THE FEATURES OF MARINE HEAVY LIQUID FUEL BURNING

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Abstract: *The marine engines use a very efficient fuel, but they have a relatively high output of NO_x emissions. The slow speed diesels tend to produce higher NO_x emissions than medium speed diesels. NO_x emissions participate to the formation of photochemical smog and acid rain. NO_x formation depends on the temperature of the burnt gas, the residence time of the burnt gas at high temperature and the existing amount of oxygen. This work presents the main theoretical characteristics of the ignition and combustion of the marine heavy fuel oil.*

Key words: *ignition, combustion, emission, low NO_x.*

1. The physical phenomena appearing at the burning of marine heavy fuels

The researches performed in the field of vaporization and burning the liquid fuels had a strong experimental feature having in view to clear up the development way of processes. During the tests made with cracked residues, the drops suspended by a quartz thread (filament) with a diameter of 0.1[mm] or by an electrode of a thermocouple, were introduced into an electric oven through which the pre-heated blast air is passing. The temperature variation of drop liquid, at its heating and vaporization, is submitted to the general laws governing the development of these processes of multicomponent fuels. So, during 2 seconds, the temperature of the drop rises quickly up to about 300 [C] and then, it slowly rises up to about 500 [C]. According to the rise of drop temperature, its dimensions change under the influence of two factors: the vaporization of lighter fractions on the surface and volume expansion. Due to these phenomena with contradictory effects up to about 450 [C], the drop dimensions don't practically change. At the temperature rise, the chemical reactions mainly have an influence over the drop dimensions. So, the resins are changed into coke (carboids) with steam and gas emissions. These emissions and the ductility of resins determine the growth of drops and the formation, as a result of cracking, of porous coked residue which is named – cenoshere. The higher the asphalt and the resin matter content in the cracked residue is, the longer the necessary time for the complete coking of drop and the bigger the dimensions of porous coked residue are. During the burning, the heat quantity received by drop from the front of the flame surrounding the drop, increases the resin-to-asphaltenes processes as well as

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the decomposition of asphaltenes with the formation of coke and finally, the cracking takes place at very high temperatures. Due to these processes, the partial or even the total coking of drop surface is induced. The surface coking, breaking the vaporization, increases the time for the overheating process of the drop, what accelerates the cracking of resins and asphaltenes in liquid phase with generation of gas and steam.

The release of gaseous fluids leads to the drop growth in the limits of membrane plasticity. If there aren't non-coked sections on the external surface of the drop, the gaseous fluids can't be blown off to the outside. In this instance, the internal pressure increases further on, leading to the membrane breaking, so, gases and liquid components outburst to the outside.

By comparing the life time of residual fuel drops with low viscosity with the life time of cracked residues [4], it has been found that the latter is longer. From those presented above result that the diameter of the drop doesn't decrease directly proportional to the consumed mass, namely, the following relation is not valid:

$$d^2 = d_o{}^2 - k\tau, \tag{1}$$

where:

d_o – the initial diameter of drop [m];
d – the diameter of drop after a time t [m];
k – the vaporization constant;
τ – the time [s].

So, by burning the residual fuel drops, the volatile matters are released burning in their gaseous phase, remaining the carbonous residue, namely, the cenosphere. This substance is composed of non-volatile components of fuel. The burning of these carbonous residues is produced on the surface and it is governed by the laws of heterogeneous combustion processes of solid fuels. Therefore, the carbonous residues have a longer time of burning to the volatile matters. The cenospheres give an increased emissivity to the flame. At the same time, they can cause losses by incomplete burning, polluting the air and acting as an abraser on the metallic parts of the circuits which lead the burning gases to the exhaust port. They usually have the shape of a sphere with a fragile and spongiest structure when they are generated by vaporization.

Their structure becomes compact and their dimensions are smaller when they are generated by burning the drops at high temperatures. So, at the air burning of residual liquid fuel drops [5], at a temperature of 700 [C], it has been found that the diameter of cenosphere is

$d_c = 0.66\ d_o{}^2$;
- and by the air vaporization of the same fuel at a temperature of 518 [C], its diameter was $d_c = 1.79\ d_o{}^{5/4}$.

The studies performed by means of x-ray diffraction showed that the cenospheres are composed of small graphitic crystallites having a height of about 18 [A] and a distance between them of about 3.5 [A] and the conditions under which they are formed, have a low influence over the mentioned dimensions.

2. The pollution emissions generated by burning the marine fuels

2.1. The pollution substances resulted from the burning of fossil fuels

By burning the fossil fuels results the following main substances according to their proportion: nitrogen (74 %), carbon dioxide (13 %) and water vapors (13 %).

