The use of carbon nanotubes in the fire extinguishing of oil and oil products

F A Dali¹, G L Shidlovsky¹, M S Khasikhanov², R U Zalaev², P R Tagirova², S S Saidulaev², L M Masaeva² and R S Erzhapova²

¹ Department of Fire Safety of Buildings and Automated Fire-Fighting Systems, St. Petersburg University, State Fire Service of EMERCOM of Russia, St. Petersburg, Russia
² Department of Life Safety, Grozny State Oil Technical University named after academician M.D. Millionschikova, Grozny, Russia

E-mail: dalee@igps.ru, shidlovsky.g@igps.ru, ipkggntu@mail.ru, zalaev-rezvan@mail.ru, t-petimat@mail.ru, saydulaev68@mail.ru, lizamasaeva@mail.ru, alikhan1201@mail.ru

Abstract. The process of quenching a flame of liquid hydrocarbons by suspensions of water with carbon nanostructures is studied. It is shown that the dispersion of carbon nanostructures in water intensifies heat transfer in liquids, which leads to their more rapid heating to boiling temperature under conditions of thermal exposure to a flame. During the experiment, it was found that the quenching time of liquid hydrocarbons by nanosuspensions is on average 3.5–5.0 times less than the time of quenching of a liquid with finely divided water.

1. Introduction
When extinguishing fires of liquid hydrocarbons by sprayed water, spraying occurs, convective entrainment of water droplets, and its penetration into the subsurface layer of the burning liquid. The low efficiency of using water as a fire extinguishing composition is associated with insufficient heat removal in the combustion zone [1].

Wetting agents and additives increase the heat sink intensity, create a film on the surface of a burning oil product. Carbon nanotubes increase thermal conductivity and change the rheological properties of liquids at low concentrations (0.01...1.00 vol. %) [2].

The aim of the study was to determine the fire extinguishing characteristics of water suspensions with carbon nanostructures when extinguishing a flame of a flammable liquid.

2. Methods and materials
Functionalized multi-walled carbon nanotubes (MWCNT) and astralen (Astr) in distilled water (DW) were used as an object of study (Fig. 1).

MWCNTs were obtained by catalytic pyrolysis [3]. Parameters of nanoparticles: \( d = 25…180 \text{ nm} \), \( l = 1…3 \mu \text{m} \). MWCNT was purified from synthesis by-products by the method described in [4]. MWCNT was placed in concentrated nitric acid (\( HNO_3 \)) 65 % (1 g MWCNT per 50 ml \( HNO_3 \)) and 35 % sulfuric acid (\( H_2SO_4 \)). After boiling, the oxidized MWCNTs were filtered off and washed with distilled water to a neutral \( pH \) filtrate, and dried at a temperature of 70–80 °C.
Astralenes were obtained by evaporation of graphite anodes in an electric arc discharge [5]. They represent a structure of curved graphite layers with a diameter of 10...150 nm, a distance between graphene layers of 0.336 nm, an average pore size of 20...60 nm. Astralenes are characterized by high thermal stability and in powder form are large agglomerates measuring about 0.5...3 microns in size [6].

Suspensions were prepared by dispersing carbon nanostructures with a volume concentration of 0.05–1.60 % vol. in DW when exposed to an ultrasound source (power 1.2 kW, frequency 50–60 Hz, processing time 30 min). Suspensions DW with a low concentration of MWCNT ($\varphi = 0.01$ vol. %). They were used as a control sample.

The following methods were used in the work: atomic force microscopy (AFM) [7]; measuring the surface tension coefficient by the droplet separation method [8]; studies of the heating rate of suspensions to a boiling point [9]; measuring the specific heat of vaporization of suspensions [10]; measuring the extinguishing time of model fires of a class “B” fire described in [11].

2.1. The study of nanostructures in suspension by atomic force microscopy

On the AFM scan of the solid residue, MWCNTs are extended structures with a diameter of $\sim 110$ nm and a length of 1–3 $\mu$m (Fig. 1, a). During the study of the topology of the Astr solid residue, clusters of particles with a diameter of 200–300 nm are observed (Fig. 2, b).

