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Extinguishing efficiency of an ammonium carbonate-based water mist in an aqueous ammonia medium for class B fires

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ABSTRACT

This study investigates the fire suppression efficiency and multi-action mechanisms of a novel binary aqueous fire-extinguishing agent (AFEA) consisting of 50 wt% ammonium carbonate $(NH_4)_2CO_3$ in an aqueous ammonia medium. Open-air fire tests were conducted using a specialized automated spray installation against standard Class 8B petrol and diesel fuel pool fires. The experimental results demonstrated that the $(NH_4)_2CO_3$-based AFEA spray achieved a rapid knockdown of volatile A-92 petrol fires within 2.0 s, requiring a minimal consumed volume of 280 ± 6 mL and outperforming the reference 40 wt% K_2CO_3 solution four-fold. Furthermore, the proposed formulation was the only agent capable of successfully suppressing high-thermal-inertia Euro-5 diesel fuel fires within a mean time of 29.7 ± 0.6 s under open-space constraints, where conventional salt solutions and tap water failed. The performance is governed by a synergistic mechanism: the endothermic pyrolytic breakdown of $(NH_4)_2CO_3$ inside the flame generates a complex mixture of gases, including carbon dioxide (CO_2), water vapor (H_2O) that dilute oxygen, while ammonia (NH_3) undergoes oxidative reactions in the high-temperature zone, further depleting local oxygen. A preliminary engineering upscaling analysis for a full-scale RVS-400 vertical steel storage tank (57 m^2 pool area) indicated that transitioning to this novel binary system could conceptually yield a 75.7% reduction in the required agent inventory (from 391.7 L to 95.4 L). These findings provide a useful technical foundation for the potential development of compact, rapid-response automated fire protection systems for industrial petroleum depots.

1. Introduction

Class B fires, involving flammable and combustible liquids such as automotive fuels and petroleum products, present severe hazards to industrial facilities, transportation networks, and chemical storage depots, with the threat dramatically escalated by systematic attacks on critical infrastructure during the Russian Federation's unprovoked aggression against Ukraine. The rapid flame propagation, intense feedback radiation, and high heat release rates characteristic of hydrocarbon pool fires make them exceptionally difficult to suppress using conventional fire extinguishing agents. For decades, aqueous film-forming foams (AFFFs) containing per- and polyfluoroalkyl substances (PFAS) served as the primary benchmark for Class B fire suppression due to their excellent film-forming and vapor-blanketing properties. However, escalating global regulations and strict bans driven by the environmental persistence, bioaccumulation, and toxicity of PFAS have forced the fire safety industry to rapidly transition toward fluorine-free and environmentally sustainable alternatives [1].

Water mist and specialized aerosol fire suppression technologies have emerged as highly promising, eco-friendly candidates to replace fluorinated foams [2,3]. Fine water mist suppresses fires primarily through physical mechanisms, including high-capacity thermal cooling via droplet evaporation, radiant heat attenuation, and localized oxygen dilution through water vapor expansion [3,4]. Despite these advantages, pure water mist exhibits inherent limitations when combating high-thermal-inertia or highly volatile Class B fires. Due to the high surface tension of water and the lack of chemical radical scavenging action, pure water mist often requires prolonged application times and massive volumetric flow rates, which can lead to structural water damage and, in worst-case scenarios, cause dangerous fuel splashing or

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boil-over phenomena [2,5].

To overcome these physical limitations, recent research has focused on the chemical modification of water mist by dissolving inorganic salts to introduce chemical inhibition pathways [2,5,6]. Traditionally, alkali metal salts – such as potassium carbonates (K_2CO_3), phosphates, and haloids – have been widely utilized [4,6]. When introduced into the high-temperature combustion zone, these salts undergo thermal dissociation, releasing metal cations (e.g., K^+) that act as potent homogeneous and heterogeneous catalysts for radical scavenging [6,7]. They intercept and terminate the highly reactive chain carriers ($H^\bullet$ and $^\bullet OH$) responsible for flame propagation.

Beyond standard alkali additives, a highly promising direction involves the utilization of transition metal salts (e.g., iron, copper, or manganese compounds) and advanced complex salts [8–10]. The flame suppression ability of transition metal elements, particularly within organometallic systems such as metallocenes, highlights their unique capability to disrupt combustion kinetics [8,11]. Transition metal ions exhibit multiple oxidation states, which enables them to participate in highly efficient cyclic catalytic radical recombination reactions directly in the gas phase [8,9]. Furthermore, complex coordination compounds, which contain multiple functional ligands, can undergo multi-stage thermal decomposition [12–14]. This unique behavior ensures a prolonged, stepwise release of active inhibiting fragments across varying temperature zones within the flame matrix. Consequently, transition metal and complex salt formulations often exhibit significantly lower critical extinguishing concentrations compared to traditional potassium-based alternatives [9,10]. Nevertheless, these advanced formulations possess distinct engineering disadvantages, including poor long-term hydrolytic stability, a tendency to accelerate the corrosion of extinguishing equipment, and heightened environmental and chemical toxicity risks [2,10].

Ammonium-based compounds, particularly ammonium carbonate $(NH_4)_2CO_3$, present an intriguing but under-investigated alternative for advanced fire suppression. Historically, various ammonium salts have been recognized for their fire-retardant properties and utilized in dry chemical powders or as aqueous additives [15,16]. Unlike fixed alkali metal salts, ammonium carbonate undergoes rapid, highly endothermic pyrolytic decomposition at relatively low temperatures (>58 °C), generating a complex mixture of gases, including carbon dioxide (CO_2), water vapor (H_2O), and ammonia (NH_3). While CO_2 and H_2O act as an inert gas providing reliable physical smothering and mass-transfer obstruction of volatile fuel vapors, the released ammonia (NH_3) plays a dual role. Although ammonia is a combustible gas capable of forming flammable mixtures with air under specific conditions, it possesses a high autoignition temperature (approximately 650 °C) and a relatively narrow flammability range, making it exceptionally difficult to ignite compared to hydrocarbon fuels. In the high-temperature combustion zone, NH_3 acts as an oxidisable gas that undergoes rapid oxidation, actively consuming local oxygen in the flame front. Concurrently, the thermal degradation of nitrogenous species yields active intermediate fractions capable of gas-phase radical scavenging, offering a comprehensive multi-action (physical and chemical) suppression matrix.

To date, the use of pure $(NH_4)_2CO_3$ as a liquid extinguishing agent remains undocumented in fire safety literature, primarily due to its volatile nature and rapid premature hydrolysis in standard aqueous solutions. Instead, prior state-of-the-art studies have been restricted to utilizing the more stable ammonium hydrogencarbonate (NH_4HCO_3) either as an additive in water-based suppressants [15] or within specialized dry chemical powders [16]. Consequently, the specific fire extinguishing kinetics, volumetric application limits, and overall efficiency of true $(NH_4)_2CO_3$ formulations deployed via water mist within challenging aqueous ammonia mediums for Class B fires remain insufficiently explored in literature.

