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EFFECT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAH) ON SOOT PARTICLES FORMATION AND THEIR EMISSION TO THE ATMOSPHERE

Formation of the soot in the flame of a heavy fuel oil (mazout) and its water emulsions, depending on the polycyclic aromatic hydrocarbon (PAH) content in the fuel, are presented. The experiments were conducted in a furnace with 1 m³ combustion chamber equipped with apparatus for measuring all thermal and chemical parameters of combustion.

It has been found that intensity of soot formation in high-temperature flame zone was higher in the case of mazout characterized by a higher content of PAH. The experiments showed that this is water contained in emulsified mazout that mainly affects the emission of PAH and soot to the atmosphere. The 10% content of water in mazout emulsion decreased the soot emission to the atmosphere more than twice, which was tantamount to similar decrease of PAH emission because the soot is the PAH carrier. This phenomenon is explained by a micro-explosion character of emulsion combustion.

1. INTRODUCTION

One of the important problems of liquid fuels combustion process is the presence of solid particles (soot) and unburned heavy hydrocarbons vapour in flames. The objective of these investigations leading to the understanding of soot particles formation and decay in flames was the necessity of determining the effect of soot on radiation heat transfer in a combustion chamber. Recent investigations, however, have been concentrated on the interaction of soot and polycyclic aromatic hydrocarbons (PAH) in flames [1]—[3]. This aspect is particularly essential, because PAH (of mutagenic and cancerogenic character) are adsorbed on the surface of soot particles. Thus, soot emitted to the atmosphere acts as a carrier of these dangerous substances. Submicron soot particles together with PAH penetrate deeply into the respiratory system thus being most harmful for human health. It has been recognized

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[2] that polycyclic aromatic hydrocarbons occur in hydrocarbon fuels at high boiling temperature and are formed by high-temperature pyrolysis in the flames of rich-mixtures of every fuel containing C-H bonds. Taking into consideration a very wide application of highly aromatic liquid fuels in power plants, in industrial furnaces and in various engines it is recommendable to undertake investigations which will explain the formation and interaction of soot and PAH during the combustion process of these fuels. Much data concerning the soot and PAH formation and emission have been obtained for pramixed-laminar and diffusion-laminar [4]-[7] or turbulent-diffusion flames [8], [9]. These investigations refer to the formation of soot and PAH, and so far they are most thoroughly known on a laboratory scale for one-component hydrocarbon fuels and their flow in flames is not too complicated. However, when combustion occurs under practical conditions the most important questions concerning the role of multi-component fuels (fuel composition), combustion parameters and aerodynamical flow structure in flame (turbulence) in the process of soot and PAH formation and destruction are still without answer.

2. EXPERIMENTS AND MEASUREMENTS

In the present paper investigation results of the effect of polycyclic aromatic hydrocarbons on the formation and emission of soot particles have been presented. Turbulent diffusion flames of a heavy fuel oil (employed in power and metallurgical industries) and its water-emulsion E 10 (with 10 % of water) were examined. These fuels were comparable in respect of their thermal parameters obtained in a furnace. It is well-known that liquid fuels used in the form of water-emulsions due to the phenomenon of micro-explosion of droplets in the flame initial zone intensify the processes of evaporation and combustion with nearly theoretical air excess. Such combustion of liquid fuels involves fuel economy and the reduction of NO_x and soot emission to the atmosphere, while an addition of alkaline compounds causes binding of sulfur oxides (SO_x) in the combustion gas, and as a result of this process sulfates and sulfites removable from flue gas are formed [10]-[12].

Combustion tests were carried out in a large-laboratory-scale furnace (1.0 m \times 1.0 m \times 3.0 m) imitating practical combustion conditions. The combustion chamber was equipped with apparatus for measuring thermal and chemical parameters of the flame and combustion gas. Fuel oil-water emulsions were generated in the mechanical-pneumatic emulgator with the Venturi nozzle. The burner system was composed of a fuel pressure atomizer and a mixing chamber whose design (two coaxial cylinders with orifices on the periphery and counter-current air inlet) ensured good mixing of the fuel atomized stream with the combustion air. To determine the soot and PAH parameters, samples of the combustion products were collected by a water-cooled-injection probe. Introduction of water to the samples of collected flame gases caused their sudden quenching,

favouring the hindering of possible interactions between the combustion products collected [8], [14]. First of all, it opposed the burning-out of soot particles and their deposition on the inner walls of the probe. A fiber glass filter located in the probe caught solid particles and unburned hydrocarbons (PAH among others) condensed and adsorbed on their surface. The material deposited on the filter was obtained in the Soxhlet extractor using distilled methylene chloride for 8 hours. In the present investigations soot was classified as post-extraction carbonaceous remains of the material collected on the filter. Soot thus determined was examined under the electron microscopes (Philips EM-301, Jeol EM-100C), and the quantitative image analysis was performed using the Quantimet Q 720 to establish the morphology of soot particles. To determine the soot mass concentration gravimetric analysis was made.

