Use of Catalytic Processes for Treatment of Combustion Products of Pyroxylin Powders

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Abstract

Technology of deep catalytic treatment of gases generated during the combustion of pyroxylin powders, *i.e.* the stuffing for substandard small arms ammunition, was suggested. The technology is based on ammonium carbonate dosage directly into the furnace with ammunition, gas purification in "wet" treatment devices to remove catalytic poisons (lead-antimony compounds) and resinous substances, selective catalytic reduction (SCR DeNOx) of nitrogen oxides with ammonia vapours, and catalytic oxidation of CO to harmless products.

Keywords: pyroxylin powders, furnace gases, treatment methods, catalysts, SCR DeNOx, instrumentation

INTRODUCTION

In order to dispose of substandard ammunition (cartridges) equipped with pyroxylin powder (trinitrocellulose) by thermal treatment, the "Boston" rotary furnace with a system of automatic ammunition feeding is used at the Barnaul cartridge plant (BCP JSC).

The combustion of pyroxylin powder, percussion caps, and polymer coatings of ammunition proceeds at 300−350 °C and is accompanied by the formation of significant amounts of NO_x and CO. Furthermore, waste gases from the furnace contain fine particles of heavy metal compounds, such as solid combustion products of the cap filling components (PbO, Sb_2O_3) [1].

The content of toxic materials in waste gases is many times higher than maximum permissible concentrations.

The NITI named after P. I. Snegirev, and L. N. Koshkin KBAL JSCs deals with the development of setups for safe disposal of fuzes and cartridges in Russia. Nevertheless, their installations do not envisage integrated treatment of waste gases from harmful impurities [2−4].

In order to address this task, a setup that ensures total capture of solid particles, purification from nitrogen oxides to the MPC (maximum permissible concentration) level and oxidation of CO to CO_2 is required.

Relatively large solid particles may be captured in a precipitator tank, while finely dispersed ones − in "wet" apparatuses, by alkaline solutions [5].

With a view to disposing nitrogen oxides, selective catalytic reduction with ammonia (SCR DeNOx method) may be used. The catalytic technique is also promising for CO oxidation [6]. During selective catalytic reduction of nitrogen oxides over catalysts, there proceed the following reactions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$
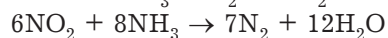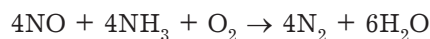
Whereas catalytic CO oxidation proceeds as follows:

$$2CO + O_2 \rightarrow 2CO_2$$
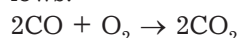
In addition to ammonia gas, reagents generating NH_3 may also be used in SCR DeNOx processes.

EXPERIMENTAL

Composition of furnace gases

Furnace gases were analysed for the organic matter content using LKhM-8MD chromatograph with a flame ionization detector. A stainless steel column with a 4 mm diameter and a 3 m length was used. It was filled with 30 % SILAR 5S on Chromosorb R; the column temperature of 120 °C and a nitrogen carrier gas flow rate of 30 mL/min.

In order to analyse carbon monoxide and dioxide in gases, LKhM-8MD thermal conductivity detector was utilised. Product separation was carried out in a stainless steel chromatographic column with a 4 mm diameter and a 1.5 m length filled with activated carbon SCT, column temperature of 120 °C, argon carrier gas flow rate of 30 mL/min.

Waste gases were investigated by GC-MS using Agilent 7890A GC chromatograph with the Agilent 7000 Series Triple Quadrupole GC/MS System using the NIST 08 MS Library (Boreskov Institute of Catalysis SB RAS, Novosibirsk).

Express analysis of a mixture of nitrogen oxides (NO and NO_2) and oxygen in exhaust gases was performed using Testo 335 electronic gas analyser with an O_2 sensor. Ammonia was determined according to the interaction with Nessler reagent in a photoelectric colorimeter.

Research for implementation of SCR DeNOx used AOK-78-55 aluminium-vanadium catalyst [7] (the manufacturer is Special Design and Engineering Bureau "Katalizator" JSC, Novosibirsk), and CO was oxidized over an iron oxide catalyst [8] (STK-05-3(F) (the producer is JSC Angarsk Plant of Catalysts and Organic Synthesis, Angarsk, Irkutsk region.).

