the fuel surface by evaporation of water draining out of foam [11, 12]. The physical characteristics of FP foam of spreading and covering performance play the key role in determining its fire extinguishing efficiency. Different from FP foam, BTP suppress fires through both physical and chemical effects, in which the chemical effect is dominant. Chemically, BTP would decompose in the flame and produce free radicals of CF_3 and Br, which would remove the active hydrogen, hydroxyl and oxygen radicals (H, OH and O) in the reaction zone. Especially the presence of Br atom guarantees the high ability of BTP in scavenging the radicals in combustion. When BTP was presented in FP foam, the chemical extinguishing effect of BTP was added to the FP foam. BTP decomposed in the combustion region to produce highly reactive species to terminate the chain reactions. Thus, the fire extinguishing performance of FP foam got improved with the increase of BTP content.

However, the addition of BTP affected the initial physical properties of compressed-air FP foam as the fact that BTP were insoluble in the foam solution, even though they were intensively mixed in the coaxial mixing chamber. As shown by the images of Figure 15, the bubbles gradually became sparse with the content of BTP increasing. At $\alpha = 15.0\%$, the bubbles even could not cover all over the pan surface. Moreover, it was found that $T_{25\%}$ decreased with the increase of α, which was shorter than that of the blank test (Figure 16). The addition of BTP damaged the stability of foam, leading to the solution more easily to drain out of foam, but meanwhile, improving the fluidity of foam on the gasoline surface in a certain extent [13].

Consequently, there was a competition between the favorable and unfavorable factors, which was determined by the additive amounts of BTP. On one hand, the addition of BTP enhanced the chemical suppressing effectiveness and slightly improved the fluidity of foam. On the other hand, its addition damaged the initial stability and covering performance of bubbles, reducing the physical extinguishing performance of FP foam. When the favorable factors were dominant, an improved fire
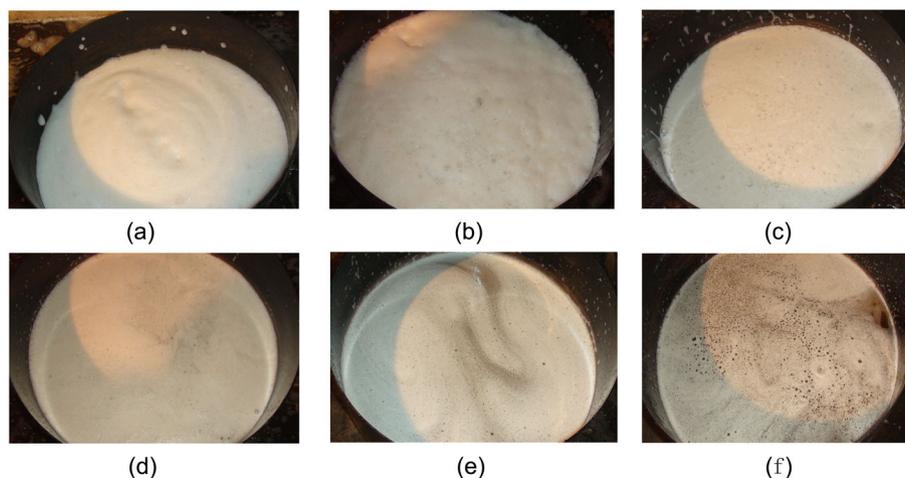
Figure 15. The initial form of the bubbles with different α: (a) α = 0; (b) α = 1.875%; (c) α = 3.75%; (d) α = 5.625%; (e) α = 7.50%; (f) α = 15.0%.
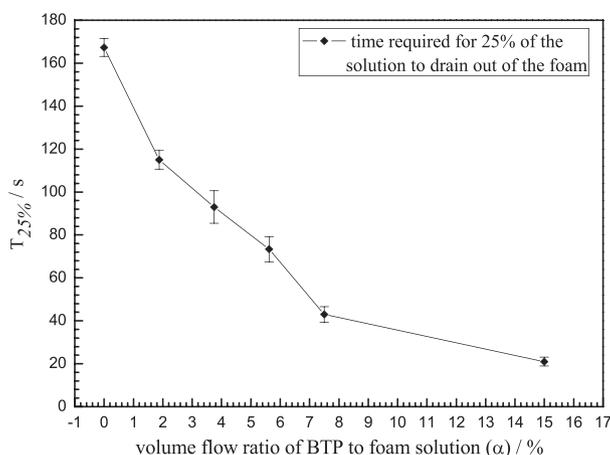
Figure 16. Effects of different α on $T_{25\%}$ (β = 9).

suppression effectiveness was exhibited. Contrarily, the extinguishing performance became weakened. The critical point emerged at α = 3.75%.

6. CONCLUSIONS

To improve the fire suppression performance of fluoroprotein foam, an efficient and degradable suppressant of bromofluoropropene (BTP) was added into the compressed-air fluoroprotein foam. Laboratory scale experiments were conducted to examine the performance of the conjunction in suppressing gasoline pool fire. The results revealed:

- The volume flow ratio of air to fluoroprotein foam solution of 9 was the optimized ratio for compressed-air fluoroprotein foam, at which the best fire extinguishing efficiency was exhibited.
- As the volume flow ratio of BTP to foam solution was 3.75%, the conjunction achieved a superior fire extinguishing performance with the fire extinguishing time reduced by 43% in comparison to that without any BTP added.
- The burn-back time of FP foam increased with the increase of BTP content, which could be as-cribed to the 'inert' effect of BTP and the resumed foaming of FP foam after BTP evaporation.

- There was a competition between the favorable and unfavorable factors for the performance improvement with BTP additive. At the content of BTP of 3.75%, the enhanced chemical effect became the significant overbalancing factor, and a minimum fire extinguishing time was achieved.

In this paper, only limited conditions were selected for examining the extinguishing performance of FP foam with BTP additive. However, the fire suppression performance is scenario dependent. Geometry and ventilation, fire size and combustible, flow rate and pressure for the fire suppressant are all important factors affecting the extinguishing performance, which will be studied in the latter work to further validate the present conclusions. It is expected that the present results obtained from the laboratory tests could provide quantitative data and guidance for the practical conjunction applications of clean gas and foam agent.

NOMENCLATURE

ER	expansion ratio, which is defined as the ratio of the volume of foam to the volume of foam solution, dimensionless
BTP	2-bromo-3,3,3-trifluoropropene
FP	fluoroprotein foam
m_{fs}	mass of the foam solution consumed for fire extinguishment, g
P	pressure, MPa
Q	volume flow, $L\,h^{-1}$
T_{ext}	the extinguishing time, s
$T_{25\%}$	the time required for 25% of solution to drain out of foam, s
T_{burn}	the time interval from ignition of burn-back pot until the fire re-involved 25% of the main burning pan, s
α	the volume flow ratio of BTP to foam solution
β	the volume flow ratio of compressed air to foam solution

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