Technology for Improving Water-Fuel Oil Emulsions Properties Using Polycarboxylic Acids

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Abstract

The technology of improving water-fuel emulsions (WFEs) properties through modification of IFO-380 marine fuel oil with aqueous solution of polycarboxylic acids surfactant was researched. Aqueous solution of the surfactant was used as water phase at WFEs production as well as emulsifier and corrosion inhibitor. It was established that viscosity, fluidity and corrosive activity of the obtained WFEs matched those of the unmodified IFO-380 marine fuel oil, while sulphur content, vanadium and coking parameters of the WFEs were lower, than those of the bunker fuel oil. An average size of water particles in the WFEs was 1–3 μm.

Introduction and Analysis

Emissions of noxious substances from combustion of marine fuels are restricted in respect of International Atmosphere Protection Programs and requirements of International Maritime Organization (**IMO**) [1]. Redrafted Annex IV of the International Convention for the Prevention of Pollution From Ships (MARPOL 73/78. Convention Annex VI), putting increasingly tougher demands on ships, came into force in July 2010. The new requirements cover almost all groups of noxious emissions, including NO_x. The Three-Tier System of Nitrogen Oxide (NO_x) Emissions Standards is being introduced in accordance with these new requirements: Tier I for pre-01.01.2011 built ships (currently valid norms for 2000 and post-2000 built ships). Tier II for post-01.01.2011 built ships (20 % reduction of NOx emissions). Tier III for post-01.01.2016 built ships (80 % NOx emissions reduction). The aforesaid requirements are not applied to ships less than 24 m in length and less than 750 kW in capacity.

The requirements towards sulphur oxides (SO_x) content in exhaust gases are equally tough [1]. As for 2012, it has been required to reduce SO_x content in heavy fuel oils to 3.5 %, and from 2020 – it must be reduced to below 0.5 %. The requirements towards noxious substances content in exhaust gases of marine engines are even tougher for the North Sea, the Baltic Sea, the English Channel, coastal waters of North America, and additional areas (SECA).

Different methods are used to reduce the content of noxious substances in exhaust gases of marine engines. The methods of fuel and/or air pre-cleaning are simple and acceptable. Mixing fuel and water to obtain stable water-fuel emulsions is the most suitable option for large two-stroke engines. Mixing air for combustion, introducing water for direct injection is not an option for two-stroke engines due to the risk of water drops getting into the combustion chamber and washing out the lubrication oil film from the cylinder. Use of alternative fuels is not common at present due to difficult operation and need to redesign the fuel system and engine.

Continuous Water Injection into air is believed to be most economically efficient for low levels (10–30 %) of NOx reduction, however insufficient experience with application of this method requires further analysis thereof.

Direct Water Injection into the cylinder is considered to be efficient for medium levels of NOx emissions reduction (40–60 %), though it requires engine modernization. This technology is economically efficient for the redesigned engines.

Notwithstanding the initially high capital costs, a relatively new method, using Humid Air Motor, is economically efficient to attain NOx emissions reduction at the medium and high levels of 60–80 %. Restricted operational background shows that equipment for this technology can be installed in the engine room and the water supply system redesigning is not necessary.

Selective Catalytic Reduction Systems and Selective Non-Catalytic Reduction Systems to restore NOx are most expensive compared to all the aforesaid technologies. Use of these technologies allows attaining practically complete reduction of NO_x emissions. These technologies are ideal for ships running in the regions of tough environmental demands [2–5].

NOx Selective Catalytic Reduction Systems are used for maximum reduction of NOx emissions. The drawback of such systems is their high cost. High level of gas purification from NOx (up to 90 %) with the aid of catalytic regenerators installed in the exhaust line of the diesel engine requires considerable additional expenses of US$ 40–70 per one kW, i.e. additional expenses per one ship with a 5000 kW power-plant make US$ 200–350 thous. for a pre-overhaul period of the diesel engine operation. The like expenses are necessary to manufacture a system for reduction of NOx in exhaust gases by 70 % of the IMO specified standard value [7].

Selective Non-Catalytic Reduction Systems are of a considerable disadvantage that restricts the application scope thereof in transport vehicles, namely, efficient purification of exhaust gases in the practically realized NOx neutralizers is ensured in a relatively narrow temperature range of 900–1200 °C. Ammonia NH_3 is most commonly used reducer, toxicity, fire and explosion risks of which require special arrangements during storage and transportation to the neutralizer reactor [5].

Use of water-fuel emulsion (**WFE**) is believed to be one of the most promising approaches. This is a simple and low cost technology to attain the medium level (30–50 %) of NOx emissions reduction for the existing ships without a need to considerably redesign the diesel engines.

Marine fuel oil cost can be reduced by 50 % through conversion of super-ships from diesel and mid-viscosity fuels to high-viscosity marine fuel oils. Normal operation of the marine engines with specific parameters is ensured through use of a rather wide range of marine fuel oil brands. For instance, both IFO 30 or IFO 180 and the cheaper IFO 380 marine fuel oils can be used. The aforesaid fuels are produced from residual oil derivatives and middle distillates [6].

Deteriorated quality of the operation process, which leads to an increased consumption of fuel and lubricants, excessive wear of the cylinder-piston group and fuel equipment is the main problem arising from conversion of diesel engines to operation on heavy fuel oils. The reason for these is poor quality of heavy fuel oils, often containing water. Purification of such fuels is a complex task since their density exceeds that of the water they contain. A more complex system of fuel treatment is required when the engines operate on heavy fuels solely. Such system should be equipped with a homogenizer, vapour-heated dual full flow filter, viscosity meter, fuel flow meter, recirculation line with a relief valve to maintain constant fuel pressure upstream the fuel pump [6].