The conversion degree (α) of nitrogen oxides and carbon monoxide was computed according to the formula:

$$\alpha = \frac{C_i - C_f}{C_i} \cdot 100 \ \%$$

where C_i and C_f are the initial and final concentrations of NO_x (CO), respectively, mg/m^3.

Treatment of furnace gases

The "Boston" furnace neutralizes both armed cartridges (powder, caps, lacquer and polymer coating) and shell casings equipped with caps only.

The production of ammunition for light weapons in BCP JSC uses pyroxylin powders of the grades VUfl, SSNf 30/3.69 cm, RVS 337, OSHf, and BT, and also percussion caps of the brands KV-16, KV-NV 16, KV-24, KV-24H, and KV-26Nf. The latter were manufactured by NPO Iskra JSC (Novosibirsk) and did not contain mercury compounds.

The average volume of gases during the combustion of 1 kg of pyroxylin powder reaches 950 L [9]. Calcium chloride, sulphur compounds, antimony, and lead are emitted into the atmosphere during the blasting of the caps.

The lacquer coating of cartridges (BL-51 lacquer) contains polyvinyl butyral, cresol-phosphate resin, linseed oil monoglyceride, cyclohexanone, and ethyl alcohol.

The polymer coating of cartridges comprises of a mixture of the composition FPCM-51 (based on polyorganosiloxane with an additive of a copolymer of butadiene with styrene) and aqueous dispersive and thermally stable Raduga lacquer (VD-KO 8180).

During the thermal action on these compounds, intermediate combustion products are generated. Many various organic compounds were determined resulting from GC-MS investigations (Table 1). Generally, all these compounds may be referred to micro impurities.

Macro impurities include nitrogen oxides, carbon monoxide, resinous substances, and solid combustion products, the content of which in flue gases is many times higher than the MPC.

In order to purify furnace gases, a process scheme involving pre-capturing the solid phase and resinous substances in devices of "wet" gas treatment, selective catalytic reduction of NO_x with NH_3 vapours, and catalytic oxidation of CO to harmless products was suggested.

With a purpose to carry out experiments directly near the source of emission of contami-

TABLE 1

Organic substances as part of exhaust gases from the "Boston" furnace

Compounds	Name
Benzene and its homologues	Benzene, toluene, ethylbenzene, 1,3-dimethylbenzene or 1,3-xylene, or metaxyllene
Biphenils	Biphenil
Condensed aromatic hydrocarbons	Naphthalene
Heterocyclic compounds	Quinoline, 2-methylquinoline, benzothiazole
Heterocyclic halogenated compounds	5-Fluoro-4-methyl-1H-imidazole
Nitrophenols	2-Nitrophenol, 2,4-dinitrophenol
Aldehydes	Benzaldehyde, glyceric aldehyde
Ketones	Bicyclo[3.3.2]decane-9-on, acetophenone, benzophenone, 4H-piran-4-on
Conjugated ketones	2-Cyclohepten-1-on
Quinone compounds	2,5-Diphenyl-2,5-cyclohexadiene-1,4-diene
Carboxylic acids	Benzoic acid

nants, a pilot plant with a 15–20 m^3/h gas output was made.

RESULTS AND DISCUSSION

Integrated scheme of furnace gas treatment

A plant for the integrated treatment of furnace gases (Fig. 1) consists of a unit for "wet" gas treatment (jet foam scrubber *1* and the absorber/condenser *2*), and also an SCR DeNOx unit of reduction of nitrogen oxides with ammonia and oxidation of CO (catalytic reactor *5*).

The pilot plant for the "wet" purification of real waste gases from the thermal furnace was tested at the industrial ground of the BCP JSC with furnace gases formed during the treatment of a mixture of cartridges and cases at a ratio of 1 : 1.

Waste gases were sampled directly from the thermal furnace. The flooding solutions were 3 % NaOH in the foam-jet apparatus and 1 % NaOH solution in the absorber/condenser.