This paper investigates the technological features of preparing a concentrated ammonium carbonate solution within an aqueous ammonia medium to stabilize the agent and prevent premature hydrolysis. Furthermore, this work focuses on analyzing the physicochemical properties and the extinguishing efficiency of the developed composition applied as a water mist, establishing the main parameters for effectively suppressing class B fires.

2. Experimental

2.1. Materials

To prepare the ammonium carbonate-based AFEA and evaluate its fire suppression performance, the following materials were utilized.

- *Extinguishing agent base* – Ammonium carbonate $(NH_4)_2CO_3$ [17] obtained as colorless crystals ($M = 96.09$ g mol^{-1}, $\rho = 1.6$ g cm^{-3}, $T_{decomposition} = 58$ °C, water solubility of 101.1 g/100 g H_2O at 15 °C, NFPA 704 rating at STP: $H = 1$, $F = 0$, $I = 1$).
- *Aqueous medium* – A 25 wt% aqueous ammonia solution (NH_4OH) used as an additive for the AFEA, prepared as a colorless liquid with a pungent, acrid odor ($M = 35.05$ g mol^{-1}, $\rho = 0.91$ g cm^{-3}, pH ≈ 12.5, p$K_b = 4.76$).
- *Class B fire sources* – Commercial 92 RON unleaded petrol (locally designated as A-92 Euro-5 automotive petrol [18], conforming to Euro-5 standard) (M = 92–110 g mol^{-1}, ρ = 0.740–0.745 g cm^{-3}, $T_{flash} \approx -40$ °C, $T_{self\text{-}ignition}$ = 255–370 °C, T_{flame} = 800–1100 °C, $r_{regression}$ = 18–20 cm h^{-1}); Euro-5 diesel fuel [19] (M = 180–230 g mol^{-1}, ρ = 0.820–845 g cm^{-3}, T_{flash} = 55 °C, $T_{self\text{-}ignition}$ = 210–250 °C, T_{flame} = 1000–1100 °C, $r_{regression}$ = 10–12 cm h^{-1}).

All reagents were purchased from commercial sources and used as received without further purification.

2.2. Preparation and characterization of the ammonium carbonate-based AFEA

The $(NH_4)_2CO_3$-based AFEA was prepared by dissolving ammonium carbonate in an aqueous ammonia solution. For this purpose, a 10 wt% aqueous ammonia solution was pre-prepared by mixing 850 mL of a 25 wt% aqueous ammonia solution with 1150 mL of water. Subsequently, crystalline $(NH_4)_2CO_3$ (1000 g, 10.4 mol) was added to 1045 mL of the 10 wt% aqueous ammonia solution. The resulting mixture was then tightly sealed in a vessel and heated to ≈ 30 °C until the crystalline salt was completely dissolved. Heating was performed under constant magnetic stirring in a hermetically sealed pressure-resistant vessel to prevent the volatilization of gaseous ammonia and shift the chemical equilibrium toward stabilization of the complex ion matrix.

The prepared 50 wt% $(NH_4)_2CO_3$ solution in aqueous ammonia was characterized using a series of physicochemical methods. The kinematic viscosity (ν) was measured via capillary viscometry using a VLA–1 viscometer with an inner capillary diameter of 0.99 mm. The surface tension (σ) was determined by Traube's stalagmometric method using an ST–1 stalagmometer. The density (ρ) was ascertained by the pycnometer (bottle) method, while the pH was measured using a 150MI pH-meter. The freezing point of the $(NH_4)_2CO_3$-based solution was calculated according to Raoult's law. The physicochemical properties of the 50 wt% $(NH_4)_2CO_3$ solution in aqueous ammonia are summarized in Table 1.

Notably, the addition of the aqueous ammonia medium significantly reduced the surface tension of the AFEA (59.5 mN m^{-1}) compared to pure water (≈72.8 mN m^{-1}) and the reference K_2CO_3 solution, which fundamentally enhances the liquid atomization during spraying. The experimental protocol for evaluating the long-term storage stability of the prepared formulation, along with the corresponding quantitative data over time, is detailed comprehensively in Section 3.1.1.

Table 1
The physicochemical properties of the $(NH_4)_2CO_3$-based AFEA.

AFEA	ρ ($g \cdot cm^{-3}$)	ν ($mm^2 \cdot s^{-1}$)	σ ($mN \cdot m^{-1}$)	pH	$T_{freezing}$ (°C)
50 wt% $(NH_4)_2CO_3$ (aqueous-ammonia medium)	1.21	1.31	59.5	12.0	−58
40 wt% K_2CO_3 (water medium) [20]	1.41	3.08	91.4	13.5	−37.5

2.3. Experimental setup and fire suppression procedures

Fire suppression experiments were conducted in accordance with the CEN (2007) standard [21]. Instead of a conventional portable fire extinguisher, a modified delivery system integrated into a specialized fire suppression installation was utilized (Fig. 1). The experimental apparatus comprised an aqueous fire-extinguishing agent (AFEA) storage container, a multi-orifice spray nozzle for mist discharge, and a composite compressed air cylinder equipped with a pressure regulator to maintain a steady system operating pressure (P_{jet}) of 0.6 MPa (corresponding to 6.12 kg cm^{-2}). The operating pressure was monitored using pressure gauges with a maximum scale limit of 1.6 MPa. Upon opening the cylinder shut-off valve, compressed air at a constant pressure entered the AFEA container, forcing the solution through the spray nozzle directly into the combustion zone.

The tests were performed at an open-air fire testing facility within the Fire Safety Laboratory of the Lviv State University of Life Safety, under an ambient temperature of 15 °C and a wind speed of 2 m s^{-1}. The test site floor consisted of concrete slabs, with a Class B circular pool fire test pan positioned at the center. The dimensions and fuel capacity of the test pan complied with the standard 8B model fire test specifications: a liquid volume of 36 L, an internal upper diameter of 0.565 m, a wall height of 0.150 m, a wall thickness of 2 mm, and a total surface area of 0.251 m^2.