Depending on the mixture quality (the air proportion in the mixture expressed in percentages, plus or minus, with the minimum air necessary for theoretical

combustion), the following substances are induced:

- carbon oxide up to 1% for rich mixtures ($\lambda \approx 1$) and 2% in the absence of air ($\lambda \leq 1$);
- oxygen up to 7% for very poor mixtures (50% air excess).

By burning also results, in small proportions, nitrogen oxides, hydrocarbons, particles, sulphur oxides. The last ones are classified in the following primary and secondary pollution substances:

- primary substances: carbon oxide (CO), radicals (HC), nitrogen oxides (NO_x), sulphur oxides (SO_2, SO_3), particles, carbon dioxide (CO_2);
- secondary substances: soot.

Among these substances:

a) those which directly harm the human body are:

- nitrogen oxides (NO_x);
- sulphur oxides (SO_x);
- carbon oxide (CO);
- some particles.

b) those which act on vegetation:

- sulphur dioxide (SO_2);
- Cl and H_2 compounds;

c) those which are the basis of acid formation:

- SO_2, SO_3, NO, NO_2;

d) those which are in the soil, that, within the biological chain: plant- animal – human being, accumulate and become noxious for the human body:

- heavy metals.

e) those which become the influence factors of climate:

- CO_2, N_2O and NO_2,

Among these noxious substances, NO_x is a pollutant with a wide range of action: in the classical marine firing plants, NO_x is formed in average quantities, their part in atmospheric pollution is significant.

The nitrogen forms five oxides, by its combination with oxygen:

- nitrogen hemioxide (nitrous oxide, nitrogen protoxide, diazot oxide) N_2O;
- nitrogen monoxide (nitrous oxide, azotic oxide) NO;
- nitrogen sesquioxide (nitrous anhydride, diazot trioxide) N_2O_3;
- nitrogen dioxide, NO_2;
- nitrogen hemipentaoxide (nitric anhydride, diazot pentaoxide) N_2O_5; we are mainly interested in nitrogen hemioxide, nitrogen monoxide and nitrogen dioxide.

2.2 The generation of NO_x emissions in the flame of marine thermal systems' furnace

The generation of nitrogen oxides during combustion takes place based on the atmospheric nitrogen and the fuel nitrogen. This system can be controlled by the initial measures proper to the combustion process. By observing the standards related to the maximum allowed level of NO_x emissions at evacuation, we can make a plan, taking into account two aspects:

1 – the control of system for generating NO_x in the furnace, by the initial measures;

2 – the cleaning of combustion gases, NO_x, by the secondary measures.

The modern combustion plants generally use both methods. In the low powered combustion plants, the cleaning of burnt gases by the secondary measures which is an expensive method and so, it is less used.

During the burning, the nitrogen monoxide (NO) is specially formed. The nitrogen dioxide (NO_2) represents fewer than 5% from the total formed nitrogen oxides (NO_x). The NO_x emissions are expressed in NO_2 because, although NO is mainly formed in the flame, then in the gas ducts and in atmosphere, it is turned into NO_2.

The special literature shows the presence of three mechanisms of forming NO_x, namely:

- the thermal mechanism of forming the nitrogen oxide from the atmospheric nitrogen necessary for burning;
- the mechanism of forming the nitrogen oxide from the fuel nitrogen;
- the mechanism of forming the prompt nitrogen oxide.

Though, for the marine generators furnaces we can't always state which is the part of each mechanism in total formation of nitrogen oxide, nevertheless it is important the systematization of these mechanisms to take measures for avoiding and limiting the NO_x generation.

Also, it is necessary to show off the main factors which have an influence over their developing rate, namely:

- the combustion parameters expressed by temperature, the oxygen concentration in the burning area and the down-time;
- the fuel specifications: thermal power, nitrogen content, content of volatile matters and reactivity.

In the Table 1 they are synthetically presented the forming reactions of nitrogen oxides, the area where they take place, as well as the values which influence their developing rate.

The reaction kinetics contains besides the reactions of forming NO from the fuel nitrogen, the reduction reactions of it by the burnt products, accordingly, the reforming reactions of N_2 and O_2. For the thermal and prompt mechanisms, the origin of nitrogen oxides, NO_x, is the atmospheric molecular nitrogen (N_2).

In case of NO induced from the fuel nitrogen, it is considered that N results from different fuel nitrogen compounds. From many tests it results that whatever the initial compound of N in fuel is, NO is formed by two compounds of –HCN form, and –NH form, respectively.