Determinations of the polycyclic aromatic hydrocarbons obtained from the extract were carried out by using the system of gas chromatograph and mass spectrometer GC-MS LKB 9000S. The concentration of each PAH was determined separately according to the formula:

$$C_{\text{PAH},i} = \alpha_i \frac{A}{B} \cdot \frac{V_1}{V_2}$$

where:

- A – area in the chromatogram corresponding with compound i ,
- B – volume of a sample injected to the chromatograph,
- V_1 – volume of a sample in the phial,
- V_2 – volume of combustion gas collected from flame,
- α_i – ratio of mass injection to area (recorded in the chromatogram) for each PAH.

For the separation of individual components a capillary column OV-1, 20 m, was used. The column temperature was constant for 10 minutes at 303 K and subjected to linear programming to 513 K at the rate of 2 K/min. The height (area) of the chromatographic peaks was utilized for the quantitative determination of PAH. The identification of individual PAH was carried out employing the mass spectra and the relative retention times obtained. They were compared with the mass spectra of standard compounds and those of standard catalogues [15]–[17].

3. RESULTS AND DISCUSSION

In the investigations carried out, types and concentration of polycyclic aromatic hydrocarbons, and soot were analyzed in the samples collected from various regions of the heavy oil and its water-emulsion E 10 flames. A considerable number of PAH in the initial flame zone were found. This was directly connected with the region of

high-temperature fuel pyrolysis being a basic phenomenon leading to the PAH forming. A greater amount of PAH of more varied types occurred in the flame of pure fuel oil. It results (among others) from the fact that during the combustion of oil the temperature in flames was higher by about 100 K than during the combustion of water-emulsion. Thus, in result the pyrolysis was far more intensive. Identified PAHs occurring in heavy oil and emulsion E 10 flames at a distance of 0.2 m from the burner are presented in table.

The total PAH concentration during the combustion of oil and emulsion E 10 is shown in fig. 1. It is clearly seen that with the increase of the distance from the burner the total concentration decreases because PAH probably undergo dehydrogenation

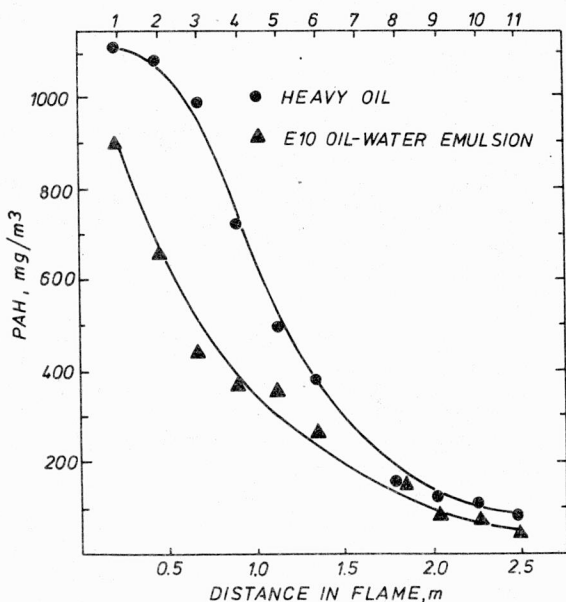


Fig. 1. PAH concentration profiles in heavy oil and E10 flames

and oxidation. Resulting from the above aliphatic hydrocarbons from C_8 to C_{24} were formed. However, in the furnace exhaust section, polycyclic aromatic hydrocarbons revealing the most strong chemical characters, i.e., benzo(a)pyrene, phenanthrene, anthanthrene, pyrene and benzo(ghi)fluoranthene, were also found. Their presence is especially dangerous for the environment, because benzo(a)pyrene is a cancerogenic substance, while other PAH show a mutagenic character. All the mentioned PAH were found both in pure oil and water-emulsion exhaust gases, but in the case of water-emulsion there was only a trace of pyrene.