Water-fuel emulsion is a special type of fuel that qualitatively and quantitatively changes the process of combustion. When heated in the cylinder, finely dispersed particles of the aqueous phase contained in fuel turn into vapour bubbles that instantly break the drops of fuel into the smallest parts. These parts are faster to heat and more intensive to interact first with oxygen formed from water dissociation, then they ignite and by mixing with the oxygen of an air burn at an accelerated rate. The aqueous phase, as a part of emulsified fuel, can be partially dissociated as the fuel oxidation progresses during the pre-flame processes. Then, the water dissociation reaction accelerates as a temperature increases in the phase of active combustion. Excessive hydrogen atoms formed at dissociation quickly diffuse in the zone of excessive oxygen, where the reaction thereof compensates for energy spent for water dissociation. An additional amount of hydrogen involved in the combustion reaction produces increased number of combustion products. Water molecules accelerate the reaction path in the oxidation processes due to a polar effect that considerably improves the orientation of the particles of active radicals in fuel [7–18].

5–10 % of water added to fuel accelerates combustion process 5–6 times. An extended range of additional combustion products improves operation of gases in the engine cylinder. Owing to more complete and accelerated combustion of fuel, continuous gasification of carbon deposits, the parts of the

cylinder-piston group and exhaust line are not contaminated with the combustion products and are less exposed to wear caused by abrasion. An increased dispersion of the residual fractions, splitting of hydrocarbon molecules exposed to cavitation into lighter fractions, and intensive mixing of a multi-component medium in high-turbulent vortexes makes for a hastened combustion reaction, thus permitting to compensate for the effect of aromatic hydrocarbons on a delay in fuel self-ignition. When the marine diesel engines are converted to operate on water-fuel emulsions, containing 17–20 % of water, fuel consumption is reduced by 12 %, nitrogen oxides NOx emissions are reduced by 30–40 %, sulphur dioxides SO_2 – by 50 %, hydrogen sulphides H_2S – by 50 % and, unburned hydrocarbons are eliminated completely. As the efficiency of fuel utilization increases, temperature of exhaust gases reduces by 8–10 $^{\circ}$C consequently reducing combustion intensity of the cylinder-and-piston group parts and consumption of high-viscosity water-free fuel by around 5 % [11].

When deciding on conversion of marine diesel engine for operation on WFE, it is reasonable to consider the level of engine boost, used fuel grade, and operation conditions of a ship. As a rule, recommended optimum concentration of water in WFE for the engines of an average effective pressure of up to 1.0 MPa, is not higher than 10–15 %. For more boosted engines it can be as much as 30–40 % depending on the demands placed on the noxious substance content in exhaust gases and on the engine operation economy. Emulsion can be prepared both immediately before fuel use in the engine, and during supplying fuel into the day tank. The properties of used fuels and availability of emulsifying additives are the determining factors in this case. Hence, it is possible to develop the guidelines on WFE use under any operational conditions of each specific marine engine by varying the concentration of water in WFE, features of the fuel equipment, and additives [7].

Materials and Methods

Water-fuel emulsion is a finely dispersed fuel-water mixture; in this case, water is the disperse phase, and fuel is the disperse medium, i.e. fine particles of water are evenly distributed within the fuel. The most optimal sizes of water particles in water-fuel emulsions developed as fuel for diesel engines are those with the size of ≈2–3 μm and those, with the size smaller than 5–10 μm. Smaller water particles negate the efficiency of micro-explosions; larger ones impair reliable operation of the fuel equipment [19].

Water-fuel emulsions are metastable liquids and their metastable state depends on the third substance, i.e. emulsifier. Most common emulsifiers are surface-active agents (**SAA**), including calciferous, magnesium, aluminium salts of higher fatty acids, various resins, natural rubber, dextrin, synthetic polymers, and polymeric non-ionic SAA, having hydrophilic and hydrophobic alternating groups. Currently SAA based on oleic acid and salts thereof, products of ethylene oxide synthesis and fatty alcohols sulphonation are widely used as emulsifiers. 1% of such emulsifier is usually sufficient to form stable water-fuel emulsions. Finely dispersed mineral powders are also used as SAA. When wetted with both phases of the emulsion at different points of the surface they kind of stick to the interphase boundary fixing the disperse phase drops [16–20].

Challenges related to creation of stable water-fuel emulsions are associated both with the selection of emulsifiers and compliance with a whole set of requirements imposed on engine fuels. First of all content of an emulsifier in the emulsion should be as low as possible, because even 0.5 % of SAA may cause enhanced deposition of carbon in the combustion chamber, and engine wobble. Moreover, emulsifiers and decomposition products thereof should not be toxic and corrosive, should not decrease water-free fuel antiknock rating. All these additional requirements add to this difficult task of creating stable water-fuel emulsions [20].

Water globules in the shell of SAA, consisting of the heaviest residual fractions, are held on the globules surface due to superficial tension of water particles. As a result, the residual fractions of bunker fuel oil (diesel) do not contaminate surfaces of the fuel filters, do not deposit in the heaters and pipelines. Long molecular compounds of high-viscosity hydrocarbons when treated in the hydrodynamic units are split into light straight-chain hydrocarbons that turn into cyclic and branched radicals as the reactions progress. Being exposed to high-frequency oscillations, long molecules of the bunker fuel oil are split in the carrying flow into shorter compounds C_2–C_5 that under the critical parameters of the treated medium, chemical reactions and phase transformations form gas fractions; molecular compounds C_8–C_{10}, fractions of distillate fuels C_{15}. Thermal treatment causes complex recombination transformations of the torn pieces of molecules into light hydrocarbon fractions with redistributed hydrogen. New qualitative characteristics of bunker fuel oil associated with the phase transformations keep properties thereof unchanged for a long time under normal conditions [21].