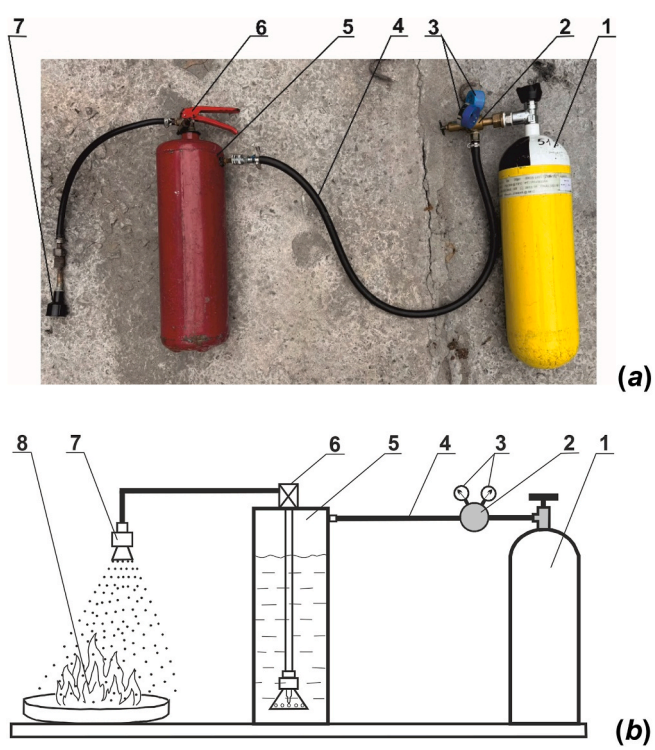

Fig. 1. General view (*a*) and schematic diagram (*b*) of the fire suppression installation: 1 – compressed air cylinder; 2 – pressure regulator; 3 – pressure gauges; 4 – connecting hose; 5 – AFEA storage container; 6 – triggering mechanism/fast-acting ball valve; 7 – multi-orifice spray nozzle; 8 – test pan with flammable liquid (Class B fire source).

To eliminate operator-induced variability and ensure maximum repeatability, the discharge system was equipped with a specialized multi-orifice water mist nozzle comprising 6 injection holes with an equivalent design orifice diameter of 1.0 mm. The nozzle was hand-held by the operator at a nominal distance of 1.5 m and an inclination angle of 45° relative to the fuel pool center. Spray discharge was initiated via a rapid-acting ball valve to avoid transient pressure lag.

This operational configuration generated a low-pressure Class I water mist according to the NFPA 750 standard [22]. Based on semi-empirical atomization correlations for hydraulic pressure nozzles – accounting for the solution's measured high density ($\rho = 1.21$ g·mL^{-1}) and reduced surface tension ($\sigma = 59.5$ mN·m^{-1}) – the volume median diameter ($D_{v0.5}$) was calculated to be approximately 100–120 μm, with a corresponding $D_{v0.9}$ of 240–312 μm. To evaluate the monodispersity (uniformity) of the generated mist, the Relative Span Factor (*RSF*) was calculated. The resulting *RSF* values, ranging from 1.6 to 2.1, indicate a highly uniform spray pattern with a minimal fraction of large satellite droplets. This strictly confirms that the droplet spectrum falls within the Class I water mist specification.

To determine the volumetric flow rates (Q_{AFEA}, L·s^{-1}), a graduated volumetric cylinder (maximum permissible error of ±0.5 cm^3) and a stopwatch (measurement uncertainty of ±0.2 s) were utilized. The combined standard uncertainty of the flow rate was calculated using the law of propagation of uncertainty. The resulting volumetric flow rates for the $(NH_4)_2CO_3$-based AFEA, K_2CO_3-based AFEA, and tap water were determined to be 0.140 ± 0.003 L s^{-1} (8.40 L min^{-1}), 0.115 ± 0.002 L s^{-1} (6.90 L min^{-1}), and 0.170 ± 0.003 L s^{-1} (10.20 L min^{-1}), respectively. Standard firefighter personal protective equipment was worn during all procedures to ensure occupational safety.

Following the established methodology, the steel fire pan was initially filled to 2/3 of its volume with water, over which a flammable liquid layer (1/3 of the volume) was added. Commercial A-92 Euro-5 automotive petrol [18] and Euro-5 diesel fuel [19] served as the combustible substances. Upon ignition, a free-burning pre-burn period was sustained for approximately 60 s until the fuel reached a steady burning state, at which point the water mist was discharged into the combustion zone.

Open-space fire suppression tests were performed using three configurations: the novel $(NH_4)_2CO_3$-based AFEA (50 wt% ammonium carbonate in an aqueous ammonia medium), a reference K_2CO_3-based AFEA (40 wt% potassium carbonate in water), and standard tap water as a blank control. The maximum water mist discharge duration was strictly limited to a cut-off time of 30.0 s. If the flame was not fully extinguished within this period, the test was terminated and recorded as a failure.

To ensure statistical reliability, all experiments were performed in triplicate ($n = 3$). The fire suppression times ($\Delta\tau$, s) and the volumes of the agent consumed during suppression (V, mL) were recorded, subjected to statistical analysis, and expressed as mean ± standard deviation (SD). For the trials designated as a failure, the discharge time and consumed volume reflect the parameters at the moment of complete depletion of the agent charge or upon reaching the maximum operational cut-off limit. The experimental results regarding the fire extinguishing efficiency are summarized in Table 2.

3. Results and discussion

3.1. Features of the $(NH_4)_2CO_3$-Based AFEA preparation technology

Ammonium carbonate, selected as the active component for the aqueous fire extinguishing agent, consists of colorless to near-white crystalline solids that exhibit instability and decompose at room

Table 2
Fire extinguishing efficiency parameters of the tested AFEAs and tap water against Class B model fires (8B) ($n = 3$).

Combustible Substance (Fuel Type)	Extinguishing Agent	Discharge Time ($\Delta\tau$, s)	Consumed Volume (V, mL)	Extinguishing Outcome
A-92 Euro-5 Petrol	$(NH_4)_2CO_3$-based AFEA	2.07 ± 0.12	280 ± 6	Successful suppression
	K_2CO_3-based AFEA	10.0 ± 0.5	1150 ± 22	Successful suppression
	Tap water	29.0 ± 0.8	4930 ± 90	Failure
Euro-5 Diesel Fuel	$(NH_4)_2CO_3$-based AFEA	29.7 ± 0.6	4200 ± 80	Successful suppression
	K_2CO_3-based AFEA	30.0 ± 0.9	3450 ± 65	Failure
	Tap water	29.0 ± 0.8	4930 ± 90	Failure

Note: For the trials designated as a failure, the recorded discharge time (≈29.0 s) reflects the exact moment of the complete depletion of the fixed liquid agent charge from the installation's storage vessel, rather than a manual cut-off.

temperature during prolonged storage. When heated to 58 °C, the solid salt undergoes complete thermal decomposition into gaseous ammonia, carbon dioxide, and water vapor according to the following reaction:

$$(NH_4)_2CO_3 \rightarrow 2NH_3\uparrow + CO_2\uparrow + H_2O.$$

In the dissolved state, $(NH_4)_2CO_3$ exhibits higher thermal stability, with substantial decomposition occurring only at temperatures exceeding 70 °C.