The formation of nitrogen oxides   Table 1

Nitrogen Oxides	Production Area	Reaction Mechanism	Factors of Influence
HERMAL NO	Flame, area after reaction	According to Zeldovich: a)air excess $O+N_2=NO+N$; $N+O_2=NO+O$ b)fuel excess $N+OH=NO+H$	-concentration of atomic oxygen; -type of reaction; -temperature higher than 1300^oC
PROMPT NO -products that will be turned into NO_x	Flam	According to Fenimore: $CN+H_2HCN+H$ $CN+H_2O-HCN+H$ $CN+N_2-HCN+N$	-concentration of atomic oxygen; -air excess factor
NO RESULTED FROM FUEL NITROGEN	Flame	$O+N_2=NO+N$; $N+O_2=NO+O$	-concentration of fuel N -concentration of O_2 - air excess factor -temperature of flame

Nitrogen Oxides	Production Area	Reaction Mechanism	Factors of Influence
NO_2	Flame	According to Fenimore: $NO+H_2O=NO_2+OH$	-quickly slowing down of burning reaction
NO_2	Smoke flues, chimneys	According to Bondestein: $2NO+O_2=2NO_2$	-temperatures of 600^oC - concentration of O_2 -time of reaction
NO_2	Free atmosphere	$O+O_2+M=O_3+M$ $NO+O_3=NO_2+O_2$	-concentration of O_2 -sun light -time of reaction -pollution degree of atmosphere

According to Zeldovich, the thermal formation of NO takes place in the flame and develops the following reactions:

a) in case of air excess, the nitrogen molecules reacts with the oxygen radicals resulted from the thermal decomposition of oxygen at very high temperatures:

$$O + N_2 \rightarrow NO+N \qquad (2)$$

The nitrogen radical resulted from this reaction and/or from thermal decomposition of molecular nitrogen, reacts with the oxygen molecule:

$$N + O_2 \rightarrow NO + O \qquad (3)$$
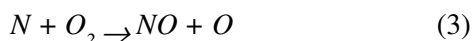
The two reactions mentioned above can also be written under the form of the following overall reaction:

$$N_2 + O_2 \Leftrightarrow 2NO; \qquad (4)$$

b) in case of fuel excess, the hydroxyl radicals (OH), generated by burning, react with the nitrogen radicals resulted from the thermal decomposition:

$$N + OH \rightarrow NO + H \qquad (5)$$
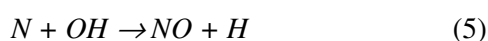
The main factors which influence the thermal formation of NO are:
- the concentration of atomic oxygen O, as a result of thermal decomposition of oxygen molecules O_2;
- the high temperature over 1300^oC;
- the time of reaction.

The equilibrium relation for the overall reaction (4) is:

$$K_{NO} = \frac{(NO)}{(N_2)^{0,5}.(O_2)^{0,5}} \qquad (6)$$

where :
K_{NO} – the equilibrium constant;
NO – the concentration of NO [%];
N_2 - the concentration of N_2 [%];
O_2 - the concentration of O_2 [%].

For the equilibrium constant, it is shown in the relation:

$$K_{NO} = 4.71e^{-9400/RT}, \qquad (7)$$

where :
R – the general constant of perfect gas [kJ/kmol K];
T – the absolute temperature [K].

In Table 2 they are presented the reaction rate constants and the activation energies for the reaction of the

mechanism of forming thermal NO. It is noted the strong temperature dependence. The reaction of the nitrogen molecules with the oxygen radical is the slowest one, so, it will represent a decisive step. The reaction of the atomic nitrogen (N), with the hydroxyl radicals (OH) is specific to the combustion conditions with λ<1.

Having in view that the fuel burning develops both under the over- and understoequimetric conditions, its part

can be neglected. For the formation of thermal NO, we can write:

$$\frac{d(NO)}{dt} = 2k_{NO}(N_2)(O_2) \qquad (8)$$

where:

k_{NO} – the constant of reaction r.

The constants and the activation energies of different reactions   Table 2

REACTION	CONSTANT OF REACTION RATE [CM^3/MOL S]	ACTIVATION ENERGY [KJ/KMOL]	TEMPERATURE T [K]
$N_2+0 \rightarrow NO+N$	$7,6.10^7$. exp(-E/RT)	316	2000-5000
$N+NO \rightarrow N_2+O$	$1,6.10^7$	≈0	300-5000
$N+0_2 \rightarrow NO+0$	$6,4 .10^3$. exp (-E/RT)	26	300-3000
$0+NO \rightarrow 0_2+N$	$1,5 .10^3$. exp (-E/RT)	126	1000-3000
$N+OH \rightarrow NO+H$	$1,32. 10^8$	0	300-2500
$N0+H \rightarrow N+OH$	$2 .10^8$. exp (-E/RT)	200	2200-34500

During the burning we can note an excess of molecular nitrogen (N_2) and the concentration of atomic oxygen will be strongly influenced by temperature. The oxygen decomposition at normal temperatures of burning is minim. For instance, at 2000 [K], it represents under 10 [ppm]. Because of high values of the activation energy, mainly for the reaction (5), the thermal mechanism depends on the temperature, so, it may be said that, in case of heavy fuel burning, its contribution is of about 50% from the total quantity of NO$_x$.