The pilot plant operated with the following parameters: gas temperature in the foam-jet apparatus, 54–55 °C; temperature at the outlet of the absorber/condenser, not higher than 35 °C. Temperature of the flooding solution was 45–49 °C in the foam-jet apparatus and 32–35 °C in the absorber/condenser.
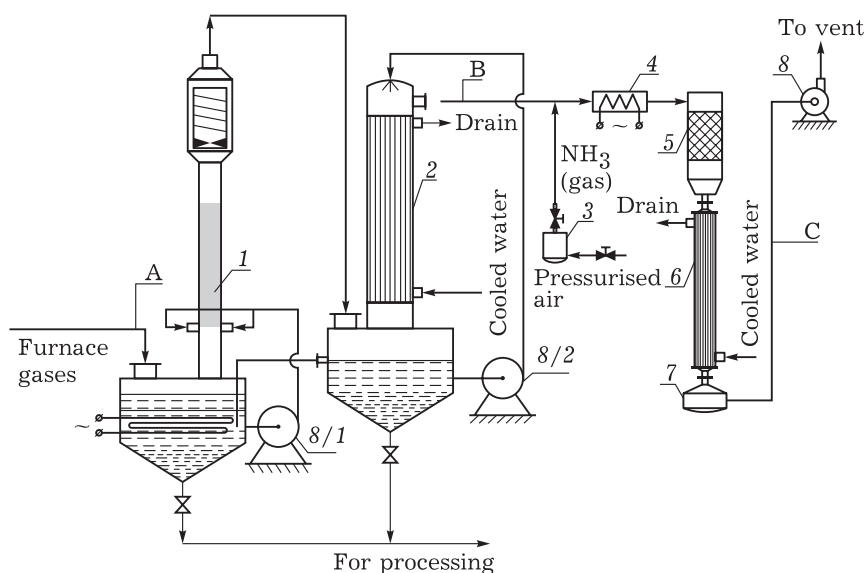

Fig. 1. Scheme of pilot plant for furnace gas treatment: *1* – jet foam scrubber; *2* – the absorber/condenser; *3* – ammonia vapour dispenser; *4* – electric heater; *5* – catalytic reactor; *6* –heat exchanger; *7* – droplet separator; *8/1*, *8/2* – water pumps; *9* – fan; A, B, C – gas sampling sites.

TABLE 2

Capture of nitrogen oxides by the "wet" stage of the pilot plant

Component	Jet foam scrubber		Absorber-condenser		Total capture degree, %
	Inlet, mg/m^3	α, %	Inlet, mg/m^3	α, %	
NO	5176	35.42	3342	80.16	87.19
	5835	39.54	3528	81.38	88.74
	5042	35.20	3267	80.10	87.10
NO$_2$	865.0	20.52	687.5	79.20	83.41
	1175	23.40	900.0	84.00	87.74
	962.0	22.30	747.5	81.70	85.78
CO	5954	0.00	5954	0.00	0.00
	7371	0.00	7371	0.00	0.00
	7768	0.00	7768	0.00	0.00

TABLE 3

Catalytic gas treatment from nitrogen oxides and CO in the pilot plant

Component	Temperature, °C	Content, mg/m^3		Degree of catalytic conversion, %	Total conversion, %
		Inlet	Outlet		
NO	273	663.0	3.8	99.43	99.93
	273	657.0	3.5	99.47	99.94
	271	650.2	3.9	99.40	99.92
NO$_2$	273	143.5	1.0	99.30	99.88
	273	144.0	1.1	99.24	99.91
	271	136.8	1.1	99.20	99.89
CO	273	5954	0.0	100.0	100.0
	273	7371	0.0	100.0	100.0
	271	7768	0.0	100.0	100.0

Results on the removal of nitrogen oxides at the "wet" stage of the pilot plant are presented in Table 2.

There were almost no solid particles (<1 mg/m^3) of aerosols at the exit of the pilot plant, while purified gases contained nitrogen oxides ("red smoke"). In irrigating solutions of "wet" devices, there was the accumulation of carbonates and nitrates, and also colouring materials (Bordeaux C dye according to Technical Conditions 6-36-5763445-759−89).

It is most advisable to dispose of the residual amount of nitrogen oxides and carbon monoxide using the catalytic method.
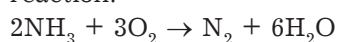
Selective catalytic reduction (SCR DeNOx) of nitrogen oxides with ammonia over AOK-78-55 catalyst was carried out in the temperature range of 270−280 °C, with the granulation of the catalyst d_g = 5.0−5.5 mm, concentrations of nitrogen oxides C_{NO_x} = 600−650 mg/m^3, ammonia C_{NH_3} = 1.0−1.1 g/m^3, and gas space velocity W = 16 600 h^{-1}.