Humic substances are known to be used as efficient SAA; they are added to provide better solubility of hydrophobic organic agents (for example, oil products). Humic substances include three components: humin, a non-recoverable residue that is neither alkali nor acid soluble; humic acids, an alkali-soluble and acid-non-soluble fraction (at pH < 2); fulvic acids, both alkali- and acid-soluble fraction. Humic and fulvic acids put together are described as humic substances. Humic substances act as analogues of detergents, reducing the superficial tension at the "oil product-water" interface [22–26].

Humic substances belong to the class of high-molecular weight aromatic polyhydroxy polycarboxylic acids. Humic substances molecules contain condensed aromatic rings, heterocycles and various functional groups (carboxy, hydroxy groups, amines, etc.) [22, 27]. By means of combined evident hydrophobic and hydrophilic parts inside the molecules, the salts of humic acids (humates) are capable of showing properties of anionic surfactants. Humates of alkaline metals (Na, K) are well adsorbed on the surfaces of the interface of emulsions (oil-water). Hence, they can be used as chemical additives to various disperse systems. Such compounds can be used, for instance, as emulsifiers and stabilizers in the process of getting fuel emulsions, etc. [28–30]. Multifunctional action of humic acids as SAA allows extending the scope of application thereof for use in other systems that traditionally utilize synthetic and usually expensive SAA [31].

Nobel Ltd. (Saint Petersburg) developed the polymer eco-surfactant TGP-F/01 that belongs to the class of high molecular aromatic polyoxipolycarboxylic acids. These often comprise condensed aromatic rings, heterocycles and various functional groups (carboxylic, hydroxylic, amines etc.). Owing to combination of hydrophobic and hydrophilic parts of the molecule such compounds are able to act as anionic surface-active compounds. Sodium or potassium solution of the TGP-F/01, being well absorbed on the oil-water interface, can be considered as a good candidate for use in various disperse systems, where it can act as an emulsifier and stabiliser. One example of such disperse systems is fuel emulsions. In the pilot study TGP-F/01 polymer ensured prolonged stability of the WFE prepared on the basis of IFO380, M100 marine fuel oil, stored at the temperature from 15 to 30 °C. The WFE containing 5–20 % water remained stable even after 12 months of production.

In accordance with the Stalagometric method weight of the drop falling from the capillary glass tube is proportional to the surface tension of liquid and the tube radius:

$$m = 2\pi R\sigma/g,$$

where g – gravitational acceleration, m/s^2; m – weight of drop of the examined liquid, kg; σ – surface tension coefficient, N/m; R – capillary tube opening radius, m.

The Wilhelmy plate method is used to determine the force (F) that has to be applied to withdraw from the liquid a thin plate immersed in it. The surface tension is calculated using the following formula

$$\sigma = F/2(l + b),$$

where F – force, N; l and b – plate width and thickness, m.

Results of the measurements are presented in Table 1.

As can be seen from Table 1, at 1 % concentration the TGP-F/01 exhibits surface-active properties reducing surface tension of aqueous solutions. At this concentration, components of the TGP-F/01 merge into micelles and their charge and properties change. Further increase of concentration of the TGP-F/01 above 10 % reduces surface tension by over 20 %.

All known technologies for manufacturing of emulsions can be divided into two groups:

1) devices with movable parts;

2) devices with external energy supply (without movable parts).

Mixers of the first group are divided into those with rotary motion and those with translational motion.

Mechanical mixing is realized in the devices jointly named as agitators. In the general case the agitators can be divided into high-speed and low-speed agitators. Mechanical agitators require high energy to obtain quality WFE.

Oscillating agitators cause the flows of liquid to occur in a vessel while rocking. When compared to the rotary

Table 1

Effect of TGP-F/01 on surface tension

Surface tension, $\sigma \cdot 10^{-3}$, N/m	Concentration of TGP-F/01 surfactant in aqueous solution, %						
	0.001	0.1	1	2	5	10	12
Stalagometric method	73	70	69	69	68	59	52
Wilhemly plate method	72	72	70	66	64	58	55
Mean value	72.5	71	69.5	67.5	66	58.5	53.5

agitators, which action is also determined by liquid friction on the vessel walls, they are advantageous in creating vertical alternating motion of particles, which does not require, this way or another, direction of the flow movement. Time required for dissolution, homogenization, or dispersion is considerably reduced under the oscillating mixing.

Ultrasonic emulsification ensures production of finely dispersed, almost homogeneous, and chemically pure emulsions. For the ultrasonic emulsification to occur, cavitation is necessary, which origin and process conditions determine the main relationships of emulsification with ultrasound intensity and frequency, temperature, pressure, existence of dissolved gases, etc. Special transformation and matching devices are used to transmit ultrasonic oscillations to the treated mediums [32].

Use of such ultrasound devices is inappropriate due to their low efficiency and high specific energy consumption.

Rotor-stator devices represent efficient equipment to provide a multi-factor pulse effect on heterogeneous liquids ensuring production of stable, finely-dispersed emulsions and suspensions, intensification of the process of dissolution and extraction of materials, modification of physical and chemical parameters of liquids, and destruction of molecular compounds [33, 34].

Concentration of a vast amount of energy and reasonable use thereof in the effective volume of RSD, through which an organized flow of the treated medium passes, high level of homogenization and dispersion are the main advantages of the devices, while high energy consumption is the drawback thereof [33, 34].

Use of static agitators, offering capability of continuous high-performance mixing cycle with a small-sized working vessel, as the main mixing equipment is an upcoming trend of the emulsification processes development. The agitator design provides for multiple readjustments of the velocity field and change in the flow direction of the mixed components.