It is seen in fig. 1 that during the combustion of water-emulsion the PAH concentration in flame and exhaust section was distinctly smaller than that obtained during the combustion of pure fuel oil. In the exhaust gas the concentrations were

more than twice smaller, i.e., that of oil is 70 mg/m^3 , and that of E 10, 30 mg/m^3 . In the earlier investigations [12] it was ascertained that during the combustion of water-emulsion the soot concentration in the exhaust gas is about 70% lower in comparison with the soot concentration in the pure heavy oil exhaust gas. Therefore, these results may point to the existence of a correlation between mutual interaction of PAH and soot in the flames of the fuels under investigation.

In fig. 2 the distribution of the total PAH concentration in comparison with the soot concentration variation in fuel oil flames is shown. It is clearly seen that the

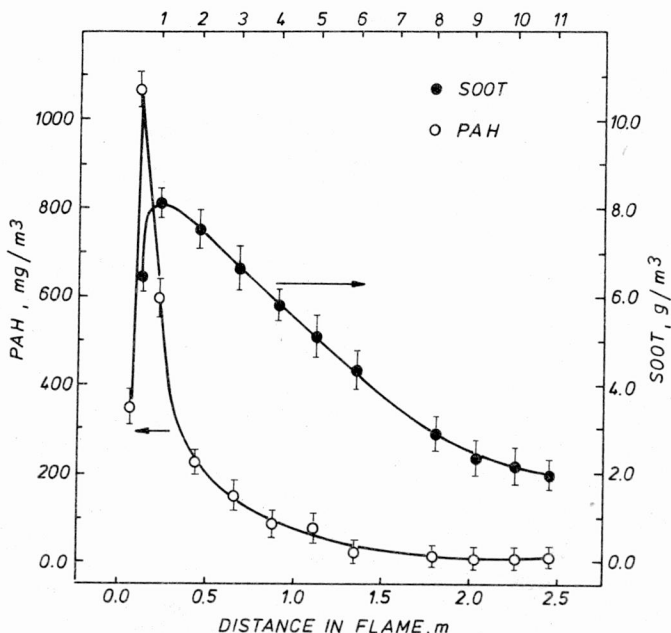


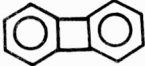
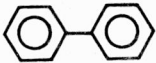
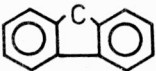
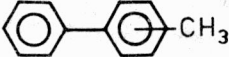
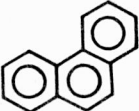
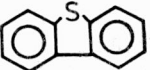
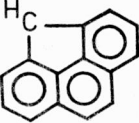
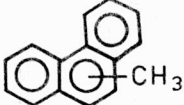
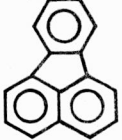



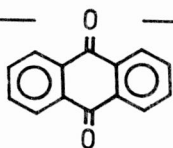
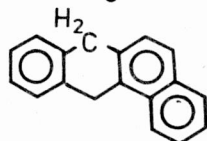
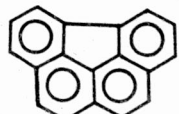
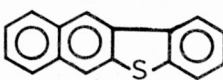
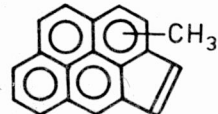
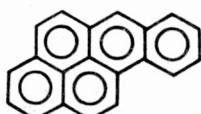




Fig. 2. PAH and soot concentration profiles in heavy oil flames

maximum PAH concentration is higher than the maximum mass concentration of soot. Furthermore, the most intensive decrease of PAH concentration occurs in the initial, high-temperature flame zones, i.e., in the zones where the largest quantity of soot was formed [18]. This confirms the suggestions of the authors of [19], [20] that polycyclic aromatic hydrocarbons can be the nuclei for the formation of soot particles in flames. The results presented in fig. 3 may be another proof of the influence of PAH on the process of soot formation. A distinct increase of soot concentration in the high-temperature region of the flame of heavy oil with higher PAH contents also proves that they can act as soot precursors. In this case the soot concentration in the exhaust section was higher, too. Moreover, the combustion of fuel oil containing more PAH caused the formation of soot particles of greater diameters (fig. 4). This fact may be explained basing on the assumption that PAH are