Catalytic oxidation of CO with air oxygen was carried out over iron oxide catalyst STK-05-3(F) in the temperature range of 270−280 °C with the granulation of the catalyst d_g = 4.0−4.5 mm, concentrations C_{CO} = 6.0−7.7 g/m^3, and gas space velocity W = 21 000 h^{-1}.

Table 3 presents experimental data on gas purification from nitrogen oxides and CO.

Analysis of chromatograms of gaseous combustion products for the powder BT points to quantitative oxidation of CO and organic compounds that are part of powder combustion products. The activity of AOK-78-55 and STK-05-3(F) catalysts did not change during the tests of the pilot plant. Excess ammonia is extensively oxidized over iron oxide catalyst STK-05-3(F) to molecular nitrogen and water vapours [10] by the reaction:

$$2NH_3 + 3O_2 \rightarrow N_2 + 6H_2O$$

Ammonium carbonate dosage to the working range of the furnace

Selective catalytic reduction of nitrogen oxides (SCR-DeNOx) requires the supply of the reducing agent, *i.e.* ammonia vapours. This may be compressed ammonia from a cylinder or one ob-

TABLE 4

Average concentrations of NO and NO_2 in exhaust gases of the "Boston" heating furnace while supplying ammonium carbonate

Parameter	Experiment number			
	I	II	III	IV
$(NH_4)_2CO_3$ feed rate, g/h	0	600	1200	1800
Number of measurements	27	44	28	16
Average concentration, mg/m^3:				
NO	326±153	305±192	274±158	238±117
NO_2	20.5±6.6	20.6±7.7	15.1±6.2	16.3±5.4

tained resulting from ammonia water evaporation. Issues with ammonia dosing complicate instrumentation for waste gas treatment from the "Boston" furnace.

An accessible and readily producible source of ammonia is ammonium carbonate $(NH_4)_2CO_3$ decomposed at T > 58 °C according to the equation [11]:

$(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$

Experiments on disposal of nitrogen oxides using $(NH_4)_2CO_3$ as the source of ammonia were carried out upon its feed to the furnace with rates of 600, 1200, 1800 g/h (portions of 50, 100, and 150 g, respectively, with an interval of 5 min).

Gas sampling for NO and NO_2 was carried out at the exit from the ventilation system used to remove furnace gases to the atmosphere, with a periodicity of 1 min. Table 4 and Figure 2 present the analysis results.

It is worth noting that $(NH_4)_2CO_3$ gasification in the "Boston" furnace (at 300−350 °C) proceeds quantitatively, as undecomposed ammonium carbonate was not found at the exit from the ther-

mal furnace. Significant fluctuations of the concentration of nitrogen oxides (especially according to NO) in exhaust gases from the "Boston" furnace (50−750 mg/m^3) are driven by time-irregular explosion of treated cartridges and caps in shell casings during their continuous dosing up to 15 000 pieces/h.

As it follows from the data in Table 4, average concentrations of nitrogen oxides decreased with an increase in the feeding of ammonium carbonate. Alongside with that, the limited number of measurements and large deviations do not make possible an unambiguous conclusion about the statistical validity of this decrease.

In order to prove the validity of hypothesis regarding the effect of feeding carbonate ammonium on the average concentration of nitrogen oxides, the statistical processing of the initial data using the Student criterion was performed to compare average values of two samplings [12] (Table 5).