Figure 1. Suspension with carbon nanostructures

Figure 2. AFM-scans of agglomerations of carbon nanostructures during dispersion in the DW: a – DW+MWCNT; b – DW+Astr.
2.2. Measurement of the surface tension of suspensions
The experimental results showed (Fig. 2) that the surface tension of the DW + MWCNT suspension increases linearly with increasing MWCNT concentration from 0.4 and at a concentration of $\phi = 1.6$ vol. % reaches 30 %. For the suspension DW + Astr, the logarithmic nature of the change in function is observed. At the initial stage, a sharp increase in the surface tension coefficient occurs at concentrations $Astr \phi = (0.05...0.5)$ vol. % relative to the suspension DW + MWCNT, but with a further increase in concentration reaches 25 % in comparison with the control sample. It was noted earlier in [12] that the surface tension of water-based nanofluids increases with increasing concentration of carbon nanostructures.

2.3. Investigation of the thermophysical properties of suspensions
During the study of thermophysical properties, it was revealed (Fig. 3) that with an increase in the MWCNT concentration to 1.0 vol. % there is a slight increase in the specific heat of vaporization of the suspension DW + MWCNT by 10–15 %, but at the same time, the heating rate to a boiling point increases linearly to 50 %. An increase in the specific heat of vaporization of the suspension DW + Astr with an increase in the concentration of Astr to 0.5 vol. % reaches 20 % in comparison with the control sample, but with a further increase in concentration it sharply decreases by 30–40 %. In this case, the kinetics of heating to the boiling point increases over the entire observed range of concentrations and reaches 50–70 % at an Astr concentration of 1.0 vol. % Thus, an increase in the specific heat of vaporization is caused by an increase in the surface tension coefficient of water suspensions with carbon nanostructures [13].

2.4. Measurement of the extinguishing time of a model fire of class “B” fire
Evaluation of the fire extinguishing ability of suspensions during the elimination of the combustion of a flammable liquid was carried out in a laboratory setup described in [11].

The free burning time of a flammable liquid was at least 60 s. The extinguishing of a model fire site (pan diameter 450 mm, the combustible mixture is motor gasoline with an octane rating of 95 and water in a ratio of 7: 3) was carried out by a sprayed stream of suspension with a droplet diameter of 100–300 $\mu$m and a pressure of 1.0–1.5 MPa. Extinguishing time was recorded at the time of complete elimination of combustion. For each type of extinguishing agent, 5 tests were carried out, the data were averaged.

During the study of fire extinguishing characteristics, it was revealed (Fig. 4) that with an increase in the MWCNT concentration to 1.0 vol. % in suspension DW + MWCNT there was a decrease in quenching time by 70 % compared with the control sample. Extinguishing time with DW + Astr suspension at concentrations up to 0.5 vol. % decreased to 80-90 %. The increase in quenching time at concentrations...
φ>0.5 (for DW + Astr) and φ>1.0 (for DW + MWCNT) is associated with intensive aggregation of nanostructures [3] and leads to a decrease in the fire extinguishing efficiency of suspensions.

![Figure 4. Thermophysical properties of suspensions](image)

It was noted that the specific consumption of extinguishing agent during fire fighting with a suspension of DW + MWCNT decreased by 3.5 times, and for a suspension of DW + Astr by 4.5–5 times.

When quenching with suspensions of water with carbon nanostructures, more intense vaporization in the combustion zone is observed in comparison with the control sample.

![Figure 5. Extinguishing characteristics suspensions](image)

3. Results
The mechanism for extinguishing liquid hydrocarbon fires by sprayed water suspensions with CNS is based on lowering the temperature in the combustion zone to the extinction temperature, at which there is no release of a sufficient amount of hydrocarbon vapor necessary for further continued combustion. A significant factor in changing the properties of nanostructures is the giant resonances of electromagnetic fields on the surface of nanoparticles [14], which determines a significant change in the properties of nanomaterials with a low concentration of CNS due to van der Waals interactions [15].

The mechanism of heat transfer in suspensions with CNS is based on the influence of the Brownian motion of carbon nanoparticles and the formation of a highly thermally conductive liquid layer at the
“liquid – solid particle” interface. The process of boiling nanosuspensions depends on the properties of the base liquid, the type and concentration of nanoparticles contained in it, which largely determines the nature of heat and mass transfer with phase transformations, the heat transfer process on the surface of evaporating drops, and the nature of boiling (film or bubble) in the volume of the liquid [16]. The phenomenon of vaporization depends on the surface tension forces in the liquid during the breaking of the bond between neighboring liquid molecules and the movement of molecules into the gaseous medium [12].

