

# A probabilistic concept of assessment of amount of noxious substances contained in exhaust gas emitted from self-ignition engines

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## ABSTRACT



*A probabilistic concept of toxicity assessment of exhaust gas emitted from self-ignition engines was presented. Without such assessment it is not possible to determine pro-ecological merits of various transport means driven by self-ignition engines, including inland waterways passenger ships. In the concept a model of starting-up process of self-ignition engines was taken into consideration. The model was presented in the form of a semi-Markovian process, discrete in states and continuous during service. The states of the process are : the cold engine state ( $s_1$ ), warm engine state ( $s_2$ ) and hot engine state ( $s_3$ ). It made it possible to determine probabilities of the starting-up of engines from its particular states. For determination of mass of noxious substances contained in exhaust gas it is necessary to know the probabilities. Usefulness of the model in assessing amount of the noxious substances results from that during the starting-up of such engines many noxious substances are produced.*

**Keywords :** engine start-up, self-ignition engine, noxious substance

## INTRODUCTION

Presently, has been carried out research work on manufacturing the bio-degradable fuels having energy properties similar to those of fuel oils and being pro-ecological as much as possible, and which could be used to ship diesel engines instead of fuel oils. However before taking any decision on application of an alternative fuel to self-ignition engines it is necessary to perform a comparative analysis of combustion processes of fuels of the kind in such engines. It means that the following parameters of energy transformation in the engine should be considered {see Fig. 1. [13]} : overall efficiency of engine ( $\eta_o$ ), heat emission coefficient ( $w_e$ ), heat utilization coefficient ( $w_{wc}$ ), heat generation coefficient ( $w$ ), pressure increase rate ( $\varphi_p$ ) etc, and content of such noxious substances in exhaust gas should be also analyzed, as : carbon monoxide (CO), hydrocarbons ( $C_nH_m$ ), nitric oxides ( $NO_x$ ), solid particles and sulfur compounds ( $SiO_2$ ,  $SiO_3$ ,  $H_2SO_3$ ,  $H_2SO_4$ ), aldehydes etc. Such analysis should show either that some alternative fuels make it possible to achieve better energy indices, or that they are more pro-ecological or even have both the merits. It can be based on laboratory tests. However no positive opinion on possible substitution of diesel oil for a given alternative fuel can be given without service tests of self-ignition engines. Only on the basis of such tests it can be unambiguously stated whether a given alternative fuel assessed fully applicable to diesel engines by means of laboratory tests will not cause a relatively greater wear of their main parts such as : injection system, piston-cylinder system and crankshaft bearings. Hence for the above mentioned analysis identification of combustion processes of diesel oil and alternative fuels in the aspects of energy, ecology and engine wear, is required.

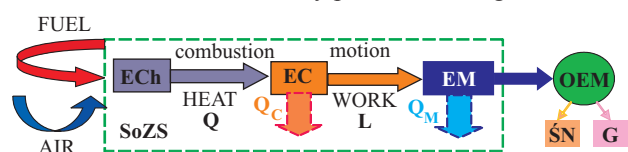
In this work in the frame of such identification an original probabilistic method for assessing mass of possible noxious substances emitted from self-ignition engine has been proposed. In the method a model of starting-up the engine was taken into account. It was demonstrated that such model can be built in the form of

semi-Markovian process. The presented proposal of assessment of toxicity of exhaust gases during start-up of the engine is important as environmental pollution by noxious substances is usually the highest just during engine start-ups.