Flow hydrodynamic (static) agitators are the mixers rigidly installed in the pipelines or circulation circuits and using energy of the process flows. The key advantages of these mixers include simple manufacture of the working parts, fast replacement thereof, absence of dead zones in the channels, small displacement of the mixing zone, and high strength and air-tightness. All these features allow to use these devices under the conditions of high temperatures and pressures [35].

According to the main purpose, the Shell Marine Fuel Specifications divide marine fuels as follows:
– Marine Gas Oil (MGO);
– Marine Diesel Oil (MDO);
– Intermediate Fuel Oil, Thin Fuel Oil (IFO, TFO);
– Heavy Fuel Oil, Residual Fuel Oil (HFO, RFO);
– Bunker Fuel Oil (BFO).

The indices of fuel quality are regulated by the international (ISO 8217:2010 Marine fuels) and national (state) (GOST R 54299-2010 Marine fuels – for Russia) standards and specifications. The international and national standards only specify most common requirements towards the most important fuel parameters. The international practice uses the earlier developed designation of medium- and high-viscous fuels: IFO-30; IFO-40; IFO-180; etc., where digits correspond to a value of kinematic viscosity values expressed in cSt units at 50 °C.

Marine fuels IFO-30, IFO-180, IFO-380 are produced from residual and medium-distillate oil products. Marine fuels IFO-30, IFO-180, IFO-380 are the analogues of G class marine residual fuels produced according to ISO 8217. IFO-30 is an analogue of ISO-F-RMC10, IFO-180 is an analogue of ISO-F-RMF 25, IFO-380 is an analogue of ISO-F-RMA 35.

Usually conversion of engines to high-viscosity fuels, leads to increase in operational expenses due to the following reasons:
– higher maintenance costs;
– higher specific fuel consumption due to lower combustion value;
– loss of dry-and-ash-free fuel due to fuel purification;
– shorter engine cleaning intervals;
– use of higher quality and more expensive engine oils.

Transportation, pumping, storage and heating of high-viscosity heavy fuel oils causes increased of water content in the form of individual local clusters. Use of specifically prepared water fuel oil emulsions (**WFOE**) as fuels is an efficient method of eliminating the above-mentioned negative factors. The problems that make the environmental situation even harder include on top of other things continuing accumulation of hundreds of thousands of oil-containing ballast waters. The sources of this problem are industrial enterprises, ocean and river fleet.

In many cases, the content of water in marine fuel oils considerably exceeds the admissible limit values (a water-cut of 12–16 % instead of 1.0 % is set by the standards). Due to the fact that the densities of marine

fuel oil and water are just one step away from each other, water does not settle on the bottom but is unevenly distributed in fuel in layers. Marine fuel oil drying through water evaporation is an energy-consuming process that also results in the loss of volatile fuel components. Dewatering is mainly performed through sedimentation. Separation of bunker fuel oil-water phases in settling pits takes considerable time and is inefficient, owing to almost similar densities of bunker fuel oil and water. The problem of utilization and purification of such waters cannot be solved chemically or biologically, as it demands large additional areas and high capital and maintenance expenses.

Use of WFOE gives considerable economical effect: 3–5 % increased of combustion efficiency, reduced emission of contaminants (CO, ash, nitrogen oxides, benzapyren and other carcinogenic polycyclic aromatic hydrocarbons) to the atmosphere.

Research Methods and Equipment

Use of agitators, the principle of operation of which is based on pulsations of velocity and pressure in flows of liquid, is one of the most efficient methods applied for resolution of the like problems. Such agitators include flow hydrodynamic mixers utilized in chemical, oil chemical, food, pulp and paper, and other industries to intensify processes of preparation of various emulsion compositions. Flow hydrodynamic mixers allow continuous cycle mixing of high

Fig. 1. Diagram of the prototype unit:
1 – flow hydrodynamic mixer; *2* – gear-type pump;
3 – jacketed process vessel; *4* – flow-meter; *5* – temperature
sensor; *6* – pressure gage; *7* – ball valves; *8* – heat exchanger line;
9 – pressure line; *10* – waste liquid discharge line;
11 – intake line; *12* – emulsion component tank;
13 – emulsion component supply line

efficiency and with a small effective volume. Economic efficiency due to use of such systems is associated with a smaller consumption of steel in the equipment, smaller production areas, smaller capital costs of construction required for premises, and reduced labour costs in connection with maintenance and servicing as opposed to the large efficient volume capacitive mixing equipment.

Water-fuel oil emulsion with the TGP-F/01 additive and water-fuel oil emulsion with distilled water (**WFOE-DW**) were obtained through cyclic mixing in a proprietary prototype hydrodynamic agitator, the schematic diagram of which is given in Fig. 1.

The prototype unit includes flow hydrodynamic mixer *1* with the inlet connector coupled via pressure line *9* to the outlet connector of gear-type pump *2*, and the outlet connector coupled via waster liquid discharge line *10* to process vessel *3* equipped with the jacket where treated liquid is cooled down or heated. Pressure line *9* is connected to a sample and discharge line equipped with ball valve *7*. The jacket is fitted with the lines for heat-transfer medium *8* or coolant supply. Process vessel *3* is connected to the inlet connector of gear-type pump *2* via supply line *11* and has the liquid supply lines equipped with ball valves *7*. Speed of the shaft of the gear-type pump electric engine is adjusted by means of frequency converter VFS11-4110PL-WN. Pressure at the inlet and outlet connectors of the flow hydrodynamic agitator is measured by pressure gage *6* (MT-100) and temperature of the treated liquid is measured by the temperature meter *5* (SH-04016). Emulsion component is supplied to the inlet connector of gear-type pump *2* from vessel *12* via line *13*.