PAH identified in heavy oil

Name	Molecular weight	Formula	Structure
Naphthalene	128	$C_{10}H_8$	
Methylnaphthalene	142	$C_{11}H_{10}$	
Biphenylene	152	$C_{12}H_8$	
Biphenyl	154	$C_{12}H_{10}$	
Fluorene	166	$C_{13}H_{10}$	
Methylbiphenyl	168	$C_{13}H_{12}$	
Phenanthrene	178	$C_{14}H_{10}$	
Dibenzo(b,d)thiophene	184	$C_{12}H_8S$	
4H-cyclopenta(def)phenanthrene	190	$C_{15}H_{10}$	
Methylphenanthrene	192	$C_{15}H_{12}$	
Fluoranthene	202	$C_{16}H_{10}$	
Pyrene	202	$C_{16}H_{10}$	

and E10 flames (0.2 m from the burner)

Name	Molecular weight	Formula	Structure
Anthracendione	208	$C_{14}H_8O_2$	
Benzofluorene	216	$C_{17}H_{12}$	
Benzo(ghi)fluoranthene	226	$C_{18}H_{10}$	
Benzo(b)naphtho(2,3-d)thiophene	234	$C_{16}H_{10}S$	
Methylcyclopenta(cd)pyrene	240	$C_{19}H_{12}$	
Benzo(a)pyrene	252	$C_{20}H_{12}$	
10-azabenz(a)pyrene	253	$C_{19}H_{11}N$	
Anthanthrene	276	$C_{22}H_{12}$	
Coronene	300	$C_{24}H_{12}$	
7,8-thiabenz(o)ghi)perylene	306	$C_{12}H_{10}S$	

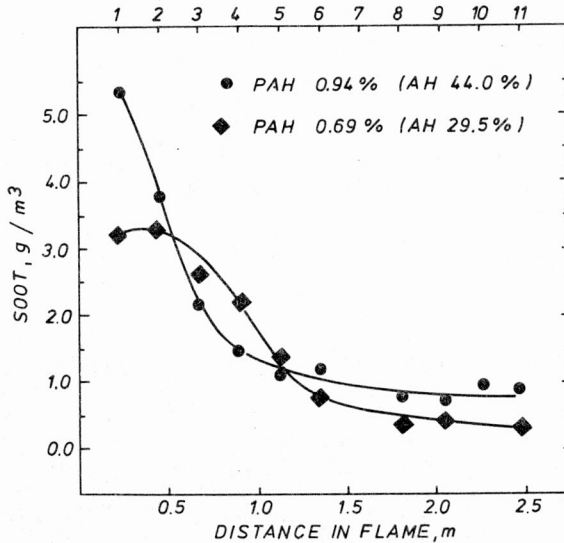


Fig. 3. Soot concentration profiles in various heavy oil flames

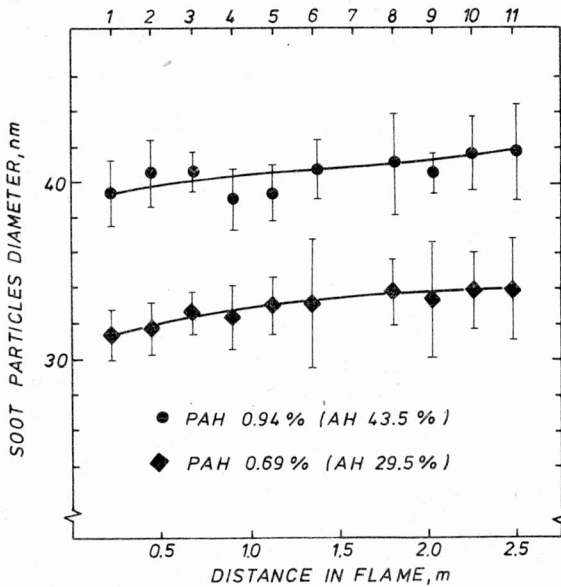


Fig. 4. Profiles of soot particle diameters in various heavy oil flames

the nuclei of soot particles' formation. Thus, in the flame of heavy fuel oil with higher contents of PAH, larger quantities of nuclei exist followed by a larger number of initial particles, their faster growth by coagulation and (in consequence) their greater sizes. The above results were obtained for fuel oils with two different contents of

PAH. The combustion processes of heavy liquid fuels with a wider range of PAH contents are being carried out at present [21], [22]. Their objective is to confirm the results obtained so far.