## ENERGY AND PRO-ECOLOGICAL FEATURES OF COMBUSTION PROCESS IN SELF-IGNITION ENGINES

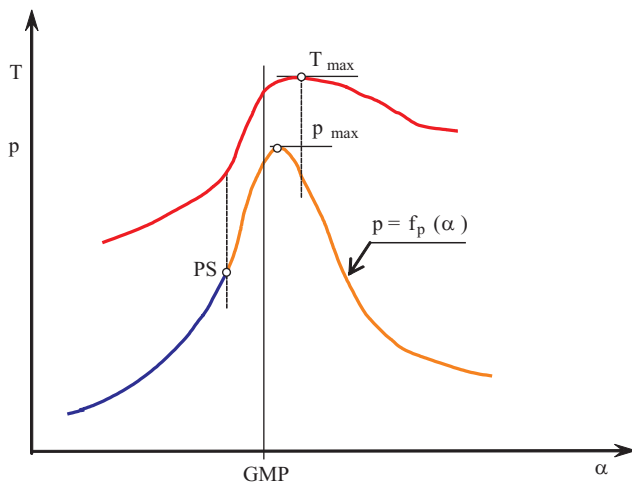
Combustion process in working volumes of self-ignition engines should ensure possibly the best energy indices as well as high engine reliability and durability and low environmental pollution [2, 9, 10, 13, 14]. Diesel engines for inland waterways passenger ships are fed with diesel oil. It would be advisable to use an alternative fuel having more pro-ecological merits, instead of diesel oil. Therefore the necessary knowledge of combustion processes of the above mentioned fuels should deal with transformation of chemical energy contained in the tested fuels (Fig. 1) into heat energy and next mechanical one, as well as its various effects. Moreover, application of an alternative fuel should not cause any faster wear of engines on which their reliability and durability as well as operational safety depend. In analyzing the run of combustion process in cylinders of self-ignition engines special attention should be paid to problems of emission of noxious substances the largest amount of which is produced during engine start-ups.

During operation of an arbitrary self-ignition engine the double transformation of energy occurs [2, 10, 13]. Such energy transformation is schematically presented in Fig. 1.



**Fig. 1.** An example schematic diagram of energy transformation in self-ignition engine : **ECh** – chemical energy; **EC** – heat energy; **EM** – mechanical energy; **SoZS** – self-ignition engine;  $Q_c$  – thermal load;  $Q_m$  – mechanical load, **OEM** – energy consumer; **SN** – screw propeller; **G** – electric generator.

Degree of perfection of energy transformation in self-ignition engines with taking into account the transferring of a part of transformed energy through its particular structural elements to surroundings, i.e. the dissipated energy ( $E_s$ ), is determined by using the overall efficiency of engine. The efficiency depends on losses occurring during work of engine, which are proportional to the dissipated energy ( $E_s$ ). The energy constitutes the difference between the energy delivered to the engine ( $E_d$ ) and the useful energy ( $E_u$ ) produced by the engine in operation. The delivered energy ( $E_d$ ) is chemical energy contained in the fuel injected to engine combustion chambers, and the useful energy ( $E_u$ ) – mechanical energy delivered to energy consumers, e.g. screw propellers in the case of ship main engines (Fig.1). The investigations which have been done so far and concerned the run of combustion process in particular cylinders with taking into account not only fuel properties but also their working condition, made it possible to obtain a very high efficiency of self-ignition engines [2, 9, 10, 13, 14]. However not only the energy aspect is important. Important are also the contaminations contained in exhaust gases of the engines. Hence in shipboard conditions the combustion process cannot be assessed only on the basis of realization of pressure and temperature changes in cylinders (Fig.2) [9, 13, 14].



**Fig. 2.** Schematic diagram of run of pressure and temperature changes in cylinder of self-ignition engine :  $p$  – pressure,  $T$  – temperature,  $\alpha$  – crankshaft rotation angle,  $p_{max}$  – maximum pressure,  $T_{max}$  – maximum temperature;  $PS$  – the beginning of fuel combustion in cylinder;  $GMP$  – upper dead centre of piston [16].

Among factors which significantly influence run of combustion process the following can be rated [9, 13, 14] :

- a) physical and chemical properties of fuel, especially its chemical content, cetane number (LC), auto-ignition point ( $T_{sz}$ ) and viscosity ( $\nu$ )
- b) engine design features, especially type of its combustion chamber, compression ratio ( $\epsilon$ ), air temperature ( $T_d$ ) and pressure ( $p_d$ ) at the beginning of air inlet to cylinder
- c) engine's main dimensions such as : the cylinder diameter ( $D$ ) and piston stroke ( $S$ ), piston material, injector type and run of process of fuel injection to combustion chamber
- d) operational parameters of engine such as : torque load ( $M_o$ ), rotational speed ( $n$ ), injection pressure ( $p_w$ ), combustion air factor ( $\lambda$ ), ignition advance angle ( $\alpha_{ww}$ ), cooling water temperature at inlet to engine ( $T_{wd}$ ), amount of residual exhaust gases from the preceding cycle ( $\gamma_r$ ).