The salt is highly soluble in water, featuring a solubility coefficient (k_s) of 100.1 g per 100 g of H_2O at 15 °C. However, since ammonium carbonate is formed by a weak base (ammonium hydroxide) and a weak acid (carbonate acid), its dissolution in water triggers simultaneous cationic and anionic hydrolysis processes:

$$(NH_4)_2CO_3 + H_2O \leftrightarrows NH_4OH + NH_4HCO_3.$$

Although both hydrolysis products act as weak electrolytes, their respective dissociation constants differ significantly. Cationic hydrolysis of the ammonium ion (NH_4^+) leads to acidification of the medium. The dissociation constant (K_b) of aqueous ammonia ($NH_3{\cdot}H_2O$) is $1.76{\cdot}10^{-5}$ ($pK_b = 4.75$). Conversely, anionic hydrolysis of the carbonate ion (CO_3^{2-}) promotes an alkaline environment. The second-stage dissociation constant of carbonic acid (K_{a2} (H_2CO_3)) is $4.69{\cdot}10^{-11}$ ($pK_{a2} = 10.33$). Because carbonate acts as a substantially weaker conjugate acid (indicated by its lower dissociation constant), its proton affinity and propensity for hydrolysis are much stronger. Consequently, the alkaline effect of the carbonate hydrolysis dominates over the acidic effect of the ammonium hydrolysis.

To establish a mathematically justified baseline for the medium behavior, the pH of a concentrated aqueous ammonium carbonate solution can be determined. For a salt derived from a weak base and a weak acid, the first-approximation pH value is independent of the salt concentration (provided it is sufficiently high) and is expressed as:

$$pH = 7 + \frac{1}{2}pK_{a2} - \frac{1}{2}pK_b$$

Substituting the corresponding dissociation parameters at 25 °C into the equation yields:

$$pH = 7 + \frac{1}{2}(10.33) - \frac{1}{2}(4.75) = 7 + 5.165 - 2.375 = 9.79$$

Thus, the theoretical pH value is 9.79. In practice, however, concentrated solutions typically exhibit lower actual values, ranging between 9.0 and 9.5. This discrepancy stems from several physicochemical factors inherent to highly concentrated systems.

- *Ionic strength of the solution:* In concentrated environments, ionic activity coefficients deviate significantly from unity, altering the effective concentration of species.
- *Stepwise salt hydrolysis:* The secondary reaction stage generates a certain equilibrium concentration of hydrogen carbonate ions (HCO_3^-), which possess a lower inherent alkalinity.
- *Ammonia volatility:* Continuous evaporation of a fraction of gaseous ammonia shifts the chemical equilibrium, driving a downward drift in pH.

The development of a robust preparation technology for $(NH_4)_2CO_3$-based AFEA must account for these critical operational constraints.

- *Chemical instability:* Ammonium carbonate remains highly volatile. Upon prolonged contact with ambient air, it degrades via ammonia (NH_3) and carbon dioxide (CO_2) desorption, transforming into ammonium hydrogen carbonate (NH_4HCO_3).
- *Medium pH dynamics:* As ammonia volatilizes, the pH drops progressively toward the 7.8–8.2 range, which is characteristic of pure hydrogen carbonate solutions.
- *Concentration dependence:* Maximizing the concentration of pure $(NH_4)_2CO_3$ is essential to maintain the working solution pH as close to the target threshold of 9.4 as possible.

Consequently, if pure water is used as the sole solvent to prepare the $(NH_4)_2CO_3$-based agent, the active salt concentration drops rapidly due to unchecked hydrolysis. Instead of a highly concentrated $(NH_4)_2CO_3$ solution, the resulting AFEA will degrade into a low-concentration aqueous solution of ammonium hydrogen carbonate (NH_4HCO_3). This occurs because a substantial portion of the newly formed NH_4HCO_3 precipitates due to its poor aqueous solubility. Crucially, the solubility of ammonium hydrogen carbonate at 20 °C is only 21.6 g per 100 g of water, which is nearly five times lower than that of ammonium carbonate.

To suppress these unfavorable hydrolysis pathways and prevent agent degradation, the reaction equilibrium must be shifted to the left by deliberately elevating the initial pH of the system. This technological challenge is effectively resolved by substituting pure water with a 10 wt % aqueous ammonia solution, which exhibits an intrinsic pH of 12.0, as the primary solvent matrix. The highly alkaline ammonia environment stabilizes the maximum concentration of dissolved $(NH_4)_2CO_3$, thereby preserving its peak fire-extinguishing efficiency for Class B fires. This formulation approach completely suppresses premature hydrolysis, prevents compound precipitation within storage systems, and ensures the rapid, intensive liberation of volatile chemical chain-inhibitors directly inside the combustion zone.

3.1.1. Experimental validation of operational storage stability

To validate the theoretical baseline established in Section 3.1 and evaluate the long-term shelf-life readiness of the developed formulation, empirical storage stability monitoring was performed. Samples of the optimized 50 wt% $(NH_4)_2CO_3$ solution prepared within the 10 wt% aqueous ammonia solvent matrix were stored under ambient laboratory conditions (20 ± 2 °C) inside tightly sealed high-density polyethylene (HDPE) vessels. As detailed in the technological constraints, tight or hermetic sealing is a mandatory operational requirement to prevent the continuous open-air volatilization and desorption of the ammonia stabilizer.

Upon sealing the containment vessels, a localized dynamic liquid-vapor equilibrium was rapidly established within the headspace, successfully halting the downward drift in pH and stabilizing the volatile nitrogenous fragments. The experimental samples were kept under continuous monitoring for a duration exceeding 6 months. Periodic physicochemical inspections revealed that the formulation remained completely static and unchanged throughout the entire multi-month testing matrix.

Quantitative tracking via hydrometer measurements confirmed zero net mass or volume loss of the agent, and the active salt concentration remained stable within the margin of error (fluctuations under 0.4%), avoiding any chemical degradation into less soluble fractions. This was further corroborated by visual and microscopic examinations, which confirmed the absolute absence of crystalline precipitation, phase separation, or sedimentation. This long-term stability provides direct empirical proof that the highly alkaline ammonia environment successfully shifts the carbonate-bicarbonate chemical equilibrium backward, completely suppressing the forward hydrolysis reaction and preventing the formation of poorly soluble ammonium hydrogen carbonate (NH_4HCO_3). These findings verify that when maintained in standard sealed configurations common to pressurized water-mist or gas-extinguishing hardware, the proposed AFEA composition retains its full physicochemical integrity and long-term fire suppression readiness.

3.2. Evaluation of fire extinguishing efficiency and physicochemical suppression analysis

3.2.1. Comparative fire suppression performance

The experimental results demonstrate a significant disparity in fire suppression efficiency among the evaluated agents, with the novel $(NH_4)_2CO_3$-based AFEA exhibiting superior performance, particularly against highly volatile Class B hydrocarbons.