Another factor which influences the formation of thermal NO is the time of reaction. The reaction, dependent on

temperature, which is complicated enough, is slow and up to the reach of an equilibrium concentration, there is a certain time. If we succeed in removing the reactants from the reaction area before reaching the equilibrium and their transfer in a lower temperature area, it will generate less NO than it might usually form at the burning temperature.

From those mentioned above, it results the following considerations:

- the formation of thermal NO will take place where the burning develops at temperatures over 1300 [C];
- a certain reduction of burning temperature in the furnaces with a high

thermal load (heat density) it will form more NO than in those with low thermal load, due to high temperature. This explanation is related to the law of exponential dependence of the phenomenon on the forming reaction of thermal NO;

- in the high thermal load furnaces, it will form more NO than in those with low thermal load due to high temperature.

- having in view that the time for forming NO is different for each plant, the primary measures for reducing the

formation of thermal NO_x are used.

2.3. The mechanism for forming the prompt nitrogen oxide

The prompt nitrogen oxide is also formed in the flame as a result of the interaction of radicals of CN and CH types with molecules of H_2, H_2O and N_2. Firstly, the cyanides HCN are formed. According to Fennimore and Becker the reactions are developed in this way:

$$CN + H_2 \rightarrow HCN + H; \qquad (9)$$

$$CN + H_2 0 \rightarrow HCN + Ohl; \qquad (10)$$

$$CH + N_2 \rightarrow HCN + N \qquad (11)$$
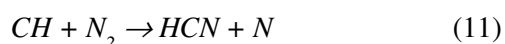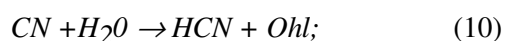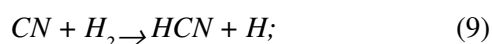
The cyanides formed, are turned into radicals having the form NH_i (i = 0, 1, 2, 3). These generate the nitrogen oxide NO in the presence of atomic oxygen or radicals OH.

The main factors which have an influence over the formation of prompt nitrogen oxide are: the concentration of atomic oxygen and the air excess factor.

The mechanism for forming the prompt NO, also due to the atmospheric nitrogen molecules, can be represented in this way:

$$N_2 \xrightarrow{CH/C_2/C} CH/HCN \rightarrow NH_{i \to NO}^{\to N_2} \quad (12)$$

The formation of atomic nitrogen and the compounds CN is possible only in the flame areas under substoequiometrical burning conditions rich in fuel.

Therefore, it can be considered that the contribution of this type of mechanism to the formation of total quantity of NO is negligible (under 10 [ppm]).

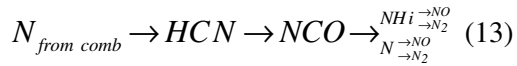## 2.4. The mechanism for forming the nitrogen oxides from the fuel nitrogen

The nitrogen oxide resulted from the fuel nitrogen is also formed in the flame by a complex mechanism, partially unknown. It is known that, firstly, the radicals of CN form are generated, of which development in the presence of oxygen leads to the formation of NO.

The main factors which determine the quantity of NO are: the nitrogen content of fuel, the concentration of oxygen in the flame, the time of reaction and the flame temperature. The mechanism for forming the thermal nitrogen oxide is much slower than that for forming the prompt nitrogen oxide.

The formation of NO from the fuel nitrogen develops faster than the formation of thermal NO but much slower than the formation of prompt NO.

The compounds based on fuel nitrogen result from the decomposition of proteins and nucleic acid from the fossil material. It is a matter of aliphatic compounds as primary, secondary and tertiary amines (RNH_2, R_1R_2NH, $R_1R_2R_3N$) or aromatic compounds as pyridine (C_5H_5N) and imidol (C_4H_5N).

The mechanism that is the basis of forming NO based on the fuel nitrogen is schematically presented in this way:

$$N_{from\ comb} \rightarrow HCN \rightarrow NCO \rightarrow {}^{NHi \rightarrow NO}_{N \rightarrow N_2} \ {}_{\rightarrow N_2}^{\rightarrow NO} \quad (13)$$

It is noted that the secondary compounds of HCN, NH_i and/or CN types are formed from the fuel nitrogen. These will react generating NO and N_2, respectively.

The activation energy for molecular nitrogen generation is lower than that necessary for the formation of nitrogen oxide. This minimum difference, of only 21–35 [kJ/mol], explains the reduced influence of temperature over these two mechanisms.

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