The factors have impact on : ignition lag, quality of fuel spraying, velocity of conversion of fuel complex combustible particles into simpler ones such as :  $H_2$ , C, S and CO which can be oxidized, rate of pressure rise ( $\phi_p = dp/d\alpha$ ), temperature ( $T_{ks}$ ) and pressure ( $p_{ks}$ ) in the end of compression.

Correctness of run of combustion process can be assessed also by means of such parameters as [22] : heat emission coefficient ( $w_e$ ), heat utilization coefficient ( $w_w$ ), heat generation coefficient ( $w_{wc}$ ), heat generation rate ( $w$ ), the ratio of the maximum heat generation rate ( $w_{max}$ ) and ignition-lag ( $\tau_{zz}$ ).

From the heat generation characteristics it results that in order to ensure maximum transformation of the heat ( $Q$ ) into the work ( $L$ ) (see Fig. 1) it is necessary to form combustion process in such a way as to generate the largest amount of  $Q$  in the initial phase of combustion process, as close to GMP as possible (Fig.2). However it should be observed that then dynamic combustion indices grow. Therefore both combustion time and amount of the heat generated in the initial phase of combustion should be so selected as to obtain a compromise between heat utilization economy and mechanical load on engine crankshaft assembly system, as well as noise associated with its operation. Also, run of process of oxidation of combustible fuel components and formation of compounds noxious to the environment, should be taken into account. Primary products of oxidation resulting from chain reactions constitute peroxides and hydro-oxides which next undergo disintegration. The disintegration products enter into reaction with oxygen, which results in forming aldehydes, acids, water vapour, carbon monoxide (CO) (very noxious) and dioxide ( $CO_2$ ), and is associated with heat reduce. Carbon monoxide is also produced in such processes as [1] :

- ❖ low-temperature oxidation of hydrocarbons
- ❖ disintegration of RCHO aldehydes
- ❖ high-temperature dissociation of  $CO_2$ .

From research on fuel combustion processes it results that physical, but not chemical, factors have significant influence on emission amount of particular noxious components of exhaust gas, and that their emission is tightly mutually connected and the possible lowering of emission of one of them may cause increasing emission of another. Therefore all undertakings aimed at lowering content of noxious components in exhaust gas must result from a compromise to obtain minimum noxious effects of detrimental impact of the components to the environment.

From the literature sources [1, 5, 6, 15] it results that prevailing amount of noxious components in exhaust gas is produced during start-up of engine. Hence in order to predict amount of noxious compounds in exhaust gas a model of engine starting-up process should be elaborated with taking into account at least three engine states, namely : cold, warm and hot, in which such process is possible.

### **SEMI-MARKOVIAN PROCESS OF SELF-IGNITION ENGINE STARTING-UP**

The three distinguished thermal states of self-ignition engine, which can exist just before its starting-up, namely : the cold state ( $s_1$ ), warm state ( $s_2$ ), and hot state ( $s_3$ ), can be taken as values of the stochastic process  $\{U(t) : t \in T\}$ , assumed to be the model of the real starting-up process of engine. According to [6, 4, 16] such model can be presented in the form of a semi-Markovian process having the set of states :

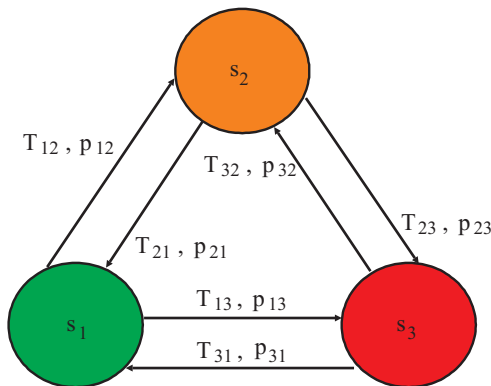
$$S = \{s_1, s_2, s_3\} \quad (1)$$

and the following interpretation of the states :

- ☆ the cold state  $s_1$  which makes it possible to start up the engine in ambient conditions (in ship engine room) characteristic of a low temperature ( $T$ ), not greater than 290 K as a rule
- ☆ the warm state  $s_2$  which makes it possible to start up the engine in conditions of pre- heating the engine ( $T > 300$

K), performed before its starting-up, and which was in the state  $s_1$  before the pre-heating process is commenced  
 ☆ the hot state  $s_3$  which makes it possible to start up the engine in its working conditions which result from the necessity to stop it even under large load and then to start up it again.