- **Petrol Fire Scenarios:** The $(NH_4)_2CO_3$-based AFEA achieved complete extinguishment of the A-92 automotive petrol fire in a mere 2.07 ± 0.12 s, requiring a minimal solution volume of 280 ± 6 mL. In contrast, the reference K_2CO_3-based AFEA required 10.0 s and a substantially higher volume of 1150 ± 22 mL to suppress the flame. This represents a more than four-fold increase in both suppression time and fluid consumption. Standard tap water completely failed to extinguish the petrol fire; even after a continuous 29.0 s discharge and a total volumetric expenditure of 4930 ± 90 mL, the flame remained unsuppressed, confirming the ineffectiveness of pure water mist against rapidly burning, volatile liquid fuels.
- **Diesel Fire Scenarios:** The Euro-5 diesel fuel fire presented a more challenging suppression scenario due to the distinct thermal properties and high-boiling fractions of heavier hydrocarbons. Notably, the $(NH_4)_2CO_3$-based AFEA was the only agent capable of successfully suppressing the diesel fire within the benchmark period, achieving complete extinguishment at almost 30 s with a consumed volume of 4200 ± 80 mL. To evaluate the operational safety margin and reproducibility of this agent against diesel fuel, three identical replicate tests were performed. The fire was successfully extinguished in all trials, with exact suppression times recorded at 30 s, 29 s, and 30 s, yielding a mean suppression time of 29.7 s and an exceptionally low standard deviation (SD = 0.58 s). While this operational window directly borders the established 30 s pass/fail criterion –reflecting the high thermal stability and challenging combustion profile of Euro-5 diesel – the minimal statistical variability indicates that the suppression mechanism operates deterministically. This high repeatability confirms that the active agent consistently achieves a reliable knockdown at the upper boundary of the safety limit, rather than representing an accidental or stochastic success. Conversely, both the K_2CO_3-based AFEA and tap water proved ineffective under these conditions. The application of the K_2CO_3 solution for 30.0 ± 0.9 s (consuming 3450 ± 65 mL) failed to knock down the flame, while tap water application for 29.0 ± 0.8 s (expending 4930 ± 90 mL) showed no suppressive effect.

The profound performance gap established by these empirical metrics provides direct evidence that the suppression mechanism of the $(NH_4)_2CO_3$ matrix extends far beyond basic physical cooling. Mathematically, the extreme reduction in fluid consumption (only 280 ± 6 mL for petrol) and the rapid 2.07 ± 0.12 s extinction time cannot be attributed solely to the sensible heat capacity or latent heat of vaporization of the water carrier. This quantitative efficiency confirms that the active thermal decomposition of stabilized ammonium carbonate introduces highly cooperative chemical and gas-phase pathways, which fundamentally differentiate its behavior from traditional fixed alkali metal salts like K_2CO_3. These combined physical and chemical interactions are structurally visualized and analyzed in the following subsection.

The complete failure of pure tap water mist to suppress both petrol and diesel fires under the tested configuration warrants a detailed physical analysis of the spray-plume interaction, as water mist has historically succeeded under different operational boundaries [3,23]. In our experimental configuration, tap water was discharged at a relatively high volumetric rate (≈10.2 L min^{-1}), expending 4930 ± 90 mL over 29.0 ± 0.8 s). However, due to the medium-pressure localized application, the downward aerodynamic momentum of the water mist droplets was entirely counteracted by the intense upward buoyant convective thermal plume generated by the liquid fuel pool fires. This intense updraft deflected the pure water droplets away from the core flame reaction zone, preventing critical penetration to the fuel surface. Furthermore, because the tests were conducted in an open-space environment without total flooding confinement, oxygen displacement via steam volume expansion was heavily mitigated. This highlights that for high-heat-release Class B fires, pure water mist lacks the requisite physical suppression efficiency unless assisted by high-pressure momentum or, as demonstrated here, by chemical additives like $(NH_4)_2CO_3$ that introduce powerful cooperative mechanisms: physical oxygen dilution by CO_2 and water vapor, local oxygen depletion driven by the rapid oxidation of released combustible NH_3 within the high-temperature zone, and homogeneous gas-phase radical inhibition.

3.2.2. Physicochemical suppression mechanisms and spatial visualization

The exceptional fire suppression efficiency of the novel $(NH_4)_2CO_3$-based advanced fire extinguishing agent is governed by a complex, multi-stage mechanism combining physical cooling, gas-phase dilution, and chemical inhibition within the combustion zone. To eliminate speculative assumptions, these interconnected pathways are directly mapped onto the macro-physical phenomena captured during experimental testing.

- *Thermal Decomposition:* Upon entering the high-temperature flame zone, the mist droplets undergo rapid endothermic dissociation. This flash pyrolysis absorbs a substantial amount of thermal energy directly from the reaction front, which is macroscopically initiated during the first 0.5 s of application.
- *Gas-Phase Dilution:* The thermal breakdown of the solute and solvent yields a mixture of carbon dioxide (CO_2) and water vapor (H_2O) that act as non-combustible gases diluting both the vaporized fuel and oxygen concentrations at the fuel-air interface, alongside volatile ammonia (NH_3). The volumetric expansion of these gases physically displaces the volatile petrol vapors, contributing to the flame front destabilization.
- *Chemical Radical Scavenging:* In the gas phase, these decomposition products are hypothesized to act as efficient chemical inhibitors. According to established combustion kinetic models, nitrogen-containing intermediate fragments are anticipated to terminate the chain reactions by scavenging key radical carriers ($H^{\bullet}$, $^{\bullet}OH$, and $O^{\bullet\bullet}$) responsible for flame propagation. This proposed chemical inhibition pathway, supported by literature on nitrogenous suppressants, offers a significant kinetic advantage over pure water alternatives, providing the requisite chemical kinetics to force complete extinction before the water carrier can evaporate fully.

A step-by-step spatial visualization of the petrol flame suppression process during the injection of an $(NH_4)_2CO_3$-based AFEA misted solution is detailed via sequential video frames (Fig. 2).

Fig. 2. Time-lapse photographic sequence of Class B fire (A-92 Euro-5 automotive petrol) suppression in an open space using misted $(NH_4)_2CO_3$-based AFEA solution, illustrating the evolution from transient flare-up to complete quenching (time interval between frames: 0.5 s).

- *Transient Flare-up (τ = 0.5 s):* Within 0.5 s of mist discharge, a localized increase in flame intensity is observed. This transient phenomenon provides visual evidence of the initial chemical interplay between the gaseous thermal decomposition products of the agent and the highly active flame radicals. This primary phase of the inhibition reaction is temporarily accompanied by a brief release of thermal energy, consistent with the early-stage radical recombination kinetics observed in ammonium-based suppressants.
- *Soot Suppression and Spectral Emission Shift (τ = 1.0 s):* At 1.0 s, the yellow-orange color of the flame becomes slightly lighter and shifts toward a translucent appearance. This visual transition strongly indicates the rapid suppression of soot formation pathways. According to established combustion literature, the chemical action of NH_3 decomposition intermediates disrupts the growth of polycyclic aromatic hydrocarbons (PAHs). This is further coupled with the characteristic emission spectrum of excited intermediate complexes formed within the heavily inhibited reaction zone.
- *Complete Quenching (τ = 1.5 – 2.0 s):* By 1.5 s, the flame front undergoes rapid thermal and chemical degradation, achieving complete extinction and absolute disappearance by 2.0 s.