The following method was used to make WFOE. Warmed-up marine fuel oil IFO-380 was supplied into the prototype unit at 60 °C. Warm marine fuel oil was transferred through the hydraulic system under a pressure of about 0.1 MPa and heated the unit hydraulic system to 70 °C. Upon warming up the unit, the warmed-up marine fuel oil was discharged from the unit and a new weighed portion of the marine fuel oil pre-heated to 60 °C was loaded and closed hydraulic loop circulation was started. Then a weighed amount of the TGP-F/01 aqueous solution was supplied to the inlet connector of the gear-type pump to ensure its even distribution and pre-mixture with marine fuel oil, circulating in hydraulic circuit of the 6 litres unit.

The hydraulic parameters were determined at a set speed of shaft of the electric pump engine, to ensure controlled supply of the liquid. The main parameters registered included pressure measured at the mixer's inlet connector, temperature measured at the pump
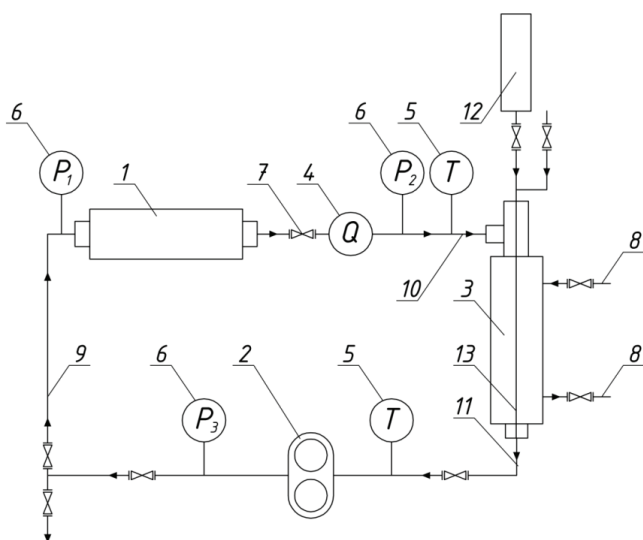
inlet connector and at the mixer's outlet connector. As the used hydraulic system was closed and liquid was pumped in a closed cycle, close to zero pressure was always registered at the mixer outlet connector.

To ensure even distribution of the coarse-dispersed mixture of marine fuel oil with the aqueous solution of the TGP-F/01 across the hydraulic system, pump delivery rate was increased to a set value and the mixture was circulated through the hydrodynamic mixer 10 times (cycles). The resulting emulsion was discharged and next portion of warmed up marine fuel oil was supplied to prepare next sample of the emulsion.

Ten cycles of WFOE treatment were performed. Average inlet pressure constituted 1.6 MPa, average flow rate through the mixer was equal to 15 m^3/h, an average pre-treatment temperature was 60 °C, an average post-treatment temperature was 68 °C.

The following samples of the water-marine fuel oil emulsion were prepared:

1) 2 % WFOE – 100 ml of the TGP-F/01 aqueous solution (25 % concentration) and 4.9 l of marine fuel oil;

2) 5 % WFOE – 250 ml of TGP-F/01 aqueous solution (5 % concentration) and 4.75 of marine–fuel oil;

3) 10 % WFOE – 250 ml of TGP-F/01 aqueous solution (5 % concentration), 250 ml of distilled water, and 4.5 l of marine fuel oil;

4) 15 % WFOE – 250 ml of TGP-F/01 aqueous solution (5 % concentration), 500 ml of distilled water, and 4.25 l of marine fuel oil;

5) 20 % WFOE – 250 ml of TGP-F/01 aqueous solution (5 % concentration), 750 ml of distilled water, and 4.0 l of marine fuel oil;

6) 5 % WFOE-DW – 250 ml of distilled water and 4.75 l of marine fuel oil;

7) 10 % WFOE-DW – 500 ml of distilled water and 4.5 l of fuel oil;

8) 15 % WFOE-DW – 750 ml of distilled water and 4.25 l of marine fuel oil;

9) 20 % WFOE-DW – 1000 ml of distilled water and 4.0 l of marine-fuel oil.

Results and Discussion

Parameters of the WFOE samples were determined in the laboratories of Tambov State Technical University and Mortestservice (Saint Petersburg). The resulting values are given in Tables 2–4.

Flash point is a fuel warming up temperature, at which vapours ignite when an open flame source approaches them. It is determined by the fraction composition and depends on the boiling and evaporation points of the fuel.

Flash point of the WFOE reduces as concentration of the TGP-F/01 in the fuel increases. Most likely, intensive hydrodynamic and cavitation treatment forces polycarboxylic (humic) acids and IFO-380 components to form compounds, flash points of which are lower than flash point of the original IFO-380.

Table 2

Kinematic viscosity, density and flash-point of the marine fuel oil and the WFOE containing the TGP-F/01

Parameter	Bunker fuel oil IFO-380	2 % WFOE	5 % WFOE	10 % WFOE	15 % WFOE	20 % WFOE
Kinematic viscosity	Kinematic viscosity at 7 days after the treatment					
at 80 °C, sCt	30.5	31.5	28.7	32.0	34.2	32.6
at 50 °C, sCt	106	112.6	104.3	105.9	120.7	116.0
Kinematic viscosity	Kinematic viscosity at 1 hour after the treatment					
at 80 °C, sCt	30.5	27.2	31.5	29.6	31	29
at 50 °C, sCt	106	93	118	109	114	109
Kinematic viscosity	Kinematic viscosity at 10 minutes after the treatment					
at 80 °C, sCt	30.5	31.8	28.6	33.7	41	40
at 50 °C, sCt	106	129.2	133.7	144	152	140
Closed cup flash point, C	95	101	104 (weak)	no	no	no
Density at 20 °C, kg/cm^3	981	961	971	971	973	976