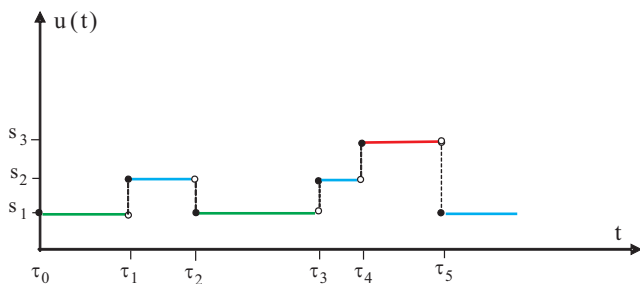
The graph of states of the considered starting-up process,  $\{U(t) : t \geq 0\}$ , of self-ignition engines is shown in Fig.3.



**Fig. 3.** The graph of states of starting-up process of an arbitrary diesel engine :  $s_1$  – cold state,  $s_2$  – warm state,  $s_3$  – hot state,  $p_{ij}$  – probabilities of transition of the process from the state  $s_i$  to the state  $s_j$ ,  $T_{ij}$  – duration time of the state  $s_i$ , provided that the process passes to the state  $s_j$ ;  $i, j = 1, 2, 3$ .

The triple-state process is of continuous realizations. It is semi-Markovian process [3, 4, 16] and – in the considered application – the simplest one out of those having practical importance.

Hence the set of the starting-up states of self-ignition engines,  $S = \{s_1, s_2, s_3\}$ , can be considered as the set of values of the stochastic process,  $\{U(t) : t \in T\}$ , of constant (uniform) intervals and realizations continuous on the right. The example realization of the process is presented in Fig. 4.



**Fig. 4.** An example of realization of the process,  $U(t) : t \in T$ , of self-ignition engine :  $\{U(t) : t \in T\}$  – engine starting-up process,  $t$  – time of operation;  $s_1$  – state of full serviceability;  $s_2$  – state of partial serviceability;  $s_3$  – state of non-serviceability.

The initial distribution of the considered process  $\{U(t) : t \in T\}$  (see also Fig.3 and 4) is, for self-ignition engine, determined by the formula :

$$P_i = P\{U(0) = s_i\} = \begin{cases} 1 & \text{for } i = 1 \\ 0 & \text{for } i = 2, 3 \end{cases} \quad (2)$$

and, the functional matrix of the process is as follows :

$$Q(t) = \begin{bmatrix} 0 & Q_{12}(t) & Q_{13}(t) \\ Q_{21}(t) & 0 & Q_{23}(t) \\ Q_{31}(t) & Q_{32}(t) & 0 \end{bmatrix} \quad (3)$$

In the case of main engine of any ship it may be expected that its stays in ports would be long enough the engine to be cooled down up to the cold state after some time. Hence the repeated start-up of engine to continue the voyage will be per-

formed from the state  $s_1$ . Moreover, the engine may be at idle running for a short time before starting-up. In consequence, the starting-up of engine may also commence from the state  $s_2$ . Also, the cases of the starting-up of main engines from the state  $s_3$  cannot be omitted that is usually associated with manoeuvres in ports or during moving through canals.

Hence for the presented process  $\{U(t) : t \in T\}$ , of the initial distribution (2) and functional matrix (3), one can determine the following limiting distribution [3, 4, 16] :

$$P_1 = \frac{\pi_1 E(T_1)}{H} ; P_2 = \frac{\pi_2 E(T_2)}{H} ; P_3 = \frac{\pi_3 E(T_3)}{H} \quad (4)$$

and :

$$\pi_1 = \frac{P_{31} + P_{12}P_{32}}{2 + P_{12}P_{23}P_{31} + P_{13}P_{21}P_{32}}$$

$$\pi_2 = \frac{P_{32} + P_{12}P_{31}}{2 + P_{12}P_{23}P_{31} + P_{13}P_{21}P_{32}}$$

$$\pi_3 = \frac{1 - P_{12}P_{21}}{2 + P_{12}P_{23}P_{31} + P_{13}P_{21}P_{32}}$$

$$H = \pi_1 E(T_1) + \pi_2 E(T_2) + \pi_3 E(T_3)$$

where :

$P_1, P_2, P_3$  – probabilities of the event that self-ignition engine is started up from the states :  $s_1, s_2, s_3$ , respectively

$\pi_j$  – limiting probability of the Markov chain which is inserted into the process  $\{U(t) : t \in T\}$ , and describes possible occurrence of the state  $s_j$ ,  $j = 1, 2, 3$

$p_{ij}$  – probability of transition of the process  $\{U(t) : t \in T\}$  from the state  $s_i$  to the state  $s_j$

$E(T_j)$  – expected value of duration time of the state  $s_j$ , ( $j = 1, 2, 3$ ).