Ultimately, these findings highlight the high viability of the developed $(NH_4)_2CO_3$-based solution as an optimized medium for advanced mist fire suppression technologies targeting Class B hazards. When the AFEA mist penetrates the flame zone, the 50 wt% $(NH_4)_2CO_3$ aqueous-ammonia matrix undergoes instantaneous flash evaporation and thermal-oxidative destruction.

Based on classical kinetic models of nitrogenous compounds in flames, the liberated ammonia (NH_3) readily participates in an oxidation reaction within the flame boundary. By consuming the surrounding atmospheric oxygen, it actively starves the combustion zone of its essential oxidant. This secondary process generates molecular nitrogen and additional water vapor according to the following integer stoichiometry:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Given that all generated gaseous products (N_2, CO_2, and H_2O) possess inherent, highly effective fire-suppressant properties, the 50 wt % aqueous-ammonia solution of ammonium carbonate delivers a potent dual-action effect. Consequently, this formulation demonstrates immense potential for high-efficiency mist-based mitigation of volatile liquid hydrocarbon fires.

3.3. Quantitative kinetic parameters and volumetric efficiency of fire suppression

To provide a rigorous quantitative evaluation of the fire suppression performance of the tested formulations against Class B hazards, two key kinetic and volumetric parameters were introduced. The application rate (I_{sp}, $L \cdot m^{-2} \cdot min^{-1}$), which characterizes the volumetric discharge rate of the agent per unit area of the fire source until complete extinguishment, was calculated using Eq. (1):

$$I_{sp} = \frac{V}{S \cdot \Delta\tau} \cdot \frac{60}{100} \tag{1}$$

where V is the total volume of the fire extinguishing agent consumed during suppression (mL), S is the surface area of the model fire pan (0.251 m^2), and $\Delta\tau$ is the fire extinguishing time (s).

It should be noted that while water mist suppresses fires primarily via gas-phase cooling, thermal radiation blocking, and volumetric oxygen dilution rather than direct fuel surface cooling, normalized scaling against the fuel surface area (S) is adopted here strictly as a standardized geometric baseline. This parameter provides a consistent methodological framework to evaluate and directly compare the relative kinetic and chemical efficacy of the modified formulations against the reference solutions under identical delivery conditions.

Furthermore, to benchmark the performance of the novel formulation against the traditional salt-based reference, the relative extinguishing efficiency coefficient (E_{rel}) was established based on an integrated time-volume criterion:

$$E_{rel} = \frac{V_{K_2CO_3} \cdot \Delta\tau_{K_2CO_3}}{V_{(NH_4)_2CO_3} \cdot \Delta\tau_{(NH_4)_2CO_3}} \tag{2}$$

where $V_{K_2CO_3}$ and $\Delta\tau_{K_2CO_3}$ represent the consumed volume and suppression time for the reference 40 wt% K_2CO_3 solution, respectively, while $V_{(NH_4)_2CO_3}$ and $\Delta\tau_{(NH_4)_2CO_3}$ denote the corresponding values achieved by the proposed $(NH_4)_2CO_3$-based AFEA.

The calculated parameters revealed a profound enhancement in fire suppression kinematics when employing the ammonium carbonate-based agent. During the A-92 petrol fire tests, the $(NH_4)_2CO_3$-based AFEA exhibited an exceptionally high application rate of $I_{sp} = 33.47\ L\ m^{-2} \cdot min^{-1}$ (calculated based on a characteristic individual trial with an exact extinguishment time of $\Delta\tau = 2.0$ s), enabling a near-instantaneous knockdown of the flame matrix within 2 s. In contrast, the reference K_2CO_3 solution demonstrated a lower specific intensity ($I_{sp} = 27.49\ L \cdot m^{-2} \cdot min^{-1}$), requiring a prolonged interaction time of

10.0 s to interrupt the combustion process. Substituting these experimental values into Eq. (2) reveals that the novel $(NH_4)_2CO_3$-based formulation achieves an $E_{rel} = 20.5$. This indicates that the developed agent is more than 20 times more integratedly efficient than its potassium carbonate counterpart on volatile petrol substrates (Fig. 3).

This drastic inflation of fire extinguishing efficiency cannot be explained solely by physical cooling. The underlying mechanism relies on the rapid, highly endothermic thermal decomposition of ammonium carbonate directly inside the high-temperature flame zone, as detailed in Section 3.1. The simultaneous *in-situ* generation of ammonia (NH_3) and carbon dioxide (CO_2) exerts a dual suppressive effect: it rapidly dilutes the oxygen concentration at the fuel-air shear layer below the lower flammability limit (LFL) and blocks the mass transfer of volatile hydrocarbon vapors. Simultaneously, the thermal dissociation of ammonia yields active nitrogen-containing intermediates that act as potent radical scavengers, chemically terminating the $H^{\bullet}$ and $^{\bullet}OH$ chain carriers responsible for flame propagation.

The dominance of this chemical inhibition pathway becomes even more apparent in the Euro-5 diesel fuel tests. Due to the high thermal inertia and elevated boiling point of diesel fractions, traditional cooling and surface-blanketing agents usually fail unless applied at massive flow rates. This limitation was confirmed by the complete failure of both tap water and the K_2CO_3 solution, which were unable to suppress the diesel fire within the 30-s benchmark period. Conversely, the $(NH_4)_2CO_3$-based AFEA successfully extinguished the diesel fire at $\Delta\tau = 29.7$ s with an application rate of $I_{sp} = 33.47$ L m^{-2}·min^{-1} ($V = 4200$ mL).

This success proves that the combined gaseous dilution and radical scavenging mechanisms are robust enough to overcome the intense feedback radiation of heavy hydrocarbon pool fires, where the identical value of I_{sp} between the two fuel scenarios stems from the higher consumed volume being precisely proportional to the extended suppression time under a constant system flow rate (Fig. 4).

3.4. Preliminary upscaling estimation and engineering Implications for industrial class B hazards

To evaluate the potential practical applicability of the developed aqueous fire-extinguishing agents (AFEAs) beyond laboratory constraints, the experimental data obtained from the model fire tests ($S = 0.251$ m^2) were upscaled to a conceptual full-scale industrial hazard scenario. It must be emphasized that in practical fire engineering, open-air full-surface flammable liquid storage tanks (such as the RVS-400 type, with a nominal surface area of 56.7 m^2, approximated as 57 m^2) are conventionally protected by foam extinguishing systems, while water spray or deluge systems are restricted to tank shell cooling and exposure protection according to international standards (e.g., NFPA 11, NFPA 15, and EN 13565). Therefore, the following scaling analysis is intended strictly as a theoretical mass-balance exercise to evaluate the chemical scale-up performance of the novel agent on a larger volatile fuel surface area, rather than a direct engineering recommendation for open-air tank protection. The practical deployment of the developed water-mist formulation is primarily envisioned for enclosed or semi-enclosed industrial hazards, such as fuel pump rooms, indoor process areas, and machinery spaces.