By the rules of mathematical statistics, the hypothesis is not considered to be refuted at $0.05 < \gamma < 0.95$ and proved at $\gamma > 0.95$. Thus, ac-
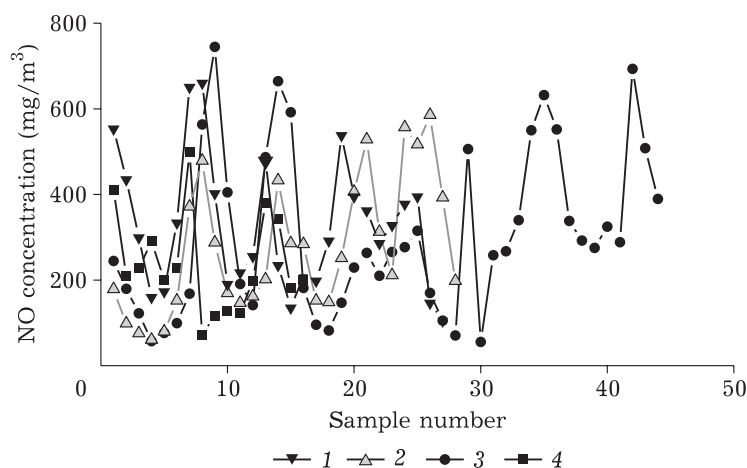

Fig. 2. Changes in the NO concentration in exhaust gases from the thermal furnace at different feed rates of ammonium carbonate, g/h: *1* − without reagent, *2* − 600, *3* − 1200, *4* − 1800.

TABLE 5

Results of the estimation of hypothesis validity

No. Experiment (supply, g/h)	NO			NO$_2$		
	I	II	III	I	II	III
II (600)	0.6926	−	−	0.4752	−	−
III (1200)	0.8935	0.7591	−	0.9988	0.9991	−
IV (1800)	0.9756	0.9047	0.7926	0.9817	0.9781	0.2418

cording to calculation results, the following conclusions can be drawn:

− when feeding $(NH_4)_2CO_3$ at a rate of 600 g/h (experiment II), there are no proven improvements in the content of NO and NO$_2$ in emissions;

− while supplying ammonium carbonate at a rate of 1200 g/h (experiment III), the contents of NO and NO$_2$ in emissions are significantly reduced;

− with $(NH_4)_2CO_3$ feed at a rate of 1800 g/h (experiment IV), there are no significant improvements in results compared to experiment III;

− the maximum level of validity is reached when comparing results of experiments II and III according to the concentration of NO$_2$.

As it follows from the findings, introducing ammonium carbonate facilitates a primary decrease in the average concentration of NO and NO$_2$ prior to their feeding into the gas treatment system. Upon an 1800 g/h dosage of carbonate ammonium, this decrease reaches 27.13 % for NO and 20.19 % − for NO$_2$.

The ammonia unreacted in the working volume of the furnace would take part in selective catalytic reduction of nitrogen oxides (SCR DeNOx).

Process flow diagram for integrated treatment of furnace gases

In order to treat waste gases from the "Boston" furnace, process scheme was suggested (Fig. 3) It involves the following:

− capturing the solid phase and resin from waste gases in a precipitator extender (1);

− treatment of waste gases in the jet foam scrubber (2) and then in the absorber/condenser (3) to capture the fine solid phase (PbO, Sb$_2$O$_3$) and water-soluble gaseous harmful compounds (NO$_2$, SO$_2$);

− selective catalytic reduction of nitrogen oxides with ammonia to harmless N$_2$ and H$_2$O;

− catalytic oxidation of CO to CO$_2$ in the catalytic reactor (5).