The presented starting-up states of any self-ignition engine are associated with relevant thermal states which represent those occurring in practice. Hence the proposed model may be used to determine mass of noxious substances contained in exhaust gas.

During starting-up the cold engine (state  $s_1$ ) an increased emission of hydrocarbons ( $C_nH_m$ ) and carbon monoxide (CO) occurs. Hence the starting-up of engine in a low temperature makes emission of carbon dioxide ( $CO_2$ ) lower. However, emission of solid particles increases, but emission of nitric oxides ( $NO_x$ ) decreases. It is due to a low temperature of fresh charge, that makes forming such compounds more difficult.

The reason of the situation are too low temperatures of surfaces of the elements which form combustion chamber, exhaust gas system and cooling system, [1, 7, 11, 12].

Too low temperature of cylinder walls causes intensive flame extinguishing (break of chain of chemical reactions). It leads to combustion quality worsening. As a result appears a greater amount of not fully combusted hydrocarbons in various forms, and a greater emission of CO and soot, in particular. The greater emission of soot results from a low temperature of engine cylinder interior, that is not conducive to burning-out the soot. According to [1] The absence of the soot burning-out phenomenon takes place in the case of lowering the temperature in the cylinder below  $500 \div 600^\circ C$ , which happens even if there is a sufficient amount of oxygen in it.

Too low temperature of exhaust gas system, like low temperature in cylinder volume, is not conducive to carbon dioxide (CO<sub>2</sub>) forming. It results from the fact that combustion of carbon monoxide (CO) formed in low temperatures and carbon dioxide (CO<sub>2</sub>) forming is possible only in the temperature more than 300°C [1].

Also, too low temperature of engine elements due to low temperatures of cooling water, makes full combustion developing more difficult. Moreover, low temperature of lubricating oil makes it much more viscid, that causes an increase of engine resistance to motion and thereby a loss of output power and increased fuel oil consumption. It results in an increased emission of noxious components of exhaust gas, especially CO, except of nitric oxides (NO<sub>x</sub>).

During cold engine starting-up intensive wall effect occurs. It takes place when temperature of fuel-air mixture near the combustion chamber walls is too low to trigger correct combustion process, because of excessive loss of the heat transferred from the produced exhaust gas to the combustion chamber walls. As a result significant drop of temperature of fuel-air mixture in the boundary layer occurs, as much down as below its ignition temperature. According to the chain theory, the flame extinguishing results from decreased concentration of active particles of intermediate combustion products. Limiting value of the concentration, below which flame cannot be maintained, is function of pressure, temperature and content of combustible mixture in a given engine working volume.

### DETERMINATION OF MASS OF NOXIOUS SUBSTANCES DURING STARTING-UP PROCESS OF ENGINE

Analyzing research results on combustion process running (Fig. 2) one can state that during the process different conditions for forming the above mentioned noxious compounds occur in exhaust gas. Moreover, it is known that properties of fuel oil, including sulfur content in it, influence the exhaust gas toxicity [1, 8, 9, 14].

Sulfur content in diesel oil has significant impact on emission of noxious compounds, mainly solid particles, as it lowers engine life-time by accelerated wear of its elements being in contact with exhaust gas. During combusting sulfur compounds in engine working volume sulfur dioxide (SiO<sub>2</sub>) and trioxide (SiO<sub>3</sub>) is formed, which, in contact with water particles, produce sulfurous, (H<sub>2</sub>SO<sub>3</sub>), and sulfuric, (H<sub>2</sub>SO<sub>4</sub>), acid, respectively. A part of sulfur particles in the form of sulfur ions is absorbed by surface of solid particles and then discharged together with them to the environment.