The application rate (I_{sp}, L·m^{-2}·min^{-1}) and the specific agent consumption (q_{sp}, L·m^{-2}) were determined using Eqs. (3) and (4):

$$I_{sp} = \frac{Q_{AFEA}}{S} \cdot 60 \tag{3}$$

$$q_{sp} = \frac{V_{AFEA}}{S} \tag{4}$$

where Q_{AFEA} is the volumetric flow rate (L·s^{-1}), V_{AFEA} is the consumed volume converted to liters (L), and S is the pan surface area (m^2).

For large-scale conceptual sizing and to account for open-air adverse factors (e.g., thermal updrafts, wind fluctuations, and uneven mist distribution over a large radius), a standard safety factor ($k = 1.5$) was integrated into the calculation of the required total volumetric flow rate (Q_{req}, L·s^{-1}) and the minimum required agent volume (V_{req}, L) for the target area (A_{target}):

$$Q_{req} = \frac{k \cdot I_{sp} \cdot A_{target}}{60} \tag{5}$$

$$V_{req} = k \cdot q_{sp} \cdot A_{target} \tag{6}$$

where $A_{target} = 57$ m^2. The estimated minimum discharge time (τ_{dis}, s) required for complete suppression is derived from the ratio of V_{req} to Q_{req}. The calculated upscaled parameters for this conceptual scenario are summarized in Table 3.

Crucially, this scaling approach must be interpreted strictly as a preliminary theoretical estimation rather than a definitive engineering design basis. Large-scale pool fires exhibit fundamentally different physical environments than laboratory-scale setups. At a 57 m^2 scale, the fire environment is dominated by immensely stronger thermal plume dynamics, massive radiative feedback to the fuel surface, high air-entrainment flows, and acute sensitivity to crosswinds. These macro-

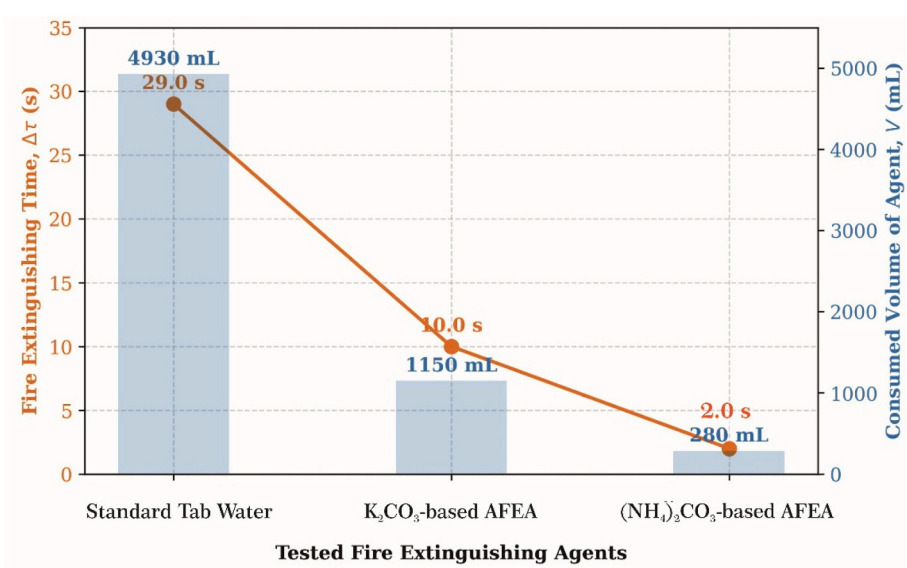

Fig. 3. Comparative kinematic and volumetric parameters for A-92 petrol fires.

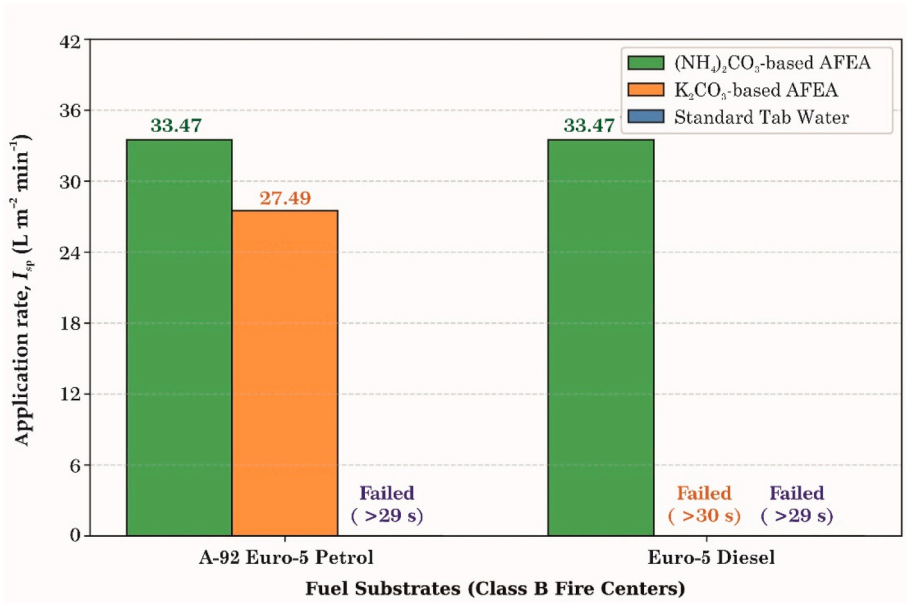

Fig. 4. Application rate (I_{sp}) for petrol and diesel suppression scenarios.

Table 3
Preliminary upscaled engineering parameters and theoretical agent capacity for a conceptual 57 m^2 petrol fire hazard.

Parameter	$(NH_4)_2CO_3$-based AFEA	K_2CO_3-based AFEA
Application rate, I_{sp} (L·m^{-2}·min^{-1})	33.47	27.49
Specific agent consumption, q_{sp}, (L·m^{-2})	1.1155	4.5817
Required total flow rate for 57 m^2, Q_{req}, (L·s^{-1})	47.7	39.2
Minimum required agent volume, V_{req} (L)	95.4	391.7
Estimated minimum discharge time, τ_{dis} (s)	2.0	10.0

physical phenomena present severe delivery challenges for misted sprays. The intense upward velocity of the thermal plume can easily deflect, decelerate, or prematurely evaporate low-momentum fine droplets before they can penetrate the flame front and reach the combustion root. Therefore, transitioning this technology to actual industrial hardware necessitates engineering modifications. Real-world systems must utilize specialized high-velocity or dual-fluid nozzles capable of imparting sufficient spray momentum to overcome the plume's drag, ensuring that the misted $(NH_4)_2CO_3$ matrix successfully penetrates the reaction zone to deploy its chemical and physical mechanisms.