Heating the irrigating solution in the tank of foam-jet apparatus (2) using heaters make it possible to enhance generating water vapours that ensure a vapour condensation agglomeration of fine aerosol particles when condensing in cooled absorber/condenser (3), which facilitates their efficient capture therein.
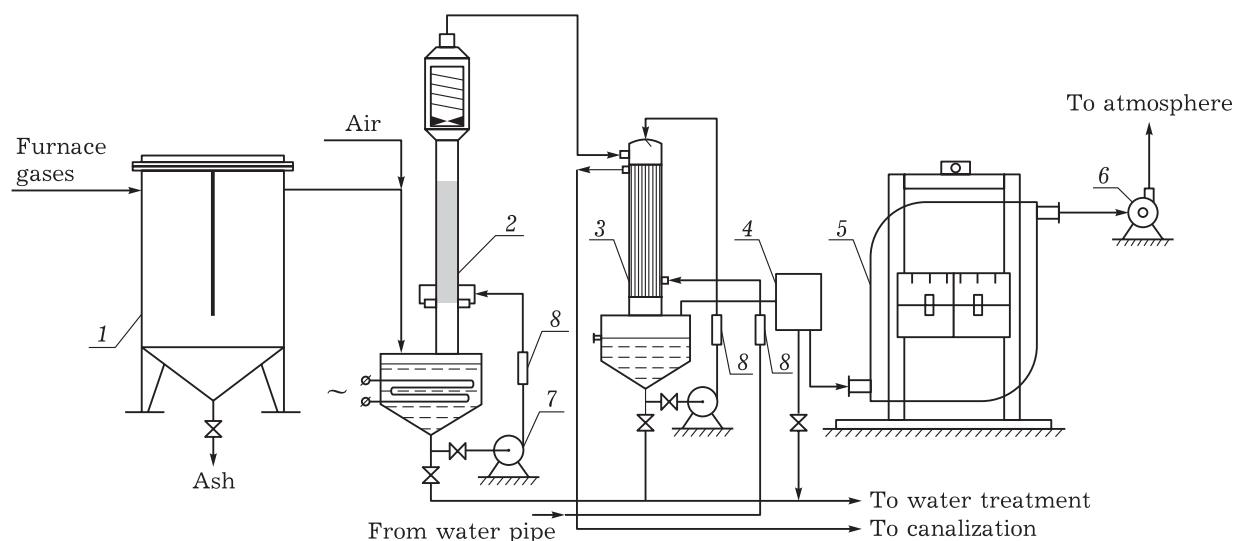

Fig. 3. Process scheme for integrated gas treatment: 1 − expander-precipitator; 2 − jet foam scrubber; 3 − the absorber/condenser; 4 − mist-trap; 5 − catalytic reactor; 6 − fan; 7 − water pumps; 8 − flow rate meters.

Ammonium carbonate dosage into the "Boston" thermal furnace should correspond to the quantity of ammunition supplied to disposal for generating ammonia in sufficient quantity.

CONCLUSION

The capture of solid particles, selective catalytic reduction (SCR DeNOx) of nitrogen oxides, and catalytic post-combustion of carbon monoxide are ensured resulting from the implementation of the suggested technology for the integrated treatment of furnace gases. The use of feeding ammonium carbonate to the thermal furnace for generating ammonia enhances process efficiency.

Acknowledgements

REFERENCES

1 Andreev K. K., Termicheskoe Razlozhenie i Gorenie Vzryvchatykh Veshchestv, Izd. 2d, M.: Nauka, 1966. 346 p. (in Rus.).

2 Pat. RU 2413174, 2011.

3 Pat. RU 2318177, 2008.

4 Maslyaev N. M., Maslyaev Yu. N., Telyshev V. I., IX Mezhd. Konf. "Aktual'nye problemy utilizatsii raket i boepripasov", Moskva, 23–24 October, 2013. (in Rus.).

5 Ramm V. M., Absorbtsiya Gazov, Izd. 2d, M.: Khimiya, 1976. 656 p. (in Rus.).

6 Popova N. M., Katalizatory Ochistki Gazovykh Vybrosov Promyshlennykh Predpriyatiy, M.: Khimiya, 1991. 176 p. (in Rus.).

7 Strelnikov E. A. Ochistka Khvostovykh Gazov Azotno-kislotnogo Proizvodstva ot Oksidov Azota (I, II, IV), Avtoref. diss. kand. khim. Nauk, M., 2006. (in Rus.).

8 Akhmerov O. I., *Vestn. Kazan. Tekhnol. Un-ta*, 2004, No. 1, P. 120–123. (in Rus.).

9 Danilin G. A., Ogorodnikov V. P., Zavolokin A. B., Osnovy Proektirovaniya Patronov k Strelkovomu Oruzhiyu: Ucheb., Spb.: Izd. Balt. Gos. Tekhn. Un-ta, 2005. P. 267. (in Rus.).

10 Ostrovsky Yu. V., Zabortsev G. M., Gusev M. A., Sobachinskiy N. N., Kuchin N. M., *Khim. Prom-st' Segodnya*, 2014, No. 5, P. 50–56. (in Rus.).

11 Goronovskiy I. T., Nazarenko Yu. P., Nekryach E. F., Kratkiy Spravochnik po Khimii, 5th izd., Kiev: Nauk. dumka, 1987. (in Rus.).

12 Kobzar' A. I., Prikladnaya Matematicheskaya Statistika, M.: Fizmatlit, 2006. 816 p. (in Rus.).