4. SUMMARY.

Combustion of liquid fuels is one of the seriously harmful sources of the emission of soot and polycyclic aromatic hydrocarbons to the atmosphere. Taking into consideration the environmental protection, the emission of soot and PAH should be reduced to the minimum level, thus resulting in the lowering in the air the concentration of these substances dangerous for life. The presence of PAH in flames is closely connected with the process of formation and growth of soot particles. Therefore, the recognition of the soot and PAH formation mechanism is helpful in the prediction of their emission. During the experiments carried out it was found that the combustion of the heavy fuel oil in the form of water-emulsion lowers the concentrations of PAH and soot in flame and their emission to the atmosphere. An essential influence on the decrease of the quantity of PAH and soot in the exhaust gases is exerted by micro-explosion phenomena of the water-emulsion droplets at the initial flame zone. The results obtained indicate that polycyclic aromatic hydrocarbons are precursors of soot particles during their formation and growth in flames and emission to the atmosphere.

REFERENCES

- [1] Proceedings of the NATO Workshop (Obernai) *Soot in Combustion Systems and Its Toxic Properties* (J. Lahaye and G. Prado, Eds.), Plenum Press, New York 1983.
- [2] Proceedings of the International Symposia *Polynuclear Aromatic Hydrocarbons*, Battelle Memorial Institute, Columbus, Ohio.
- [3] Proceedings of the Symposia (International) on Combustion, the Combustion Institute, Pittsburgh.
- [4] HOMANN K. H., WAGNER H. Gg., *Some New Aspects of the Mechanism of Carbon Formation in Premixed Flames*, Eleventh Symposium (Int.) on Combustion, p. 371, the Combustion Institute, 1967.
- [5] BITTNER J. D., HOWARD J. B., *Composition Profiles and Reaction Mechanism in a Near-Sooting Premixed Benzene (Oxygen) Argon Flame*, Eighteenth Symposium (International) on Combustion, the Combustion Institute, 1981.
- [6] CRITTENDEN B. D., LONG R., *Combustion and Flame*, Vol. 20 (1973), p. 359.
- [7] KERN J., SPENGLER G., *Erdöl und Kohle*, Vol. 23 (1970), p. 813.
- [8] PRADO G., LEE M. L., HITES R. A., HOULT D. P., HOWARD J. B., *Soot and Hydrocarbons Formation in a Turbulent Diffusion Flame*, Sixteenth Symposium (International) on Combustion, p. 649, the Combustion Institute, 1977.
- [9] CIAJOLO A., BARBELLA R., MATTIELLO M., D'ALESSIO A., *Axial and Radial Measurements of Soot and PAH in a Light Oil Flame*, Nineteenth Symposium (International) on Combustion, p. 1369, the Combustion Institute, 1982.
- [10] KORAL A. A., SLUPEK S., KOKKINOS A., SHALER A., MISKOVSKY N. M., ESSENHIGH R. M., *Smoke*