Increase of cetane number (LC) of diesel oil makes content of carbon monoxide (CO) and hydrocarbons (C<sub>n</sub>H<sub>m</sub>) in exhaust gas, smaller. According to [26], the rise of cetane number, e.g. from 40 to 50, decreases CO emission by 25% and C<sub>n</sub>H<sub>m</sub> one - by 40%. Moreover, increase of the LC of diesel oil leads to a lower level of noise generated by engine : e.g. in the case of the diesel oil of LC = 48, engine noise level reaches 76 dB(A), and for LC = 60 - that of 73 dB(A).

Decrease of the diesel oil density (ρ) from 0, 845 [kg/dm<sup>3</sup>] to 0, 825 [kg/dm<sup>3</sup>] results in the drop of particulate matter emission by 5 ÷ 10% [16]. Such decrease of content of polycyclic aromatic hydrocarbons is favourable. For instance, by lowering the content of the hydrocarbons in diesel oil from 9% to 1% it is possible to reduce amount of particulate matter in exhaust gas by about 5% [16].

Toxicity of exhaust gas can be reduced also by introducing special additions which are able to lower content of noxious

compounds in it. Nonetheless, mass of noxious substances which may be contained in exhaust gas, should be known in any case both before and after actions aimed at lowering their content.

Mass of emitted noxious substances can be determined by means of the following formula [1] :

$$e_k = \frac{v_{\text{mix}} \rho_k K_H C_k}{s} 10^{-6} \quad (5)$$

where :

$k = 1, 2, \dots, n$  – number (kind) of noxious substance

and :

- $e_k$  – mass of a polluting substance [g/km]
- $v_{\text{mix}}$  – volume of diluted exhaust gas in the normal conditions [dm<sup>3</sup>/test]
- $\rho_k$  – density of polluting substance in the normal conditions [g/dm<sup>3</sup>]
- $K_M$  – correction factor of humidity of mass of nitric oxides
- $c_k$  – concentration of a substance polluting the environment [ppm]
- $s$  – distance covered by a ship during conducting the tests [km].

The emission  $e_k$  ( $k = 1, 2, \dots, n$ ) is different depending on whether the starting-up commences from the cold state ( $s_1$ ), warm state ( $s_2$ ), or hot state ( $s_3$ ). During ship voyage of the length ( $s$ ) when the test has to be conducted, many engine start-ups may be performed from its different states. The emission from the same engine will be also different as it depends also on technical state of equipment of its fuel system, and kind of fuel oil on which it works. Important are also ambient conditions in which the engine has to start up. Therefore it can be assumed that the mass of emitted noxious substances derived from the formula (5) constitutes realization of the emission which can be taken as the random variable  $E_k$ . Hence the mass of noxious substances can be expressed, by taking into account the relations (4) and (5), in the form of the expected value as follows :

$$E(E_k) = \frac{(p_{31} + p_{12}p_{32})E(T_1)}{M} e_{1k} + \frac{(p_{32} + p_{12}p_{31})E(T_2)}{M} e_{2k} + \frac{(1 - p_{12}p_{21})E(T_3)}{M} e_{3k} \quad (6)$$

and :

$$M = E(T_1) + p_{12}E(T_2) + (1 - p_{12}p_{23})E(T_3)$$

where :

- $E(E_k)$  – expected value of the random variable  $E_k$
- $e_k$  – mass of  $k$ -th substance polluting the environment, ( $k = 1, 2, \dots, n$ )
- $p_{ij}$  – probability of transition of the engine starting-up process  $\{U(t) : t \in T\}$  from the state  $s_i$  to the state  $s_j$ ,  $i \neq j$ ;  $i, j = 1, 2, 3$
- $E(T_j)$  – expected value of duration time of the state  $s_j$  ( $j = 1, 2, 3$ ).

The formula (6) results from the fact that all relations given in the formula (4) which determines the probabilities  $P_1, P_2$  and  $P_3$ , as well as the relation (5) were taken into account.

## FINAL REMARKS AND CONCLUSIONS

- The largest emission of noxious substances contained in exhaust gas occurs during the starting-up process of engines.
- Therefore it was proposed and demonstrated that to assess amount of emitted substances a semi-Markovian, triple-state model of engine starting-up process, i.e. that to which the three states : cold, ( $s_1$ ), warm, ( $s_2$ ), and hot, ( $s_3$ ) are attributed, can be applied.
- Usefulness of the model for determining mass of the noxious substances emitted to the environment during engine starting-up was made evident. It was assumed that the masses of polluting substances,  $e_k$ , where  $k = 1, 2, \dots, n$  {n-kind (number) of a given noxious substance}, possible to be determined, constitute realizations of the random variable  $E_k$  which represents emitted mass of noxious substance of k-th kind.