When evaluating the practical industrial implementation of this upscaled configuration, a multi-faceted qualitative lifecycle assessment encompassing economics, material compatibility, and safety is required.

- *Procurement and Formulation Economics:* Both ammonium carbonate and aqueous ammonia are mass-produced, low-cost industrial commodities heavily utilized in chemical sectors. Consequently, the basic chemical procurement cost is highly competitive, offering a significant economic advantage on a commercial scale over proprietary fluorinated firefighting foams (AFFF), halocarbon gas alternatives, or specialized dry chemicals.
- *System Footprint and Hardware Requirements:* The primary engineering asset of the developed agent lies in the 75.7% reduction in the theoretically required fluid volume (95.4 L for the novel agent versus 391.7 L for the K_2CO_3 baseline). In large-scale automated installations, this downscaling directly translates to much smaller, lighter storage pressure vessels and a minimized structural footprint on industrial sites, yielding substantial savings in initial system hardware Capital Expenditure (CapEx).
- *Material Compatibility and Corrosion Management:* Because the stabilized aqueous ammonia solvent matrix is highly alkaline (pH ≈ 12.0), it accelerates galvanic corrosion in traditional carbon steel or copper-based piping. Large-scale systems must utilize corrosion-resistant metallurgy, specifically Grade 304 or 316 stainless steel, or high-density polymer (HDPE) linings for storage configurations. While premium alloys elevate the cost per unit mass of hardware, the sharply reduced volumetric requirement minimizes the total surface area and mass of the required piping network, effectively offseting the overall material cost penalty.
- *Personnel Safety and Gaseous Emissions:* The industrial deployment of an ammonia-stabilized matrix requires strict operational protocols due to the localized release of gaseous NH_3 during pyrolytic suppression. This technology is optimally tailored for automated, fixed local-application water-mist installations protecting unoccupied or isolated industrial zones (e.g., automated processing bays, pump rooms, or closed fuel transfer stations). The short-term hazard of localized ammonia exposure must be balanced against the major mitigation advantage: reducing the estimated suppression time from 10.0 s to a rapid 2.0 s drastically curtails thermal radiation exposure to surrounding structural elements and process equipment, prevents structural buckling of adjacent piping, and completely arrests the prolonged, massive generation of highly toxic Class B combustion products such as carbon monoxide (CO), dense black soot, and carcinogenic polycyclic aromatic hydrocarbons (PAHs). Furthermore, the simultaneous co-generation of dense water vapor (H_2O) from the mist acts as an *in-situ* scrubbing medium, accelerating the knockdown and dissolution of airborne ammonia fractions, thereby limiting the downstream environmental footprint.

4. Conclusions

Based on the experimental fire safety testing and mathematical evaluation of the fire suppression performance of various aqueous agents against Class B pool fires, the following conclusions can be drawn.

1. The novel aqueous fire extinguishing agent (AFEA) formulated with 50 wt% $(NH_4)_2CO_3$ in an aqueous ammonia medium demonstrated high fire suppression efficiency. During model 8B fire test scenarios, it achieved a rapid knockdown of highly volatile A-92 petrol fires within 2.07 ± 0.12 s, requiring a minimal consumed volume of 280 ± 6 mL. This performance outclassed the reference 40 wt% K_2CO_3 solution, which required 10 s and a four-fold higher liquid volume (1150 ± 22 mL) to suppress the same flame matrix.
2. Comprehensive kinetic and volumetric evaluation based on the integrated time-volume criterion revealed that the $(NH_4)_2CO_3$-based AFEA achieved a relative extinguishing efficiency coefficient (E_{rel}) of 20.5 compared to the potassium carbonate baseline. This improvement in suppression performance is highlighted by a high application rate ($I_{sp} = 33.47$ L m^{-2}·min^{-1}), confirming its capability to rapidly disrupt intense combustion zones.
3. The proposed formulation proved to be the only agent capable of successfully suppressing heavy hydrocarbon Euro-5 diesel fuel fires under the benchmark open-space constraints, achieving complete extinguishment at a mean time of 29.7 ± 0.6 s with an application rate of 33.47 L m^{-2}·min^{-1}. Conversely, both the 40 wt% K_2CO_3 solution and pure tap water failed to mitigate the diesel fire within the testing limits, highlighting the limitations of traditional cooling or single-action salt solutions against substrates with high thermal inertia.
4. The high efficiency of the $(NH_4)_2CO_3$-based AFEA is governed by a synergistic multi-action mechanism. Beyond the conventional physical cooling provided by the fine water mist, the rapid, endothermic pyrolytic breakdown of ammonium carbonate directly inside the flame structure generates massive volumes of non-combustible gases. While carbon dioxide (CO_2) and water vapor (H_2O) act as non-combustible gases that physically dilute oxygen concentrations at the fuel-air interface, the simultaneously released ammonia (NH_3) operates as an oxidisable gas, rapidly consuming local oxygen within the high-temperature zone. Concurrently, the generated nitrogen-containing active intermediates act as potent radical scavengers, terminating the chain carrier reactions ($H^\bullet$ and $^\bullet OH$) responsible for fire propagation.
5. A preliminary engineering upscaling analysis based on a conceptual 57 m^2 industrial fire footprint (equivalent to the surface area of an RVS-400 tank, utilizing a standard safety factor of $k = 1.5$) was conducted to evaluate the conceptual feasibility of the system. The theoretical model indicates that transitioning to the novel $(NH_4)_2CO_3$-based system could reduce the minimum calculated agent inventory from 391.7 L (for the K_2CO_3 baseline) to 95.4 L. Recognizing that full-surface open-air tank fires are conventionally protected by foam systems, this 75.7% conceptual reduction in agent volume highlights the exceptional technical viability of the formulation for designing highly compact, rapid-response automated water-mist installations. Such systems are optimally tailored for protecting enclosed or semi-enclosed industrial sectors, including fuel pump rooms, indoor processing bays, and distribution depot infrastructure, where rapid flame knockdown and minimized hardware footprints are critical.

CRediT authorship contribution statement

Volodymyr-Petro Parkhomenko: Writing – original draft, Visualization, Investigation. **Borys Mykhalichko:** Writing – original draft, Methodology, Conceptualization. **Helen Lavrenyuk:** Writing – review & editing, Formal analysis, Data curation. **Nadiia Hodovanets:** Validation, Supervision, Project administration. **Oleg Mykhalichko:** Visualization, Software, Investigation.

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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