- Point and Heat Transfer Characteristics of Oil/Water/Air Emulsions in a Hot Wall Furnace*, Spring Meeting: Central States Section of the the Combustion Institute, 1976.
- [11] SŁUPEK S., NOCOŃ J., MALCZEWSKI W., RYCOMBEL S., *Influence of Carbon Hydroxide Addition to Heavy Oil Emulsion on the Level of SO_x Elimination from Combustion Gases*, *Metalurgia i Odlewnictwo*, T. 9, z. 4 (1983), p. 349.
- [12] SŁUPEK S., CZAKON A., KOZIŃSKI J. A., MALCZEWSKI W., SOŁTYSIK L., *Investigations of Soot and NO_x Formation During Combustion of Fuel Oil-Water Emulsion* (unpublished), contract 3.351.53, University of Mining and Metallurgy, Cracow 1985.
- [13] SŁUPEK S., KOZIŃSKI J. A., *Prediction of Soot Concentration*.
- [14] JAGODA I. J., PRADO G., LAHAYE J., *An Experimental Investigation into Soot Formation and Distribution in Polymer Diffusion Flames*, *Combust. Flame*, Vol. 37 (1980), p. 261.
- [15] STENHAGEN E., ABRAHAMSON S., McLAFFERTY F. W., *Registry of Mass Spectral Data*, J. Wiley, New York 1974.
- [16] McLAFFERTY F. W., *Interpretation of Mass Spectra*, W. A. Benjamin Inc., Massachusetts 1973.
- [17] KARCHER W., FORDHAM R. J., NELEN A., De PAUS R., DUBOIS J., GLAUDE Ph., *Molecular Spectra of Polycyclic Aromatic Hydrocarbons*, [in:] *Polynuclear Aromatic Hydrocarbons: Physical and Biological Chemistry* (M. Cooke, A. J. Dennis, and G. L. Fisher, Eds.), p. 405, Battelle Memorial Institute, 1982.
- [18] KOZIŃSKI J. A., *Soot Formation in Flames of Heavy Liquid Fuels Modified by Water*, Ph.D.Thesis, University of Mining and Metallurgy, Cracow 1986.
- [19] BITTNER J. D., HOWARD J. B., *Role of Aromatics in Soot Formation*. [in:] *Alternative Hydrocarbons Fuels: Combustion and Chemical Kinetics* (C. T. Bowman and J. Birkeland, Eds.), p. 335, Progress in Astronautics and Aeronautics, Vol. 62, American Institute of Aeronautics and Astronautics, 1978.
- [20] HOWARD J. B., LONGWELL J. P., *Formation Mechanisms of PAH and Soot in Flames*, [in:] *Polynuclear Aromatic Hydrocarbons: Formation, Metabolism and Measurement* (M. Cooke and A. J. Dennis, Eds.), p. 27, Battelle Memorial Institute, 1983.
- [21] SŁUPEK S., KOZIŃSKI J. A. et al., *Soot and PAH Formation in Heavy Oil-Water Combustion Gas*, Central Programme of Basic Research 02.08, pr.2.4.3, University of Mining and Metallurgy, Cracow 1987.
- [22] SŁUPEK S., KOZIŃSKI J. A., *PAH and Soot Behaviour During Combustion of Heavy Oil-Water Emulsions*, 38th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, paper no. 399, Atlantic City 1987.

WPLYW WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH NA POWSTAWANIE SADZY I JEJ EMISJĘ DO ATMOSFERY

Przedstawiono proces powstawania sadzy w płomieniu ciężkiego paliwa ciekłego (mazutu) oraz jego wodnych emulsji w zależności od zawartości wielopierścieniowych węglowodorów aromatycznych (WWA) w paliwie. Badania prowadzono w piecu o objętości komory spalania około 1 m³, wyposażonym w aparaturę pomiarową umożliwiającą określenie wszystkich parametrów termicznych i chemicznych procesu spalania.

Stwierdzono, że intensywność formowania się sadzy w wysokotemperaturowej strefie płomienia była wyższa dla mazutu o większej zawartości WWA. Badania wykazały zasadniczy wpływ wody w emulsji mazutu na emisję WWA i sadzy do atmosfery. Zawartość 10% wody w emulsji mazutu obniża ponad dwukrotnie emisję sadzy do atmosfery, co było równoznaczne z podobnym zmniejszeniem emisji WWA, gdyż sadza jest nośnikiem WWA. Zjawisko to tłumaczy się mikroeksplozyjnym charakterem procesu spalania emulsji.

ВЛИЯНИЕ МНОГОЯДЕРНЫХ АРОМАТИЧЕСКИХ УГЛЕВОДОРОДОВ НА ОБРАЗОВАНИЕ САЖИ И ЕЕ ЭМИССИЮ В АТМОСФЕРУ

Представлен процесс образования сажи в пламени тяжелого жидкого топлива (мазута), а также его водных эмульсий в зависимости от содержания многоядерных ароматических углеводородов (МАУ) в топливе. Исследования вели в печи объема камеры сжигания ок. 1 м³, снабженной измерительной аппаратурой, способствующую определению всех термических и химических параметров процесса сжигания.

Было установлено, что интенсивность образования сажи в высокотемпературной зоне пламени была выше для мазута большего содержания МАУ. Исследования обнаружили принципиальное влияние воды в эмульсии мазута на эмиссию МАУ и сажи в атмосферу. Содержание 10% воды в эмульсии мазута понижает свыше двухкратно эмиссию сажи в атмосферу, что было равнозначно с похожим понижением эмиссии МАУ, ибо сажа является носителем МАУ. Это явление объясняется микровзрывчатым характером сжигания эмульсии.