Table 3

Physical-chemical characteristics of marine fuel oil and WFOE with the TGP-F/01

Physical-chemical parameters	Marine fuel oil IFO-380	5 % WFOE	10 % WFOE	15 % FOE	20 % WFOE
Kinematic viscosity, sCt :					
at 50 ºC, sCt	100.2	104.5	97.4	115.3	111.4
at 80 ºC, sCt	28.4	29.3	27.8	31.5	30.7
at 100 ºC, sCt	15.3	15.7	15	16.7	16.3
Density at 15 °C, kg/cm^3	964.9	967.9	969.9	969.5	975
Mass fraction of water, %	0.25	5.1	8.7	8.7	15.3
Closed cup flash point, ºC	100	86	86	76	74
Ash content, %	0.1	0.35	0.35	0.22	0.37
Hot filtering deposit, %	0.03	0.12	0.13	0.1	0.14
Freezing point, ºC	24	27	24	27	27
Sulphur content, %	1.76	1.61	1.55	1.44	1.16
Coke ability	6.45	6.73	6.38	6.24	5.62
Stability	N2	N2	N2	N1	N1
Vanadium content, mg/kg	72	50	39	44	37
Average particle size, μm	–	1	3	4	5

Density of the WFOE containing the TGP-F/01 was visually lower than the density of the original untreated marine fuel oil. Measured density of the samples of WFOE with the TGP-F/01 in 1 hour and in 7 days of storage at a room temperature demonstrated that the density of WFOE and the original marine fuel oil was almost the same. The density insignificantly increased with an increase in the concentration of water in WFOE. When assessed visually, a difference could be seen in the pace of discharge of the original marine fuel oil and WFOE containing the TGP-F/01 from the system. WFOE appeared to have lower density and was discharged faster than the original marine fuel oil or WFOE without the TGP-F/01. This phenomenon can be explained by the fact that upon discharge from the system, some structural changes occur in the WFOE due to post-discharge reduction of pressure and temperature in post-discharge. When the WFOE containing the TGP-F/01 are treated at elevated temperature and pressure, some structural changes that occur in the WFOE cause temporary reduction of viscosity. Upon discharge from the system, some reverse changes, such as relaxation of the WFOE, may take place. Measurements of viscosity of WFOE stored after treatment do not demonstrate reduction of viscosity compared to the untreated marine fuel oil.

Presumably, change in density occurs by the following mechanism.

An intensive hydrodynamic and thermal treatment at 70 °C changes structure of the marine-fuel oil. High-molecular paraffin hydrocarbon compounds and asphalt-resin matters are torn into shorter molecular

Table 4

Physical-chemical characteristics of WFOE and WFOE-DW

Physical-chemical parameters	5 % WFOE	10 % WFOE	5 % WFOE-DW	10 % WFOE-DW
Kinematic viscosity, sCt :				
at 50 °C, sCt	104.5	97.4	126	138
at 80 °C, sCt	29.3	27.8	34	36
Density at 15°C, kg/cm^3	967.9	969.9	967	968
Closed cup flash point, °C	86	86	64	72
Ash content, %	0.35	0.35	0.14	0.126
Freezing point, °C	27	24	27	30
Sulphur content, %	1.61	1.55	1.85	1.74
Coke ability	6.73	6.38	6.6	5.9
Vanadium content, mg/kg	50	39	58	51
Average particle size, μm	1	3	5	7

compounds, causing viscosity decrease. Addition of special additives into the treated bunker fuel oil makes for the process of breaking of high-molecular compounds. Depending on the properties of the additive, viscosity of the treated marine fuel oil can be significantly decreased compared to the untreated marine fuel oil.

Presumably, during the storage the WFOE restores structure of the original marine fuel oil containing conglomerates of paraffin and water particles. Density values of the untreated marine fuel oil and the WFOE indicate that the restored structure of the marine fuel oil is less dense, that is why density of the WFOE is lower than that of the untreated marine fuel oil.

Density of the WFOE slightly increases as the water content in marine fuel oil increases.

We can draw a preliminary conclusion that TGP-F/01 reduces viscosity of the WFOE, i.e. viscosity of WFOE without TGP-F/01 would be higher.

The density of WFOE increases with the increased water concentration in the emulsion. It conforms to the physical laws, as water density is higher than marine fuel oil density. It may be so that WFOE becomes slightly denser at storage and transportation.

Examination of the structure of WFOE was performed at the Central scientific-research institute of naval fleet (Saint-Petersburg) using optical-electronic device «Wideomat». To determine the particle size and structure, samples of the WFOE were heated to 800 °C and homogenised. WFOE drops were applied to the slides and analysed in the device. Optical examination of samples was performed at 360-fold magnification. Water globule sizes were calculated using specialized computer software.

Images of samples of the original IFO-380 marine fuel oil and the WFOE are presented in Fig. 2.

Analysis of the WFOE sample allows to conclude that resinous molecules encapsulate water globules forming developed interphase surface. Thickness of the resinous shell is commensurable to the size of water globules. Resinous films of asphalt-resinous and solid-resinous structures also form shell around water globules and mechanical particles (solid particles).

The most homogenous and fine-dispersed water-fuel structure was obtained in 5 % WFOE and 10 % WFOE solutions. Average size of water particles constituted 1 μm in the 5 % WFOE solution and 3 μm in the 10 % WFOE solution. Average size of water particles in the 15 % and the 20 % WFOE solutions was larger and constituted 3 and 5 μm, respectively. Irregularly distributed water globules could be seen in the two latter solutions. In the 15 % WFOE-DW and the 20 % WFOE-DW solutions particle size was even larger and constituted 12 and 13 μm, respectively.