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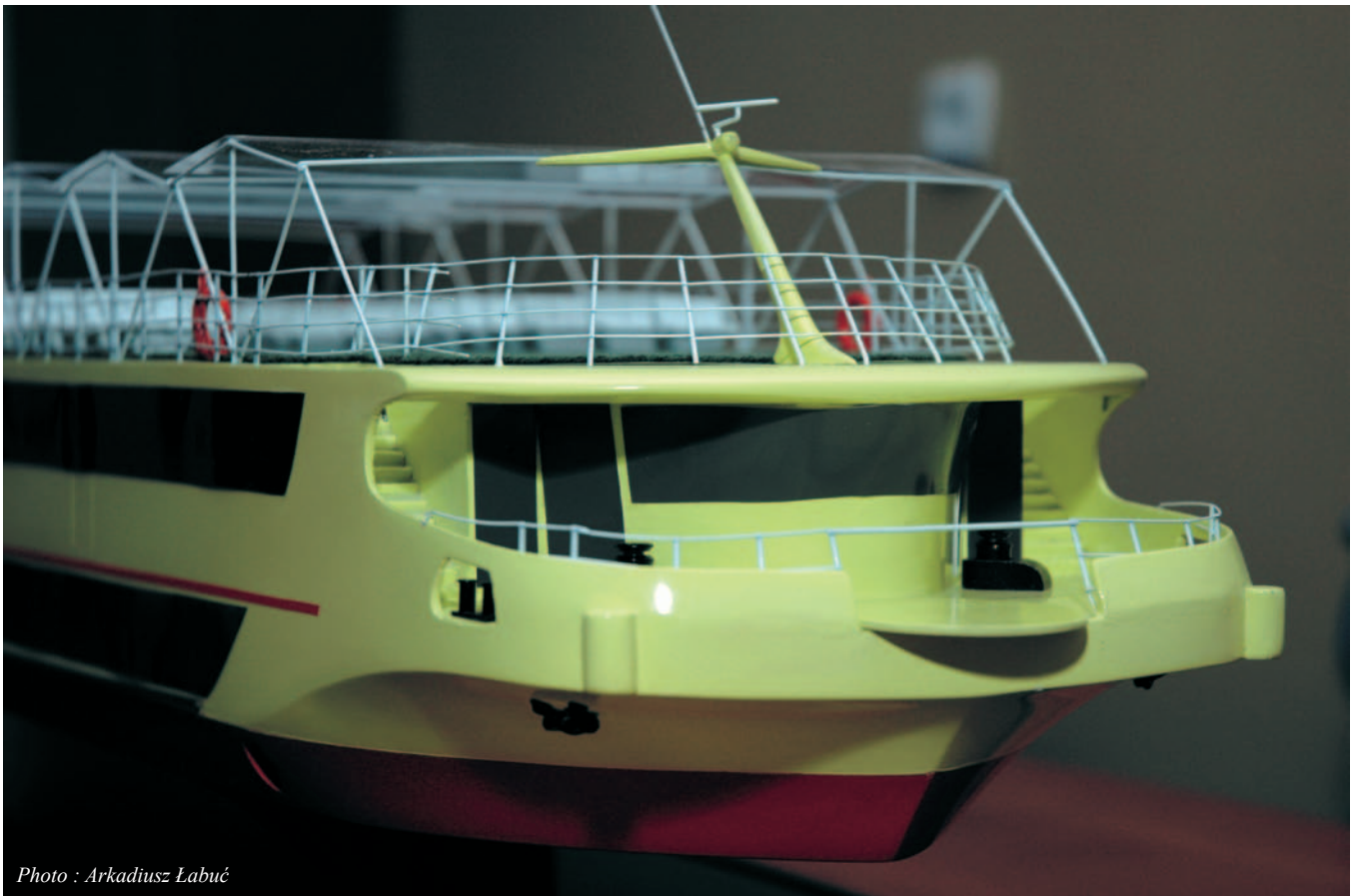


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