It can be concluded that suspensions based on water with CNS are extinguishing agents with a predominantly cooling and diluting effect. When droplets of suspensions enter the combustion zone, intense heating occurs to the boiling point, followed by evaporation and cooling of the combustion zone. With a sufficient amount of water vapor in the combustion zone, flame extinction is observed. In this case, an increase in the specific heat of vaporization entails an increase in the amount of selected heat energy from the combustion zone. Increase Astr concentration to 0.5 vol. % and MWCNT up to 1.0 vol. % in suspensions significantly increases the extinguishing efficiency of Extinguishing Agents. A further increase in the concentration of nanoparticles leads to aggregation of CNS, which reduces the effective thermal conductivity of the suspensions and the specific heat of vaporization.

4. Conclusion
The dependence of the specific consumption and the quenching time of the flame of burning liquid hydrocarbons on the concentration of CNS (MWCNT, astralen) is obtained. The results indicate that suspensions are effective extinguishing agents for extinguishing burning liquid hydrocarbons at a relatively low concentration of carbon nanostructures. Dispersion of CNS intensifies the heat transfer in sprayed droplets of extinguishing agents, which leads to their more rapid heating in conditions of heat exposure to the flame. The effectiveness of controlling the properties of suspensions depends on the physicochemical properties of the base liquid and nanomaterials, as well as on the parameters of the external action.

References
[1] Nolan D P 2014 Handbook of fire and explosion protection engineering principles: for oil, gas, chemical and related facilities (William Andrew)
[2] Yu W and Xie H 2012 A review on nanofluids: preparation, stability mechanisms, and applications J. of Nanomater. 11 DOI: 10.1155/2012/435873
[3] Zhao Q, Jiang T, Li C and Yin H 2011 Synthesis of multi-wall carbon nanotubes by Ni-substituted (loading) MCM-41 mesoporous molecular sieve catalyzed pyrolysis of ethanol J. of Indust. and Engineer. Chem. 17(2) 218–22 DOI:10.1016/j.jiec.2011.02.009
[4] Sun Y P, Fu K, Lin Y and Huang W 2002 Functionalized carbon nanotubes: properties and applications Accounts of chem. Res. 35(12) 1096–104 DOI: 10.1021/ar010160v
[5] Shames A I, Katz E A, Panich A M et al 2009 Structural and magnetic resonance study of astralen nanoparticles Diamond and Related Mater. 8(2–3) 505–10 DOI: 10.1016/j.diamond.2008.10.056
[6] Ponomarev A and Iudovich M 2015 Multi-layered carbon nanoparticles of the fulleroid type US Patent No 9,090,752. 28 July.
[7] Voigtländer B 2016 Scanning probe microscopy (Berlin: Springer-Verlag AN) DOI 10.1007/978-3-662-45240-0
[8] Ding Y, Alias H, Wen D and Williams R A 2006 Heat transfer of aqueous suspensions of carbon nanotubes (CNT nanofluids) Int. J. of Heat and Mass Transfer 49(1–2) 240–50 DOI: 10.1016/j.ijheatmasstransfer.2005.07.009
[9] Khaleduzzaman S S, Mahbubul I M, Shahrul I M and Saidur R 2013 Effect of particle concentration, temperature and surfactant on surface tension of nanofluids Int. Communicat. in Heat and Mass Transfer 49 110–4 DOI: 10.1016/j.icheatmasstransfer.2013.10.010
[10] Suriyawong A and Wongwises S 2010 Nucleate pool boiling heat transfer characteristics of TiO2-water nanofluids at very low concentration Experim. Thermal and Fluid Science 34(8) 992–9 DOI: 10.1016/j.expthermflusci.2010.03.002
[11] Tanvir S and Qiao L 2012 Nanoscale res. Lett. 7(1) 226–36 DOI: 10.1186/1556-276X-7-226
[12] Amiri A., Shanbedi M., Amiri H et al 2014 Appl. Therm Eng. 71(1) 450–9 DOI: 10.1016/j.applthermaleng.2014.06.064
[13] Ponomarev A N, Yudovitch M E, Gruzdev M V and Yudovitch V M 2008 A nonmetallic nanoparticles in a superficial electromagnetic field. Topological factor of mesostructures interference. Voprosy materialovedeniya Mater. issues 60(4) 59–64 Retrieved from: http://www.crism-prometey.ru/science/editions (in Russian).
[14] Dzyaloshinsky I E, Lifshits E M and Pitaevsky L P 1961 The General Theory of the Van der Waals Forces Uspekhi Fizich. Nauk: Successes of phys. Sci. 123(3) 381–422
[15] Das S K, Choi S U S, Yu W and Pradeep T 2007 Nanofluids: science and technology (John Wiley & Sons) 397 p DOI: 10.1002/9780470180693.ch1