Closed cup flash point of the WFOE with TGP-F/01 was lower than that of the original marine fuel oil. Hypothetically when the emulsion is treated, the longer molecules of hydrocarbons are broken down and more volatile and more combustible components are formed. This effect is positive as fuels containing more combustible components burn more completely. However, fuel fire hazard increases as the flash point decreases.

The content of sulphur and vanadium decreased with an increase in the concentration of water in the WFOE. Supposedly, these chemical elements formed compounds that could not be detected. When burning, reduced emissions of SO_2 is expected from the WFOE. Besides for the reduced emissions of contaminants, the corrosiveness of fuel decreases as the content of sulphur and vanadium therein lowers. When the engines operate on fuels with low vanadium and sulphur content, the fuel equipment will be subject to lesser wear and corrosion.

Presence of vanadium leads to formation of ash of high melting point that causes an intensive high-temperature corrosion of the exhaust valve and seats thereof, and also of boiler super-heater pipes. Presence of sodium makes for ash formation. Nitrogen is mainly coming to the air combustion zone with vapours of seawater.

When combusted, fuels even with low content of vanadium and sodium form salts and compounds (for instance, $Na_2V_6O_7$) with a melting point close to the temperature of discharged gases. Vanadium oxides, formed during combustion, together with ferrous compounds act as catalysts in the process of oxidation of sulphur gas SO_2 to SO_3. The latter, combined with water vapours forms sulphuric acid.

Melting point of vanadium oxide V_2O_5 is around 680 °C. Under normal conditions it is removed from the cylinder as a solid matter together with combustion products. If there are sodium compounds in fuel, melting point of V_2O_5 drops considerably to 400 °C and lower. When temperature of the hot engine parts, for instance, of the exhaust valves, exceeds melting point of the oxide, the latter sticks to metal of the mounting sockets and edges, forming active corrosive deposits thereon, preventing tight closure of the valves. In this case, the valves are often overheated that in turn results in intensive growth of deposits. Further on, being exposed to impact stresses, these deposits partially detach and exhaust gases, being in the cylinder under high pressure and therefore moving at high speeds,

a)

b)

c)

d)

e)

f)

g)

h)

i)
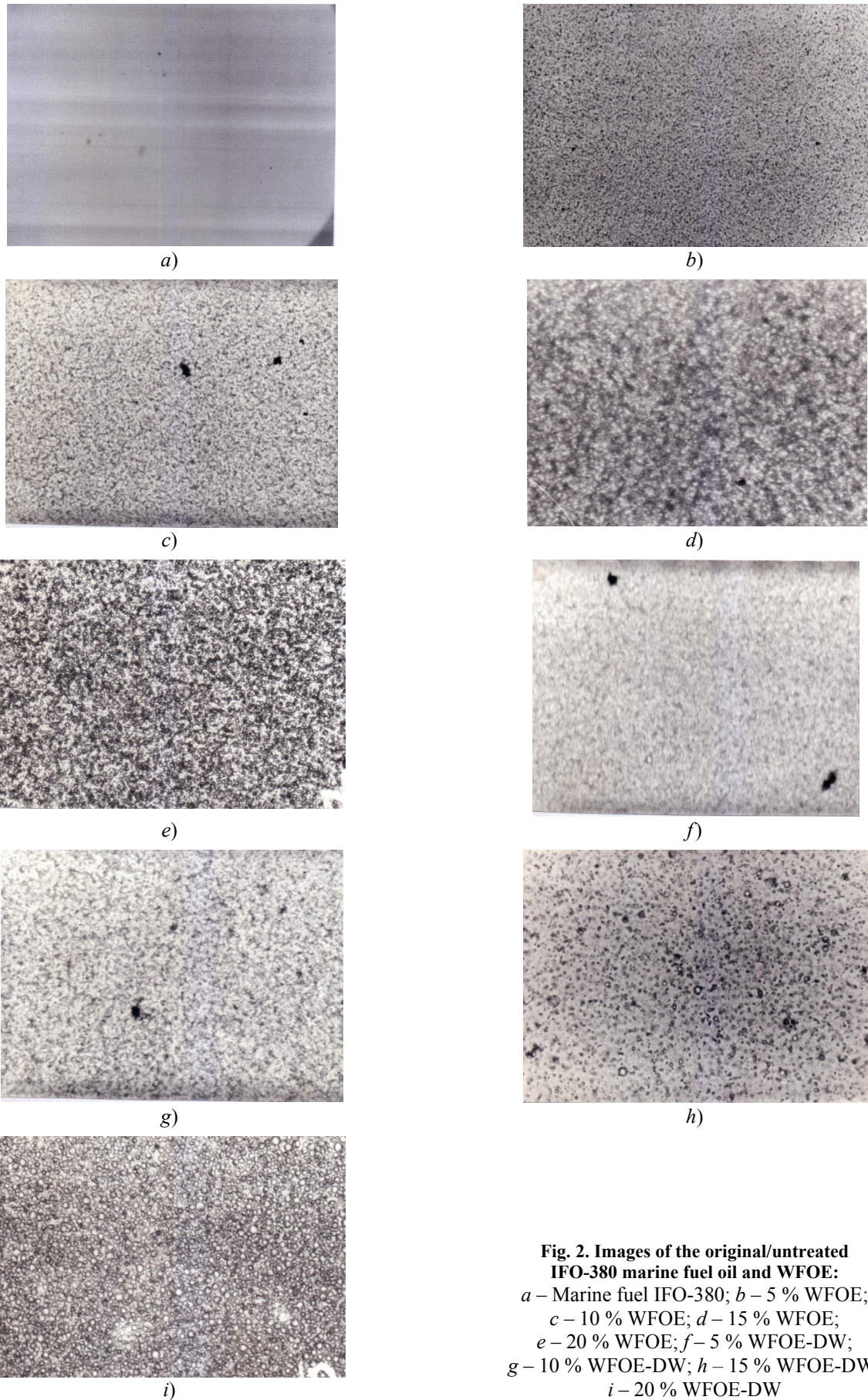
**Fig. 2. Images of the original/untreated
IFO-380 marine fuel oil and WFOE:**
a – Marine fuel IFO-380; *b* – 5 % WFOE;
c – 10 % WFOE; *d* – 15 % WFOE;
e – 20 % WFOE; *f* – 5 % WFOE-DW;
g – 10 % WFOE-DW; *h* – 15 % WFOE-DW;
i – 20 % WFOE-DW

penetrate the formed slit. As a result, in several weeks of operation grooves and channels are formed on the valve edges causing rapid early failure of the valves. Free sulphur and H_2S are not admitted in fuels of the marine engines.

Sulphites, disulphites, thiophens, and other sulphur compounds, being oil components, are less aggressive. All sulphur compounds are corrosive towards engine metal parts as in the process of fuel combustion they turn into oxides SO_2 and SO_3, responsible for electrochemical corrosion. At high temperature (more than 600 °C), sulphur trioxide SO_3 can cause gas corrosion on the exhaust valves and separate parts of piston bottom. Moreover, sulphur oxides accelerate polymerization of fuel and lubrication oil hydrocarbons, resulting in proportionally increased incrustation and lacquer formation as the sulphur oxide content increases therein.

Decreased coke ability of the WFOE at an increased water concentration, allows to expect that use of the WFOE will reduce incrustation in the engine and gumming of the engine injectors. Hypothetically, an increased ash content and hot filtering sediment can be explained by passage of mechanical particles from the system and precipitation of vanadium and sulphur salts.

Water mass fraction in the WFOE does not correspond to the actual water content in the emulsion at 10% and higher. One can presume that an intensive cavitation treatment breaks water particles into globules of several micrometres in size (based on the preliminary research data) and less. Small sizes of water particles probably do not permit complete detection of water mass fraction in marine fuel oil.

When the WFOE is used as fuel, the water phase therein can be partially dissociated as the fuel oxidation progresses during the pre-flame processes. Then, as a temperature increases in the active combustion phase, the reaction of water dissociation accelerates. An excess in the hydrogen atoms formed at dissociation is fast to diffuse in to the zone of excessive oxygen concentration, where the reaction thereof compensates for all energy spent on water dissociation. Involvement of an additional amount of hydrogen in the combustion reaction results in an increased amount of combustion products. Water molecules hasten the reaction path in the oxidation processes also due to the polar effect that considerably improves orientation of the fuel active radicals particles.

Reduced viscosity of the WFOE containing TGP-F/01 compared to the untreated marine fuel oil can reduce energy expenses for fuel transfer. Another important factor, in favour the WFOE use is the expected increased performance and lifetime of marine engine. When the emulsion is combusted, some drops hit the heated surfaces and explode thereon making for both deposits prevention and cleaning of surfaces from old ash formations.

The high content of sulphur in marine fuel oils is one of the most serious problems of combustion. Sulphur compounds escape with smoke gases, polluting the atmosphere that is currently inadmissible due to hard requirements placed on the emissions of fuel power plants. The engines of ships running in coastal waters or ports of some states (the USA, Sweden, etc.) should not operate on fuels with sulphur content higher than 1.0 %.

A preventive measure is use of sulphur trapping additives. These additives are added to smoke gases or bunker fuel oil. As major part of the additives is water soluble, addition of cheap components into emulsified water in small amounts provides a simple way for sulphur trapping and use of low quality marine fuel oils. Water-soluble polymer TGP-F/01, containing humic acids, can be an additive of this kind.

Conclusions

1. Multifunctional effects of humic substances as SAA support their use for improvement of WFOE quality parameters, and for replacement of more expensive industrial SAA products. Polymeric additive TGP-F/01, comprising a set of humic acids, exhibits good adsorbing and emulsifying properties.

2. The most homogenous and fine-dispersed water-fuel structure could be seen in the 5 % WFOE and the 10 % WFOE. Mean size of water particles was 1 μm and 3 μm in the 5 % WFOE and in the 10 % WFOE solutions, respectively.

3. The experimental studies have demonstrated that addition of the polymeric additive TGP-F/01 does not change viscosity of the original marine fuel oil IFO-380. Viscosity of WFOE containing 30 % water without TGP-F/01 was twice as high as the viscosity of the original untreated marine fuel oil. Homogenisation of the TGP-F/01 with the marine fuel oil lowers viscosity of the latter, thus indicating that the amount of energy spent on fuel transfer can be reduced.

4. The sulphur and vanadium content have decreased as the water concentration increased. It is expected that combustion of the WFOE can ensure considerable reduction in SO_2 emissions. Apart from the reduced noxious emissions, a decrease in the sulphur and vanadium content in fuel will result in a

lower corrosive ability. Addition to emulsified water of small amounts of cheap compounds may be the simplest way of trapping sulphur and may render possible use of the low-quality marine fuel oils. The water-soluble polymer TGP-F/01 composed of aromatic polyoxipolycarboxylic acids can be used as an additive of the kind.

5. Reduced coke ability of the WFOE at an increased concentration of water allows to expect that use of the WFOE will reduce incrustation in the engine and gumming of the engine injectors.

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